WBS: 1.2.5.4
QA: L

**Civilian Radioactive Waste Management System**
**Management & Operating Contractor**

# Chapter 4
# Total System Performance Assessment-Viability Assessment (TSPA-VA) Analyses Technical Basis Document

## Near-Field Geochemical Environment

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**August 14, 1998**

Prepared for:

U.S. Department of Energy
Yucca Mountain Site Characterization Office
P.O. Box 30307
North Las Vegas, Nevada 89036-0307

Prepared by:

TRW Environmental Safety Systems Inc.
1261 Town Center Drive
Las Vegas, Nevada 89134

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Prepared by:

Jerry A. McNeish for — 8/14/98
David G. Sassani — Date
Performance Assessment Operations

Darren M. Jolley — 8/14/98
Darren M. Jolley — Date
Performance Assessment Operations

Jerry A. McNeish for — 8/14/98
Yueting Chen — Date
Performance Assessment Operations

Jerry A. McNeish for — 8/14/98
Paul Domski — Date
Performance Assessment Operations

Jerry A. McNeish for — 8/14/98
Paul Mariner — Date
Performance Assessment Operations

Jerry A. McNeish for — 8/14/98
Christine Stockman — Date
Performance Assessment Operations

Checked by:

FOR — 8/14/98
F. Joseph Pearson — Date
Performance Assessment Operations

Approved by:

for — 14 Aug 98
Robert W. Andrews — Date
Performance Assessment Operations

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Near-Field Geochemical Environment

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## ACRONYMS

| | |
|---|---|
| CAM | corrosion allowance material |
| CC | central-central |
| CRM | corrosion resistant material |
| CRWMS | Civilian Radioactive Waste Management System |
| CSNF | commercial spent nuclear fuel |
| DHLW | defense high-level waste |
| DOC | dissolved organic carbon |
| EBS | Engineered Barrier System |
| ESF | Exploratory Studies Facility |
| GRSF | gas reservoir scaling factor |
| I-dry | Infiltration rate under dry climatic conditions |
| I-LTA | Infiltration rate under long-term average climatic conditions |
| MCM | microbial communities model |
| MING | Microbial Impacts to the Near-Field Geochemistry |
| NFGE | near-field geochemical environment |
| QA | Quality Assurance |
| RH | relative humidity |
| RIP | Repository Integration Program |
| SZ | saturated zone |
| TBV | to be verified |
| TFM | tracers, fluids, and materials |
| TH | thermohydrologic |
| THC | thermo-hydro-chemical |

| | |
|---|---|
| TSPA | Total System Performance Assessment |
| TSPA-VA | Total System Performance Assessment for the Viability Assessment |
| TST | transition state theory |
| UZ | unsaturated zone |
| UZRT | unsaturated zone radionuclide transport |
| VA | Viability Assessment |
| WFD | waste form degradation |
| WP | waste package |
| YMP | Yucca Mountain Site Characterization Project |

# 4. NEAR-FIELD GEOCHEMICAL ENVIRONMENT

## 4.1 INTRODUCTION

The TSPA-VA analyses of the potential high-level waste repository at Yucca Mountain, Nevada, includes a more detailed representation of the chemical processes within the potential emplacement drifts than previous analyses. This near-field geochemical environment (NFGE) component is a description of the changing composition of gas, water, colloids, and solids within the emplacement drifts under the perturbed conditions of the repository environment. The major changes are caused by the planned thermal loading of the system and the emplacement of large masses of materials that can react with water and gas in the system. Because the system will heat and then cool off, the system will continue to change. Not only will the thermal perturbation affect the movement of gas and water through the unsaturated system (thermal hydrology as described in Section 3.2), but it will also affect the composition of the gas and water. These fluids of altered composition may enter the drifts and react with the materials emplaced during repository construction. Most of these emplaced materials will be very different in chemical composition from the host rock. In the drifts, reactions with materials such as concrete may alter water and gas compositions before they react with the waste package and the waste forms, and along the flow paths for radionuclide transport in the unsaturated zone (UZ). The emplaced materials may also provide additional sources of colloids. These colloids from emplaced materials may be more effective in transporting radionuclides than natural colloids. Figure 4-1 is a general view of processes, phases, and design materials that are considered for the NFGE.

This document contains an introduction (Section 4.1) to the NFGE component of the TSPA-VA and an overview of the conceptual models being used to assess the NFGE for TSPA-VA. This initial section provides the context of the NFGE analyses within the entire set of TSPA-VA components and summarizes the major issues for the NFGE processes that were gathered from the NFGE workshop and planning activities conducted in fiscal year 1997 (Civilian Radioactive Waste Managements System [CRWMS] M&O 1997a). In Section 4.2, the conceptual process models are described and the major assumptions of the various modeling activities are discussed. Section 4.3 includes an overview of the specific inputs from the Repository and Waste Package Design groups for compositional information on design materials. Section 4.4 provides the model development and implementation for the analyses that have been done.

The results for all NFGE model analyses that have been performed for the base-case TSPA-VA analyses are presented within Section 4.5, with associated abstraction for use by the TSPA code and discussion of uncertainties. Also within Section 4.5 are the sets of parameters generated by the NFGE that are utilized either within other NFGE models, other TSPA components, or directly within the TSPA analyses. Section 4.6 contains the sensitivity studies and the results of those studies that were used within TSPA analyses. In addition to those, Section 4.6 contains the results of NFGE models that were not incorporated directly into TSPA-VA analyses, but which provide preliminary bounds on the chemical system in the potential drifts. A summary of the NFGE analyses is provided in Section 4.7 that covers the major changes for the TSPA-VA, summarizes the results given in this document, and provides direction for further work in this area.

The most direct way the NFGE may impact long-term performance is by changing the EBS that inhibits the release of radionuclides to the geosphere (to the UZ radionuclide transport component, see Chapter 7). Chemical changes to the drift environment may affect the amounts and types of mobile radionuclides and the properties of the solids through which they are transported. The NFGE is the set of compositional conditions under which the waste package corrodes, the waste forms dissolve and precipitate as secondary phases, the radionuclides mobilize from the waste form, and the radionuclides migrate through the engineered barriers. In addition to these primary effects within the engineered barrier system, perturbed fluids generated in the NFGE could react with the host rock. Such alteration may change the flow pathways in the geosphere and change conditions for UZ transport.

A set of five models has been developed to represent the NFGE. These models are:

A. The incoming gas, water, and colloids (compositions of those phases as they enter the drift)

B. The in-drift gas phase (composition of the gas phase relative to major gas sinks in the drift)

C. The in-drift water/solid chemistry (evolution of water composition reacting with major materials and the in-drift gas phase)

D. The in-drift colloids (stability and quantity of clay and iron-oxide colloids in the drift)

E. The in-drift microbial communities

The relationships between the models for the NFGE, including the general flow of information from one model to another and the major components of each submodel, are shown in Figure 4-2. In some cases, these five models contain process-level calculations to represent the evolution of water, solid, and gas reactions in the system. In other cases, the models consist of "bounding" arguments for applying observed values. There are a number of submodels for the water/solids interaction model covering steel corrosion products (iron oxyhydroxides), concrete, waste form (spent nuclear fuel), and mineral precipitates from boiling.

### 4.1.1 Overview of the Near-Field Geochemical Environment

For the purposes of Performance Assessment model components, the NFGE is defined as the environment within the drift (i.e., in-drift geochemistry). The NFGE model affects and is affected by all of the other processes (and associated models) within the Engineered Barrier System (EBS), including the coupling to thermohydrologic processes. As defined here, the NFGE component specifically focuses on major-element geochemistry within the potential emplacement drifts (see CRWMS M&O [1997a] for a discussion). The boundary of the NFGE domain defined for the TSPA-VA analyses is the drift wall. The boundary of this NFGE region (from a geochemical perspective) is defined as the rock face because (1) the dominant introduced substances masses are within the drift and delineate a very sharp compositional anomaly compared to the host rock, (2) it is also the location of the handoff for the source-term, radionuclide concentrations from the EBS to the geosphere UZ transport, and (3) additional

geochemical gradients occur within the drift, adding complexity to the possible reaction pathways.

This does not imply that geochemical processes outside the drift should be ignored. On the contrary, these in-drift geochemical analyses can only be done using initial conditions and boundary conditions "imposed" by the geosphere geochemistry. Some of these conditions are developed in a simplified manner below, but additional, separate models for the geosphere geochemistry would facilitate more detailed analyses of the NFGE. There are a number of efforts currently addressing, or planned to address, the geosphere conditions as discussed in Section 4.2 covering the boundary conditions conceptualization for the NFGE activities.

Many of the aspects that contribute to determining the NFGE are shown in Figure 4-1. Key inputs to the NFGE model include the major-element composition and thermodynamic/kinetic coefficients of the introduced, in-drift materials, the thermohydrologic behavior of the entire repository, the gas-phase composition entering the drift through time, and the aqueous-phase composition entering the drift through time. These in turn depend to a large extent on the design of the repository: the thermal load, whether and what type of backfill is used (there is no backfill in the reference design evaluated here), the waste-package material composition, and the drift lining composition (e.g., concrete or steel). Additional factors to be considered are the far-field percolation flux, the reaction and reflux of condensate water, and the drift seepage flux. The inclusion of organic materials and potential growth of microbial communities add another level of complexity to this system. All these parameters will influence to some extent our ability to discern/bound the actual NFGE using currently available models.

### 4.1.2 TSPA Component Processes and General Approach to TSPA-VA Model Development

Although the ambient geochemical system has a large capacity to moderate bulk system geochemistry, changes to the NFGE have the potential to affect waste package corrosion, waste-form dissolution, radionuclide solubility limits, and transport characteristics through the engineered barriers and perhaps even throughout the geosphere. The geochemical environment within the potential emplacement drifts will be defined by the complex interactions among the ambient and thermally perturbed fluxes of geosphere water and gas phases through the drift, the masses of introduced materials left in the drift post-closure, and the microbial communities which may form within this region of large compositional heterogeneities (West 1988; Murphy 1991; Glassley 1993; Meike and Wittwer 1993; Wilder 1996; Hardin et al. 1998).

A number of major aspects of the NFGE are shown schematically within Figure 4-1, but a full description of the near-field geochemistry is not currently possible. A comprehensive description would include evolution of the abundances and compositions of the aqueous phase, solid phases, gas phase, colloidal phases, and microbial communities in the potential emplacement drifts for the time period of interest. The connections among the TSPA-VA NFGE component and the other components of the TSPA-VA are discussed below. Below that, the development of the NFGE component models is described in the remaining sections.

#### 4.1.2.1 Connections To and From Other TSPA-VA Components

The general TSPA model architecture is based on the ability to decouple system behavior both spatially and by type of process, (i.e., it assumes weak feedback spatially and among processes). This assumption is least tenable when applied to the NFGE, which may be highly coupled in a nonlinear fashion, being influenced by thermal, hydrologic, and multicomponent chemistry. This is evident by the numerous interconnections between the NFGE and other components shown in Figure 4-3 and detailed in the discussion below. The potential effects of the coupling within the thermal-mechanical-hydro-chemical system are uncertain, but work is ongoing (both within the project and outside of it) to delineate the first-order couplings that should be addressed and to define the magnitude of the effects of representing inherently coupled processes using uncoupled, or loosely coupled, models (Manteufel et al. 1993; Chen et al. 1996a; Lichtner et al. 1996; Lichtner and Seth 1996; Wilder 1996; Hardin et al. 1997; Hardin et al. 1998). In addition, an expert elicitation evaluating coupled thermohydromechanicochemical processes in the geosphere/altered zone was held and is discussed further in Section 4.2. The coupling of the NFGE models to other aspects within the NFGE component and to other TSPA-VA components is done either in a single direction via output/input transfers at the process-model level, or by one-way, direct-connections within the TSPA analyses. The main first-order interactions between the NFGE and the other TSPA-VA components considered in the analyses are discussed below.

The NFGE component models take input from the UZ flow and thermal-hydrology components and provide output to the waste-package degradation component, the waste-form component (degradation, radionuclide mobilization, and EBStransport), the UZ radionuclide transport component, and the criticality analyses. The NFGE models, their connections to these other TSPA-VA components, and the specific inputs/outputs to/from the NFGE component are shown in Figure 4-4. These interfaces to other TSPA-VA components are discussed in more detail below.

**Unsaturated Zone Flow** - The flux of water and dissolved constituents through the NFGE is based either on the seepage flux through the drifts or on the average percolation flux at the repository horizon. Seepage flux is used for the in-drift water-solids model and the colloid model. Average percolation flux is used for the in-drift gas model because gas mobility is relatively high near the drifts and, therefore, the gas composition is in equilibrium with a larger volume of water than just the seeping water. Because of the relatively rapid movement of gas species at the drift scale, the dissolved gas constituents in the water are viewed as being available for reaction with materials in the drift. Therefore, those aqueous fluxes are included in the total available masses of gas constituents. See Chapter 2 of this document for a detailed description of the Unsaturated-Zone Flow Component of the TSPA-VA analyses.

**Thermal Hydrology** - The thermal disturbance caused by repository heating provides a number of time-dependent boundary conditions for the NFGE model, including the flux of gas into the drift, the drift temperature, and the relative abundance of air in the gas (i.e., the air-mass fraction). Thermal effects can drive changes in the fluid and gas compositions through changes to temperature-dependent phase equilibria or reaction kinetics. Such changes may also occur within the heated geosphere surrounding the EBS and change the compositions of those incoming phases. The effects of thermal perturbations may also have long-term consequences

for minerals and solids within the drift because of changes in phase stabilities, reaction rates, permeability, and porosity. In addition, if mineral dissolution/precipitation processes are extensive enough, changes to the permeability/porosity in the near-field could create feedback to the thermal-hydrologic processes, causing changes in liquid and gas movement through the potential drifts. Such thermal-hydrochemical feedback is not yet incorporated into these models, but process models are starting to address such issues (Hardin et al. 1998, Section 5.5). The effects of any thermal-mechanical interactions are considered only to the extent that they are included in the thermal-hydrology models.

These effects can lead to changes in the behavior of waste package degradation, the evolution/dissolution of the waste form, and both the hydrologic and transport properties of the engineered barrier system. Thermal-hydrologic changes to the near-field environment will affect the chemistry in the drift and may impact the rate and types of long-term radionuclide releases from the EBS into the geosphere. See Chapter 3 of this document for a detailed description of the Thermal Hydrologic Component of the TSPA-VA analyses.

**Waste Package Degradation** - The waste package degradation model defines the rate at which the various engineered barriers (inner and outer layers, etc.) of the waste package corrode, providing both the time of first penetration of the package and a time history of the number of breaches (pits and patches) in the container. This provides the state of the waste package degradation through time, as well as the area of the waste package through which mass transport can take place. See Chapter 5 of this document for a detailed description of the Waste Package Degradation Component of the TSPA-VA analyses.

The in-drift geochemistry may have impacts on the corrosion rates of waste package barrier materials. The composition of water contacting the waste package and the bulk oxidation state within the drifts are supplied by the NFGE component of the TSPA-VA for both base-case analyses and for concrete modified water sensitivity studies. In addition, the NFGE models supply bounding estimates on the mass of microbes generated within a potential emplacement drift, and on the masses (and timing) of precipitates/salts buildup for a waste package. These model results were considered within process-level sensitivity analyses of waste package degradation, but were not included within any of the total system performance assessment analyses.

The waste package materials themselves are an extensive mass of introduced materials that may have effects on the NFGE. These materials and their solid corrosion products can change the aqueous and gas compositions in the drift, as well as provide a source of iron-oxyhydroxy colloids that may enhance migration of certain radionuclides. These aspects are considered by the in-drift water-solids and the in-drift colloids models.

**Waste Form Degradation, Mobilization, and Engineered Barrier System Transport** - The degradation rates of the waste forms (including cladding) depend on the composition of the gas phase and the aqueous phase reacting with the waste form. The NFGE component provides the compositions of water and gas that may react with the waste forms, the abundances of natural (clay) and introduced (iron-oxyhydroxide) colloids, and the state of the media through which radionuclide transport will occur in the engineered barrier system. The major chemical constituents of the commercial spent nuclear fuel (CSNF) waste form have also been evaluated

for their potential to change the water chemistry from its initial composition entering the waste package.

The waste form degradation and EBS transport models define the rate of waste form reactions, the type and supply of mobile radionuclides at the waste form surface, the radionuclide transport pathways and mechanisms through the engineered barrier system, and, ultimately, the radionuclide fluxes and types of mobile radionuclides delivered to the geosphere (at the edge of the EBS, i.e., the drift wall, which represents the source term for the geosphere models). See Chapter 6 of this documents for a detailed description of the Waste Form Degradation, Mobilization, and Engineered Barrier System Transport Component of the TSPA-VA analyses.

**Unsaturated-Zone Radionuclide Transport** - The major element (nonradionuclide) composition of the water moving from the EBS into the UZ transport pathways of the geosphere is determined from the NFGE component. Radionuclide transport depends on the water composition, particularly for radionuclide retardation processes, but also for potential alteration of the pathways themselves. The potential altered fluid compositions that may migrate through the UZ are used for scenario development for altered UZ radionuclide transport sensitivity analyses. These were used in total system performance assessment sensitivity analyses to evaluate the impacts of potentially reduced sorption of actinides in a migrating alkaline plume.

The unsaturated zone radionuclide transport (UZRT) models define the movement of the radionuclides from the edge of the EBS, through the UZ, and to the start of the saturated zone (SZ). The main input from the EBS region to the UZRT model is via the EBS transport model (discussed in Chapter 6 covering the waste form models), which provides the aqueous abundances of radionuclides (and the colloidal abundances for Pu isotopes) at the edge of the engineered barrier system. See Chapter 7 of this documents for a detailed description of the Unsaturated-Zone Radionuclide Transport Component of the TSPA-VA analyses.

**Criticality** - A portion of this work considers the possibility of a critical configuration of fissile material forming within the drift (near-field) environment after release from waste packages ("external" criticality), and its potential performance consequences. This external criticality is linked directly to radionuclide transport processes in the emplacement drifts and depends on the location and time-dependant chemical changes that occur there. The NFGE models provide the context for scenario development for in-drift criticality. In addition, the changes (mainly thermal) caused by a critical event could affect the chemical environment within a drift. See Chapter 10 of this documents for a detailed description of the criticality analyses done for the TSPA-VA analyses.

### 4.1.3 Previous Treatment in YMP PA Modeling Efforts

In the previous TSPA analyses (Barnard et al. 1992; Wilson et al. 1994; Andrews et al. 1994; CRWMS M&O 1995), the NFGE was incorporated as a number of compositional variables within subsystem models, or implicitly within some of the ranges used for performance parameters (e.g., solubility-limited radionuclide concentrations). The most recent performance assessment modeling work (CRWMS M&O 1995) primarily employed the Repository Integration Program (RIP) (Golder 1996). RIP is a TSPA code with a source-term model that analyzes waste package degradation, waste form degradation and mobilization, and transport of

radionuclides through the engineered barrier system. It can use the NFGE model output parameters directly in the form of response surfaces or table lookups, which set the local environments of RIP cells representing various portions of the near-field, such as the waste form, the degraded package, and the invert. These compositional response surfaces can be used in RIP to affect waste-form degradation rates, as well as solubility-limited concentrations and equilibrium distribution of radionuclides among the phases (which would in turn affect the transport rate). These NFGE response surfaces could also be used within RIP to affect the wastepackage degradation rate. (However, for TSPA-VA they will be used directly in the external waste-package degradation model, WAPDEG, which generates first penetration rates (both pits and patches) and growth rates of breaches. Abstracted results of these simulations are then fed as additional response surfaces into the RIP package-failure module. See Chapter 5 for a detailed discussion.)

The NFGE implicitly included in previous TSPA calculations corresponds to the ambient water composition from Well J-13 and atmospheric oxygen and carbon dioxide fugacities. The impacts of pH variation and temperature variation have been incorporated explicitly into models of waste-package degradation, waste-form dissolution, and the solubility-limited concentrations of Np, Pu, and Am (CRWMS M&O 1995). A variable pH condition covering values of 6 to 9 (with 7 taken as the base-case) was incorporated implicitly into the distributions of solubility-limited concentrations to define the mobile radionuclide concentration. This range of pH reflects the range of measurements for fluids from Well J-13 (this water composition is referred to as J-13 water in the sections of the document below). Gas phase composition was assumed to be buffered to atmospheric values because of ready gas flow through the mountain.

Previous TSPA analyses have not incorporated explicitly bulk fluid compositions different from the "ambient" condition, variable gas-phase composition, colloid abundances, and changes to mineral distribution within and around the drifts. [However, because of the conservative (far-from equilibrium) spent-fuel dissolution rates and large ranges of solubility-limited concentrations used in past TSPA calculations, the impacts of some of these potential variations may have been implicitly included.] Explicit inclusion of such information is facilitated by process models that constrain and quantify the geochemical effects in the near field (e.g., pH changes) in conjunction with additional process models that delineate the impacts to performance parameters of those effects (e.g., waste form dissolution as a function of pH). Examples of geochemical code packages that can help build such process models are EQ3/6 (Wolery 1992a, b; Wolery and Daveler 1992), OS3D/GIMRT (Steefl and Yabusaki 1996), and AREST-CT (Chen et al. 1995). Models of geochemical processes constructed using such packages can be used to generate compositional response surfaces for inclusion in the TSPA-VA RIP model.

### 4.1.4 Workshop Summary/Overview

A workshop about the treatment of the near-field (in-drift) geochemical environment in this TSPA was held in March 1997. The details of the workshop activities and results are documented in *Near-Field Geochemical Environment Abstraction/Testing Workshop Results* (CRWMS M&O 1997a). A brief overview of the workshop is provided because it was the primary initiator for development of the NFGE component for this TSPA. The criteria used at the workshop to prioritize issues, the highest priority issues, and the resulting abstraction/analysis plans are listed in Table 4-1.

At the NFGE workshop, Yucca Mountain Project (YMP) personnel from the design, scientific programs, and performance assessment organizations delineated, discussed, and prioritized issues relevant to chemistry within emplacement drifts that might impact system performance. The two issues given the highest priority focused on evolution of design materials within the drift (that is, the in-drift water/solid chemistry). These two issues are, "the amount of water coming into the drift" and "the introduced material masses and compositions."[1] Three additional issues that were also given high priority for this topic are "aqueous and gas reactions with materials," "aqueous and gas reactions with the waste package," and "open versus closed system behavior." The gas composition issue given top priority was "gas flux into the drift." The third-highest overall prioritized issue relates to the in-drift water composition, "effects from reactions with introduced materials." Workshop participants gave high priority to two other issues related to drift water chemistry; "open versus closed system," and "aqueous reactions with the waste package." The highest priority issue related to in-drift colloids was assessed to be "reversibility of sorption." The issues "water composition effects" and "waste form" were also given high priority for colloids in the drift. These priorities, together with the group discussion of issues in each topic area, provided the bases for development of the component models.

The workshop itself, together with post-workshop synthesis and planning, led to the five model areas for the NFGE:

- Incoming gas, water, and colloids (compositions of those phases as they enter the drift)
- The in-drift gas phase (composition of the gas phase relative to major gas constituent sinks in the drift)
- The in-drift water/solids chemistry (evolution of water composition reacting with major materials and the gas phase in the drift)
- The in-drift colloids (stability and quantity of clay and iron-oxide colloids)
- The in-drift microbial communities.

The conceptual models for each of these areas are summarized in Section 4.2, and their specific implementations for the analyses are given in Section 4.4.

### 4.1.5 Synopsis of Current Treatment/Changes from Prior Efforts

Many of the NFGE processes cannot be represented currently in detailed mechanistic models of the chemistry completely coupled to the fluid flow and physical evolution of the system. However, pieces of the system are being constrained using experimental results (Lu et al. 1997; CRWMS M&O 1998a. Section 6.3.6.2) and models of the thermochemical behavior of the system (Wilder 1996; Glassley 1997; Hardin et al. 1998). For the TSPA-VA, explicit

[1] Although the waste package is a design material, it was considered separately from other potential repository-design materials for clarity because it is also a major component of the engineered barrier system.

consideration of the NFGE evolution constitutes a major step forward for directly including the potential chemical variations affecting source-term performance, however, this initial effort is only a relatively simplified representation of the complex interactions of this heterogeneous system.

The evolution of water that may be dripping into drifts is being assessed using both reaction mass transfer code packages such as EQ3/6 (Wolery 1992a, 1992b; Wolery and Daveler 1992) and coupled reactive transport simulators such as AREST-CT (Chen et al. 1995). Assessment of the interaction of water with concrete, steel corrosion products, and the formation of salt crusts was also done with EQ3/6, although limited equilibrium thermodynamic and kinetic data for some of these systems allow only treatment of idealized systems (e.g., cementitious systems). The AREST-CT code was used to evaluate coupled reactive transport through the CSNF waste form. These NFGE analyses used the base-case gas composition for setting gas fugacities in the calculations and were supplemented with sensitivity analyses incorporating the perturbations developed in the models addressing gas composition evolution and microbial communities effects.

The primary output from the TSPA-VA NFGE model is a set of major chemical compositional parameters over time and space within the EBS that are used by other EBS models. For example, if pH and carbonate concentration are the only parameters deemed important for waste-package or waste-form degradation, these will be the only outputs taken from the NFGE model (even though the model will predict many other species activities). The NFGE model was run for a certain number of introduced materials evolution scenarios with a finite number of incoming fluid compositions, (i.e., for only a certain number of boundary conditions to the NFGE model). These include the following chemical compositions for the input boundary water and gas: J-13 water to thermally perturbed water, and ambient pore gases to thermally perturbed gases.

This represents the initial incorporation of most of these geochemical conditions into the TSPA analyses and will likely indicate a large number of areas where revisions will be needed to the models utilized both in this TSPA component and in other TSPA components to address many of these compositional issues. These analyses currently address only the highest priority aspects of the issues within this complex chemical system. Although the work is intended to bound the conditions that may affect performance most directly, many aspects of the system will not be given much direct attention, and it should be noted that there may be some aspects that will require further evaluation (these are discussed in Section 4.7).

## 4.2 CONCEPTUAL PROCESSES APPLICABLE TO THE NFGE

There are a large number of issues and coupled processes relevant to the development of NFGE models (Hardin et al. 1997; Hardin et al. 1998). Performance assessment personnel and principal investigators within the scientific program worked together to develop abstracted models of the NFGE component of the TSPA-VA. Some of the NFGE models are based, in part, on conceptual process models developed within the *Near-Field/Altered-Zone Models Report* (Hardin et al. 1998). Such conceptual models were combined with time-dependent, abstracted results of the potential repository system thermal-hydrologic evolution (see Section 4.4), that were used as constraints for the NFGE models of gas composition. This abstraction entailed

using average constant values for defined time periods with step changes in between them. One primary result of this abstraction is that short-term transient effects (for example, lasting less than about 100 years) are included in an average manner. This was assessed as a reasonable way to proceed for this initial model development effort because the TSPA system integration model utilizes time-steps of at least 100 years (see Sections 4.4 and 11.1). This synthesized all the various process models into an abstracted representation of the NFGE through time.

### 4.2.1 General Overview of Relevant Processes

This section contains a general overview of the processes that were considered relevant for model development for the NFGE component. This overview includes three major aspects of the system: (1) ambient system conditions; (2) processes driven by thermal perturbations; and (3) processes driven by introduced materials. Below that, Section 4.2.2 is a brief discussion of the intricacies of the coupling among these processes in the NFGE. Finally, the conceptual models developed for the NFGE component of the TSPA-VA are presented in Section 4.2.3.

#### 4.2.1.1 Ambient System Conditions

The discussion below provides some general background on the geochemistry of the ambient system. A detailed review of this information has been conducted and presented in the *Yucca Mountain Site Description* (CRWMS M&O 1998a, Sections 5 and 6 in particular).

##### 4.2.1.1.1 Gas Compositions

The values of the gases $O_2$, $N_2$, and Ar in samples of pore gases from the UZ are all very close to their atmospheric values (CRWMS M&O 1998a, Section 6.2.7.2, pp. 6.2-40). Measurements of gas compositions from various UZ boreholes (Figure 4-5) demonstrate that UZ $CO_2$ gas concentrations are elevated above atmospheric $CO_2$ partial pressures (about 350 parts-per-million-by-volume [ppmv]) by about a factor of three (CRWMS M&O 1998a, Section 6.2.7.2, pp. 6.2-40). The values of UZ pore-gas composition analyzed for the site indicate that the $CO_2$ content of pore gases tends to average about 1000 ppmv (CRWMS M&O 1998a, Section 5.3.4.2.4.6, pp. 5.3-173). These elevated values could be the result of mixing of $CO_2$-rich gases generated in the soil zone with the rest of the gas volume of the mountain (CRWMS M&O 1998a, Section 5.3.4.2.4.6, pp. 5.3-173).

##### 4.2.1.1.2 Water Compositions

Analyses of the groundwater compositions at Yucca Mountain are described in detail in the *Site Description Document* (CRWMS M&O 1998a, Sections 5.3.4, 5.3.5, and 6.2). The ambient water composition could either be defined by analyzed values of saturated-zone water (e.g., Well J-13), or from the analyses performed on pore water extracted from UZ rock samples. Harrar et al. (1990) evaluated water from Well J-13 for use as a reference water composition and concluded that it could be used as such for the purpose of a reference case fluid. It was noted that fluids taken from flowing fractures at Ranier Mesa had compositions similar to the J-13 values (Harrar et al. 1990). The average composition of J-13 water from Harrar et al. (1990) is given in Table 4-2, together with averages for UZ fluids analyzed from boreholes UE-25 UZ-5 and UE-25 UZ-4 (Yang et al. 1988, 1990; Yang 1992).

Measurements of groundwater compositions from the SZ indicate that the fluids within the tuffaceous units (as represented by samples from well J-13) are predominantly dilute sodium bicarbonate fluids with high concentrations of aqueous silica (Benson et al. 1983; Ogard and Kerrisk 1984; Kerrisk 1987; Harrar et al. 1990). In general, the saturated-zone fluids have pH in the range of 7-8 (but cover 6.7 to 9.4), contain, in order of decreasing concentration, the additional cations $Ca^{2+}$, $K^{+}$, and $Mg^{2+}$, and the additional anions $SO_4^{2-}$, $Cl^{-}$, $F^{-}$, and $NO_3^{-}$. The groundwater from the deep Paleozoic carbonate aquifer (from UE-25p#1) is more highly concentrated with respect to all these constituents except aqueous silica and is characterized by pH values slightly lower than 7 (Ogard and Kerrisk 1984; Kerrisk 1987). The saturated-zone water analyses suggest that these fluids are, in general, relatively oxidized, but a couple of samples may indicate reducing conditions at depth (Ogard and Kerrisk 1984). A series of measurements of the saturated-zone system are underway to more fully determine the oxidation potential near the surface of the water table and as a function of depth into the aquifer. Measurements of the organic content of the saturated-zone fluids are below 1 ppm (Means et al. 1983).

Analyzed water compositions from the UZ tuffaceous rocks (Yang et al. 1988, 1990; Peters et al. 1992; Yang 1992) indicate that they have pH values in the range of 6.4 to 7.5 and that some constituents ($Ca^{2+}$, $K^{+}$, $Mg^{2+}$, $SO_4^{2-}$, $Cl^{-}$, and dissolved silica) are more concentrated than found in samples from the SZ tuffaceous aquifer. However, the average $HCO_3^{-}$ content measured in 83 water samples extracted from UZ nonwelded tuff was lower than that in the saturated-zone samples (Peters et al. 1992). Some of this variability may be caused by the extraction techniques used to remove water from unsaturated samples (Peters et al. 1992). No analyses of the dissolved organic content have been given in the studies of the UZ fluid compositions. Because of the intimate contact between the UZ fluids and the pore gases in the rock, these groundwaters are relatively oxidizing and the oxidation potentials are probably controlled primarily by atmospheric oxygen levels (CRWMS M&O 1998a, Section 6.2.5.2, p. 6.2-19). In the units above the Calico Hills, the pH of the water is thought to be dependent primarily on the carbon dioxide content of the gas, with some degree of $Na^{+}$-$H^{+}$ ion exchange affecting the values (CRWMS M&O 1998a, Section 6.2.5.2, p. 6.2-19).

There are clearly differences between the J-13 and UZ fluids, primarily higher Ca, Mg, Cl, and $SO_4^{2-}$ in the UZ fluids (see Table 4-2 and discussion in CRWMS M&O 1998a, Section 6.2.5.2). Whether these differences are meaningful, as well as which fluid composition most closely represents the ambient composition of fluid that moves through Yucca Mountain, is not currently completely understood. There may have been some alteration of UZ pore fluid chemistry from the extraction techniques, as discussed above. In addition, it was thought that the UZ-4 samples had lost water by evaporation, which may account for the generally higher values compared to UZ-5 analyses (Peters et al. 1992; Yang 1992). Because of low sample volumes, the UZ analyses are not as comprehensive as those for the SZ. In addition, the saturated-zone fluids are similar compositionally to both the perched water (CRWMS M&O 1998a, Section 6.2.5.2, p. 6.2-19) and to that collected flowing from fractures at Ranier Mesa (Harrar et al. 1990, pp. 6.5 and 6.6—Table 6.1). At this time, it appears that a reasonable ambient water composition moving through fractures can be represented by the J-13 composition.

#### 4.2.1.1.3 Natural Colloids

In addition to the possibility of radionuclides dissolved in the aqueous phase, another potentially mobile mass of radionuclides could come from colloids. Suspended in the aqueous phase, colloids are minute particles ranging in size from about $10^{-8}$ m (100 Å) up to about $10^{-5}$ m ($10^{5}$ Å); a range that includes viruses at the low end and bacteria at the high end (Stumm and Morgan 1981). Field studies of saturated-system radionuclide migration associated with underground nuclear tests (Buddemeier and Hunt 1988) or with actinide contaminant plumes (Penrose et al. 1990) indicate that those systems possess a highly mobile colloidal component.

In a potential repository environment there are two general types of colloids: (1) pseudocolloids, which are comprised of small particles of other materials that adsorb radionuclides and may act as a mobilizing agent; and (2) waste form colloids, which contain radionuclides as part of their structural mass. Pseudocolloids that are generated from the natural system minerals, or natural organic matter, are referred to as natural colloids. Pseudocolloids generated from introduced substances at the site are called introduced colloids. Waste form colloids include radiocolloids that are produced by agglomeration of hydrolysed actinides (e.g., Hobart et al. 1989) via direct precipitation from supersaturated solutions, and degradation colloids formed by physical deterioration of the waste material (or alteration products) itself (e.g., Bates et al. 1992). For this discussion, the various colloids are sufficiently distinguished by their sources as (1) natural colloids, (2) introduced colloids, and (3) waste form colloids. The background on natural colloids is discussed here, whereas the introduced colloids and waste-form colloids are described in the appropriate portions of Section 4.2.1.3 below.

Natural colloids occurring at Yucca Mountain include inorganic colloids consisting essentially of clays, silica, and iron oxyhydroxides (Ogard 1987; Levy 1992; Triay et al. 1996; CRWMS M&O 1998a, Section 6.1.8.5) and organic colloids such as humic and fulvic acids (Minai et al. 1992). Such colloids may be able to enhance the transport of highly sorbing radionuclides such as Pu and Am (Triay et al. 1995; CRWMS M&O 1998a, Section 6.3.6). The abundance and stability of the inorganic colloids have been characterized in a manner that facilitates incorporation into Performance Assessment models (Triay et al. 1996; CRWMS M&O 1998a, Section 6.3.6.1). The mass concentration of natural colloids of size greater than 200 nm in J-13 water was measured to be about 23 ng/ml (Triay et al. 1996), which was similar to the value of 27 ng/ml measured by Ogard (1987) for natural colloids greater than 400 nm. In order for these concentrations of natural colloids to account for 10 percent of a particular mobile radionuclide, Ogard (1987) calculated that a sorption distribution coefficient of greater than $4 \times 10^{6}$ ml/g was necessary for that radionuclide. This is much higher in general than the measured values or the values recommended to assess the effect of these colloids on trivalent and tetravalent actinides using an irreversible sorption assumption (Triay et al. 1996). The kinetic sorption and desorption rates of Pu to iron oxyhydroxides are discussed in Chapter 6 and are used to assess the bounding sorption coefficients of Pu onto these phases. Even for Pu sorption to iron oxyhydroxides (i.e., a strongly sorbing case), the values appear to indicate that major impacts to the concentrations of mobile Pu are not expected for the colloid concentrations given above (see Chapter 6 for details). However, a small release of radionuclides may occur sooner if natural colloid transport is a major aspect of radionuclide migration, compared to the case of purely aqueous species transport. In addition, as discussed below in Section 4.2.1.3, introduced materials are a potential source of colloids also. So even if the natural colloids are not very effective, there is still

potential for other colloids produced within the drift to enhance radionuclide migration. Therefore, as part of the NFGE component, a model for the stabilities/abundances of colloids has been constructed that covers both natural and introduced colloids (see Sections 4.2.3.1.3 and 4.2.3.2.3, respectively).

#### 4.2.1.1.4 Microbial Populations

Work done in several vadose zones in arid and semiarid sites indicates that the total numbers of microbes that are considered ambient populations range from $10^4$ to $10^7$ cells/g dry wt. (Kieft et al. 1993). Microbial analyses conducted in the Exploratory Studies Facility (ESF) have determined the existence of aerobic heterotrophs and autotrophs (Ringelberg et al. 1997). The organisms present include the following types: iron-oxidizing, sulfur oxidizing, and nitrifying organisms. Cell counts for autotrophs ranged between 10 and 500 cells/g dry wt. and for the heterotrophs between $3.2 \times 10^4$ to $2 \times 10^5$ cells per gram. Similar investigations were conducted on tuff samples taken from nearby Ranier Mesa and resulted in viable cell counts of about $10^4$ per g of crushed tuff (Keift et al. 1993). Kieft et al. (1993) also stated that in the various vadose systems there are many populations that are growth limited, most by water or organic carbon. However, some systems were growth limited by nitrogen or phosphorous.

### 4.2.1.2 Processes Driven by Thermal Perturbations

Water entering the drift will have variable composition as a function of time as a result of the heating of the system driving processes such as boiling/condensation and reaction of both heated and condensate waters with minerals and gases in the fractures of the host rocks (Arthur and Murphy 1989; Glassley 1993; Murphy 1993; Wilder 1996; Lichtner and Seth 1996; Glassley 1997; Hardin et al. 1998, Section 6.2.2). These reacted, or thermally perturbed, fluid compositions may flow down fracture pathways and enter potential emplacement drifts where they could undergo reaction with introduced materials or be boiled again and deposit mineral precipitates containing salts (Glassley 1993; Murphy and Pabalan 1994; Wilder 1996; Lichtner and Seth 1996). The total amounts of salts deposited within the drifts will depend to some extent on the composition of ambient water within the UZ.

As temperature increases, a number of changes may impact the geochemical behavior of the near-field environment. Mineral stabilities and phase equilibria are temperature dependent, and the rates at which reactions occur will generally increase at higher temperatures. Both continuous reactions such as the gradual dehydration or shift in cation composition of a solid phase, and discontinuous reactions such as the disappearance of a phase outside of its stability range, will occur as temperature increases (Glassley 1993; Murphy 1993; Hardin et al. 1998, Sections 5 and 6). The higher temperatures in the near-field may result in regions where attainment of thermochemical equilibrium can be assumed (Glassley 1993). Mineral transformation reactions, as well as precipitation/dissolution reactions will cause changes in porosity and permeability of the system as temperature increases (extending out into the geosphere—see Sections 5.6 and 5.7 in Hardin et al. 1998) and will result in a change in both the type and distribution of minerals present in the near-field (Glassley 1993; Wilder 1996).

The extent to which these effects may reach into the geosphere is illustrated by the potential extensive alteration of the basal vitrophyeare of the Topopah Spring tuff with concurrent large

changes in calculated porosity (Wilder 1996; Hardin et al. 1998, Sections 5.6 and 5.7). Such changes may impact the hydrologic properties of the system as well as the near-field and geosphere transport properties. The increased temperatures will vaporize much of the water in the near-field as an above-boiling zone forms in the very near-field (Glassley 1993). This transition will increase the capacity of the system to transport moisture as volatiles and will result in precipitation of all dissolved solids from boiling fluids in the near-field. Condensation of steam as water in cooler regions above the potential repository horizon will dissolve new material, which could be transported through fractures back down into the boiling zone with subsequent boiling and phase precipitation. This refluxing could produce porosity and permeability changes that may impact the near-field hydrology (Glassley 1993; Hardin et al. 1998, Section 5.6).

Because boiling of fluids will occur, mineral precipitates including salts will form in the region of boiling. Water undergoing boiling/evaporation or reacting with precipitated salts will become concentrated in a number of dissolved constituents either in close proximity to, or within, potential emplacement drifts (Hardin et al. 1998, Section 6.2.2). Such fluids represent a second end-member for reaction with the EBS. Currently these fluid compositions are primarily constrained by the results of geochemical mass-transfer calculations for simplified systems designed to simulate the evaporation/boiling that would occur within a thermally perturbed repository environment. Results from two such calculations (Murphy and Pabalan 1994; Wilder, 1996; Hardin et al. 1998, Section 6.2.2) are discussed here.

In one calculation (Wilder 1996; Hardin et al. 1998 Section 6.2.2), ~J-13 water evaporates/boils along a temperature rise from ambient to 95°C at equilibrium with atmospheric gases. These calculations represent 95 percent evaporation. The second set of calculations (Murphy and Pabalan 1994) starts with model water evolved at 75°C (heated J-13 water that has reacted with tuff), heats it instantaneously to 100 C in equilibrium with atmospheric oxygen and the calculated $CO_2$ fugacity. (This latter parameter value is higher than atmospheric values and was derived from a coupled reactive transport calculation in which both gas and fluid flow were calculated.) The compositions resulting from this second set are given up to about 99.6 percent evaporation. Even though the results of these two calculations are not directly comparable (because they represent different compositional systems and different controls on the gas phase), they appear to be roughly consistent. Relative to ambient compositions these fluids have, in general, high ionic strength (greater than 1 molal stoichiometric ionic strength for the 99.6 percent evaporated case), are enriched in alkalis, chloride, sulfate, and other ligands ($F^{\&}$, and $HCO_3^{\&}$), and have higher pH (~9.5).

Because mineral precipitation occurs throughout these calculations (calcite, silica polymorphs, etc.), these compositions do not represent simply concentrated ambient values, but are selectively concentrated. In both sets of calculations, the dissolved Ca content is low (<50 mg/kg) because calcite precipitation depletes the fluid of Ca. However, other elements that are conservative within the aqueous phase are orders of magnitude higher than at ambient conditions. For example, at the 99 percent and 99.6 percent evaporation points, chloride concentrations are about 100-times and about 250-times higher, respectively, than the average value for J-13 water (Murphy and Pabalan 1994).

Modeling results of water evaporation indicate that resultant composition may be profoundly affected by the gas phase assumed to be in equilibrium with the evaporating waterXi.e., whether the system behaves as open to the atmosphere or in a closed manner (Wilder 1996; Hardin et al. 1998, Section 6.2.2). In equilibrium with the atmosphere gas, initial ~J-13 water evolves to higher pH (>9.5) and lower Eh (~+500 mV) at high degrees of evaporation, compared to the case where the system is isolated from the atmosphere for which the final values are pH < 6.8 and Eh > +650 mv. The model results are very sensitive to the constraints on $CO_2$ fugacity (Murphy and Pabalan 1994), with different solid phases precipitating for lower $CO_2$ fugacities. These results emphasize the need to have a model that incorporates consistently the evolution of near-field gas composition, and the need to have such constraints defined for each scenario.

The NFGE component incorporates model calculations of mineral precipitation and salt formation representing the processes that will deposit minerals in the potential drifts. These analyses are meant to coarsely capture the effects of the complex process of potential salt precipitation within rock fractures during boiling, redissolution as the relative humidity (RH) increases enough for brines to form, movement of such brines into the potential drifts, and reprecipitation of salts on the waste package surface. Because the waste package surface should remain hottest and driest for the longest period, it is this place within the potential drifts that final salt precitipation is likely to occur. The conceptual model for these calculations is discussed below in Section 4.2.3.2.2.4, implementation of this model is discussed in Section 4.4.3.2.4, and the results are given in Section 4.6.2.2.3.

In addition to the mineral precipitation and water compositional changes, introduced substances such as cementitious materials (discussed below) will undergo phase transformations that will include dehydration reactions as fluids are expelled from pores and from mineral structures (Bruton et al. 1993a, 1993b; Meike et al. 1994). Model results suggest that calcite precipitation will occur at higher temperature limited only by the Ca supply (Murphy 1993), which could mean that Ca supplied from near-field cementitious materials may enhance the abundance of calcite precipitated (and retardation of $CO_2$) in close proximity to the potential repository. This aspect of the evolution of cementitious materials is one that could control, in large part, the fluid composition in equilibrium with the evolved material as discussed in the next section.

The thermally driven perturbations to the system will also affect the flux and composition of gas entering the potential emplacement drifts (Murphy 1991; Glassley 1993; Codell and Murphy 1992; Murphy and Pabalan 1994; Lichtner and Seth 1996; Wilder 1996; Glassley 1997; Hardin et al. 1998, Section 5.7.1). One major process affecting the in-drift gas composition is the boiling of the pore water, which is expected to drive out most of the air component of the gas from the drift environment (Murphy 1991; Pruess et al. 1990; Murphy and Pabalan 1994; Dunlap et al. 1997, see Chapter 3). The changes in the air mass-fraction of the gas will drive changes in the water chemistry and changes to the solid materials in the drifts because of, for example, the interaction of $CO_2$ gas with (a) water in terms of pH controls, and (b) cementitious materials in terms of calcite formation and neutralization of alkalinity. These interactions between the water, the carbon dioxide, and the introduced materials may play a key role in determining some of the major chemical conditions of the thermally perturbed system.

#### 4.2.1.3 Processes Driven by Introduced Materials

During construction of potential emplacement drifts, a number of substances that are likely to remain in the system over geologic time will be introduced into the system to create an in-drift set of solids dominated by the introduced engineered materials, rather than by the host lithology. The repository and waste package design groups have provided information on design materials compositions, masses, and locations that help to define the NFGE (see Section 4.3). These materials may include a wide variety of specific compounds, but there are three main categories that potentially will be abundant after closure (as part of the waste package or as structural components): steels (waste package and support, some ground support), cementitious materials (concrete liner, pier, and invert), and organic substances (within concrete mix).

The reaction of these materials with the water and gas fluxing through the drift will alter the composition of water that may contact both the waste packages and waste forms, and the composition of water in which radionuclides transport through the engineered barrier system. In addition, the EBS component materials will be altered by this reaction. The concrete will alter and organic constituents may provide abundant nutrients for microbes. Microbial activity may alter pH and $CO_2$ fugacity within the drift. The waste forms themselves also represent substantial solid masses that will affect fluid composition within the potential drifts for some period of time (CRWMS M&O 1997a). Some of these materials could supply colloids that may be more effective at transporting radionuclides than are natural colloids.

##### 4.2.1.3.1 Steel/Corrosion Products

Reaction of water with steel (much of which is iron [Fe], although other components are present in abundance in many steel alloys, including chromium [Cr] and nickel [Ni]) in the potential drifts will liberate metal cations to the aqueous phase. This material certainly increases the source mass for Fe in the system and could increase the concentration of dissolved Fe in the fluids. The natural groundwaters are relatively poor in dissolved Fe, and the analyzed values probably represent colloidal material (Harrar et al. 1990). The major lithologies at the site in the potential repository horizon are felsic tuffs that contain about 1 to 3 percent total iron oxide, representing a relatively low Fe content for igneous rocks (Lipman et al. 1966; CRWMS M&O 1998a, Section 3.5).

The alteration of steels will produce Fe-oxide and -hydroxide corrosion products within the drift and may form Fe-silicate minerals. As the Fe in the steel oxidizes, it represents a sink for oxygen and could be a mechanism for generating locally reducing conditions if the oxygen flux into the potential drift is low enough. Such oxidation reactions represent a source of metabolic energy for microbial activity within the potential emplacement drifts. The Fe-corrosion products will alter the sorptive properties of the EBS and affect transport of radionuclides within the drift. Colloids generated from steel corrosion products that strongly sorb radionuclides could provide additional radionuclide transport capabilities (Meike and Wittwer 1993; Triay et al. 1995). Because of the large amount of steel planned to be used in the potential repository, these types of colloids could have a large source capacity relative to the natural Fe-oxyhydroxide colloids fluxing through the drift.

Table 4-18. EQ6 Aggregate and Steel Fiber Input Information.

| Component | Phase | Value (moles) | EQ6 Relative Reaction Rate (moles reactant/moles reaction) |
|---|---|---|---|
| Coarse Agg | Annite | 178.97 | 1E-03 |
| Coarse Agg | Phlogopite | 43.79 | 1E-03 |
| Coarse Agg | Sanidine-high | 2774.84 | 1E-03 |
| Coarse Agg | Albite | 5666.94 | 1E-03 |
| Coarse Agg | Anorthite | 363.83 | 1E-03 |
| Coarse Agg | Pyrophyllite | 441.48 | 1E-03 |
| Coarse Agg | Quartz | 12441.57 | 1E-03 |
| Coarse Agg | Cristobalite-a | 15163.56 | 1E-03 |
| Fine Agg | Annite | 139.31 | 5E-03 |
| Fine Agg | Phlogopite | 37.97 | 5E-03 |
| Fine Agg | Sanidine-high | 2113.80 | 5E-03 |
| Fine Agg | Albite | 4324.45 | 5E-03 |
| Fine Agg | Anorthite | 291.29 | 5E-03 |
| Fine Agg | Pyrophyllite | 315.91 | 5E-03 |
| Fine Agg | Quartz | 11447.94 | 5E-03 |
| Fine Agg | Cristobalite-a | 13952.53 | 5E-03 |
| Steel Fiber | Fe-Metal | 3028.66 | 1E-05 |

Table 4-19. EQ3NR Input Files for Generating EQ6 Pickup Files.

| File Name: | PerAcon1.3l | perBcon1.3l | perCcon1.3l | periodD1.3l | PeriodE.3l | periodF.3l |
|---|---|---|---|---|---|---|
| Period | A | B | C | D | E | F |
| Parameter | Setting | Setting | Setting | Setting | Setting | Setting |
| Temperature | 95.0 | 95.0 | 95.0 | 70.0 | 70.0 | 30.0 |
| PH | Charge balance | Charge balance | Charge balance | Charge balance | Charge balance | Charge balance |
| Log $fO_2$ | -3.7 | -7.7 | -2.7 | -1.7 | -0.7 | -0.7 |
| $HCO_3^-$ | Log $fCO_2$ = -4.0 | Log $fCO_2$ = -10.0 | Log $fCO_2$ = -5.0 | Log $fCO_2$ = -4.0 | Log $fCO_2$ = -3.0 | Log $fCO_2$ = -3.0 |
| $Na^+$ | 461.00 mg/l | 461.00 mg/l | 461.00 mg/l | 45.788 mg/l | 45.788 mg/l | 45.788 mg/l |
| $Fe^{2+}$ | 7.16E-07 | 7.16E-07 | 7.16E-07 | Nontronite-Ca | Nontronite-Ca | Nontronite-Ca |
| $SiO_2$(aq) | 5.09E-03 | 6.13E-03 | 7.89E-03 | Cristobalite(alpha) | Cristobalite(alpha) | Cristobalite(alpha) |
| $Ca^{2+}$ | Calcite | 2.62E-06 | 1.01E-05 | Calcite | Calcite | Calcite |
| $K^+$ | 50.60 mg/l | 50.70 mg/l | 50.60 mg/l | 5.04 mg/l | 5.04 mg/l | 5.04 mg/l |
| $Mg^{2+}$ | 5.74E-06 mg/l | 1.40E-07 mg/l | 2.42E-07 mg/l | Saponite-Ca | Saponite-Ca | Saponite-Ca |
| $F^-$ | 21.90 mg/l | 21.90 mg/l | 21.9 mg/l | 2.17 mg/l | 2.17 mg/l | 2.17 mg/l |
| $Cl^-$ | 71.80 mg/l | 71.80 mg/l | 71.80 mg/l | 7.138 mg/l | 7.138 mg/l | 7.138 mg/l |
| $SO_4^{2-}$ | 1.93E-03 | 1.93E-03 | 1.93E-03 | 18.39 mg/l | 18.39 mg/l | 18.39 mg/l |
| $Al^{3+}$ | 1.46E-02 mg.l | 8.05E-02 mg/l | 1.92E-02 | Montmorillonite-Ca | Montmorillonite-Ca | Montmorillonite-Ca |
| Database | COM | COM | COM | COM | COM | COM |
| Suppressed Phases: Quartz, talc, and tridymite | | | | | | |

Table 4-20. Thermal Hydrologic Information.

| Repository Location | Infiltration Conditions | Period | Time Period (years) | Thermal Hydrologic Scenario (°C) |
|---|---|---|---|---|
| CC | I | A | 0–200 | 95 |
| CC | I | B | 200–1,000 | 95 |
| CC | I | C | 1,000–2,000 | 95 |
| CC | I | D | 2,000–4,000 | 70 |
| CC | I | E | 4,000–11,000 | 70 |
| CC | I | F | 11,000–100,000 | 30 |

Table 4-21. Abstracted Gas Information for Thermal/Hydrologic Periods.

| Period | $CO_2$ fugacity (ppm) | $CO_2$ Reservoir (moles) | $O_2$ fugacity (ppm) | $O_2$ Reservoir (moles) |
|---|---|---|---|---|
| A | 100 | 228.39 | 200 | 506.23 |
| B | 1E-04 | 230.19 | 2E-02 | 1,002.74 |
| C | 10 | 372.29 | 2,000 | 25,149.51 |
| D | 100 | 979.31 | 20,000 | 173,780.88 |
| E | 1,000 | 4,161.19 | 200,000 | 531,265.49 |
| F | 1,000 | 51,305.84 | 200,000 | 1,203,304.66 |

Table 4-22. Scaled Gas Reservoirs Used in the EQ6 Simulations.

| Period | Gas Reservoir Scaling Factor | $CO_2$ Reservoir (moles/m liner-mol Ca reacted) | $O_2$ Reservoir (moles/m liner-mol Ca reacted) |
|---|---|---|---|
| A | 3.75E-04 | 8.57E-02 | 1.90E-01 |
| B | 3.75E-04 | 8.64E-02 | 3.76E-01 |
| C | 3.75E-04 | 1.40E-01 | 9.43E+00 |
| D | 3.75E-04 | 3.67E-01 | 6.52E+01 |
| E | 3.75E-04 | 1.56E+00 | 1.99E+02 |
| F | 3.75E-04 | 1.92E+01 | 4.51E+02 |

Table 4-23. EQ3NR Calculated Fluid Compositions Used in the EQ6 Runs.

| Code | EQ3NR V7.2b | EQ3NR V7.2b | EQ3NR V7.2b | EQ3NR V7.2b | EQ3NR V7.2b | EQ3NR V7.2b |
|---|---|---|---|---|---|---|
| Input File | perAcon1.3I | perBcon1.3I | perCcon1.3I | PeriodD.3I | PeriodE.3I | periodF.3I |
| Output File | perAcon1.3O | perBcon1.3O | perCcon1.3O | PeriodD.3O | PeriodE.3O | periodF.3O |
| Pickup File | perAcon1.3P | perBcon1.3P | perCcon1.3P | PeriodD.3P | PeriodE.3P | periodF.3P |
| Period | A | B | C | D | E | F |
| Parameter | Value | Value | Value | Value | Value | Value |
| Temperature | 95 | 95 | 95 | 70 | 70 | 30 |
| pH | 8.06 | 8.05 | 8.05 | 8.94 | 8.25 | 8.12 |
| $Al^{3+}$, m | 5.41E-07 | 2.98E-06 | 7.12E-07 | 6.06E-07 | 1.52E-07 | 4.89E-09 |
| $Ca^{2+}$, m | 5.24E-03 | 2.62E-06 | 1.01E-05 | 4.27E-05 | 9.44E-05 | 3.18E-04 |
| Cl-, m | 2.03E-03 | 2.03E-03 | 2.03E-03 | 2.01E-04 | 2.01E-04 | 2.01E-04 |
| F-, m | 1.15E-03 | 1.15E-03 | 1.15E-03 | 1.14E-04 | 1.14E-04 | 1.14E-04 |
| $Fe^{2+}$, m | 7.16E+00 | 7.16E+00 | 7.16E+00 | 1.74E-15 | 1.74E-15 | 2.17E-14 |
| HCO3-, m | 8.06E-05 | 6.99E-11 | 6.97E-06 | 7.60E-04 | 1.46E-03 | 2.09E-03 |
| K+, m | 1.29E-03 | 1.30E-03 | 1.29E-03 | 1.29E-04 | 1.29E-04 | 1.29E-04 |
| $Mg^{2+}$, m | 2.36E-10 | 5.76E-12 | 9.96E-12 | 5.58E-09 | 1.47E-07 | 1.66E-05 |
| Na+, m | 2.01E-02 | 2.01E-02 | 2.01E-02 | 1.99E-03 | 1.99E-03 | 1.99E-03 |
| $SO4^{2+}$, m | 1.93E-03 | 1.93E-03 | 1.93E-03 | 1.91E-04 | 1.91E-04 | 1.91E-04 |
| SiO2(aq), m | 5.09E-03 | 6.13E-03 | 7.89E-03 | 1.79E-03 | 1.36E-03 | 4.42E-04 |

Note: concentrations in mol/kg, temperature in °C

Table 4-24. Characteristics of Cement Dissolution, after Berner (1990).

| Stage | Control | Effect |
|---|---|---|
| 1 | Alkali hydroxides (NaOH & KOH) | - 12.5<pH<14<br>- highest ionic strength |
| 2 | portlandite & CSH dissolution | - 12<pH<12.5 |
| 3 | hydrogarnet – ettringite dissolution sequence | - 8<pH<12 |

Table 4-25. Relative Reaction Rates (rk1) Used in the Sensitivity Analysis.

| Phase | Baseline rk1 | rk1 x 5 | rk1/5 | rk1 = 1.0 | rk1 = 0.1 |
|---|---|---|---|---|---|
| Ettringite | 0.1 | 0.5 | 0.02 | 1.0 | 0.1 |
| CSH17gel | 1.0 | 5.0 | 0.2 | 1.0 | 0.1 |
| Brucite | 0.1 | 0.5 | 0.02 | 1.0 | 0.1 |
| Fe-Hydrogarnet | 0.025 | 0.125 | 5E-03 | 1.0 | 0.1 |
| Al-Hydrogarnet | 0.025 | 0.125 | 5E-03 | 1.0 | 0.1 |
| Portlandite | 5.0 | 25.0 | 1.0 | 1.0 | 0.1 |
| Coarse Aggregate Phases | 1E-03 | 5E-03 | 2E-04 | 1.0 | 0.1 |
| Fine Aggregate Phases | 5E-03 | 2.5E-02 | 1E-03 | 1.0 | 0.1 |
| Iron Fiber | 1E-05 | 5E-05 | 2E-06 | 1.0 | 0.1 |

Table 4-26. Scaled Gas Reservoir Data.

| Period | Gas | Baseline (*moffg*) | 5x (*moffg*) | x/5 (*moffg*) | X=1.0 (*moffg*) | x=0.1 (*moffg*) |
|---|---|---|---|---|---|---|
| A | $O_2$ | 1.90E-01 | 9.50E-01 | 3.80E-02 | 3.75E-01 | 3.75E-02 |
| | $CO_2$ | 8.57E-02 | 4.28E-01 | 1.71E-02 | 1.69E-01 | 1.69E-02 |
| B | $O_2$ | 3.76E-01 | 1.88E+00 | 7.52E-02 | 7.42E-01 | 7.42E-02 |
| | $CO_2$ | 8.64E-02 | 4.32E-01 | 1.73E-02 | 1.70E-01 | 1.70E-02 |
| C | $O_2$ | 9.43E+00 | 4.72E+01 | 1.89E+00 | 1.86E+01 | 1.86E+00 |
| | $CO_2$ | 1.40E-01 | 6.98E-01 | 2.79E-02 | 2.76E-01 | 2.76E-02 |
| D | $O_2$ | 6.52E+01 | 3.26E+02 | 1.30E+01 | 1.29E+02 | 1.29E+01 |
| | $CO_2$ | 3.67E-01 | 1.84E+00 | 7.35E-02 | 7.25E-01 | 7.25E-02 |
| E | $O_2$ | 1.99E+02 | 9.96E+02 | 3.99E+01 | 3.93E+02 | 3.93E+01 |
| | $CO_2$ | 1.56E+00 | 7.81E+00 | 3.12E-01 | 3.08E+00 | 3.08E-01 |
| F | $O_2$ | 4.51E+02 | 2.26E+03 | 9.03E+01 | 8.91E+02 | 8.91E+01 |
| | $CO_2$ | 1.92E+01 | 9.62E+01 | 3.85E+00 | 3.08E+00 | 3.80E+00 |

Table 4-27. Equilibrium Reactions Considered in the Stage-1 Simulations and Their Equilibrium Constants as Polynomial Functions of Temperature.

| Aqueous Equilibrium Reactions | * log $K^{eq}$ |
|---|---|
| $H_2O = H^+ + OH^-$ | $a_0$=-0.1494E+02<br>$a_1$=0.4171E-0<br>$a_2$=-0.1917E-03<br>$a_3$=0.4950E-06<br>$a_4$= -0.6159E-09 |
| $CO_2(aq) + H_2O = H^+ + HCO_3^-$ | -0.6576E+01<br>0.1198E-01<br>-0.1362E-03<br>0.4131E-06<br>-0.5483E-09 |
| $HCO_3^- = H^+ + CO_3^{--}$ | 0.1062E+02<br>-0.1397E-01<br>0.1143E-03<br>-0.3352E-06<br>0.4687E-09 |
| $HSiO_3^- + H^+ = SiO_2(aq) + H_2O$ | 0.1033E+02<br>-0.1707E-01<br>0.4438E-04<br>0.3611E-07<br>-0.9495E-10 |
| $CaCO_3(aq) + H^+ = Ca^{++} + HCO_3^-$ | 0.7500E+01<br>-0.2156E-01<br>0.7888E-04<br>-0.1821E-06<br>0.8651E-10 |
| $CaHCO_3^+ = Ca^{++} + HCO_3^-$ | -0.1091E+01<br>0.3525E-02<br>-0.9368E-04<br>0.3085E-06<br>-0.4615E-09 |
| $NaCO_3^- + H^+ = Na^+ + HCO_3^-$ | 0.9810E+01<br>-0.2859E-02<br>0.1433E-03<br>-0.3573E-06<br>0.3362E-09 |
| $NaHCO_3(aq) = Na^+ + HCO_3^-$ | -0.3675E+00<br>0.8192E-02<br>-0.9257E-06<br>-0.4679E-07<br>0.2168E-09 |
| $NaCl = Na^+ + Cl^-$ | 0.8298E+00<br>-0.1559E-02<br>-0.2947E-04<br>0.1183E-06<br>-0.2367E-09 |

Table 4-27. (continued).

| Aqueous Equilibrium Reactions | * log $K^{eq}$ |
|---|---|
| $NaHSiO_3(aq) + H^+ = Na^+ + SiO_2(aq) + H_2O$ | 0.8425E+01<br>-0.5331E-02<br>-0.2584E-04<br>0.2532E-06<br>-0.4395E-09 |
| $UO_2(CO_3)_3^{---} + 3H^+ = UO_2^{++} + 3\ HCO_3^-$ | 0.9493E+01<br>-0.4015E-03<br>-0.5581E-04<br>0.1200E-06<br>-0.2995E-09 |
| $UO_2(CO_3)_2^{--} + 2H^+ = UO_2^{++} + 2\ HCO_3^-$ | 0.4492E+01<br>-0.3047E-01<br>0.4683E-04<br>-0.7901E-07<br>-0.7331E-10 |
| $UO_2(CO_3)\ (aq) + H^+ = UO_2^{++} + HCO_3^-$ | 0.9531E+00<br>-0.1163E-01<br>-0.3975E-08<br>0.8229E-07<br>-0.3169E-09 |
| $UO_2(OH)_3^- + 3H^+ = UO_2^{++} + 3H_2O$ | 19.2227 |
| $UO_2(OH)_2\ (aq) + 2H^+ = UO_2^{++} + 2H_2O$ | 10.3155 |
| $UO_2(OH)^+ + H^+ = UO_2^{++} + H_2O$ | 0.5910E+01<br>-0.3035E-01<br>0.1067E-03<br>-0.2529E-06<br>0.2606E-09 |
| **Gaseous-Aqueous Equilibrium Reactions** | |
| $CO_2(g) + H_2O = H^+ + HCO_3^-$ | -0.7676E+01<br>-0.4984E-02<br>-0.2707E-04<br>0.1083E-06<br>-0.2044E-09 |
| $O_2(g) = O_2(aq)$ | 2.660<br>0.1142E-1<br>-0.9291E-4<br>0.2735E-6<br>-0.3402E-9 |

* The numbers under the column of log $K^{eq}$ are the polynomial coefficients of equilibrium constants as a function of temperature. That is, $\log K^{eq} = a_0 + a_1T + a_2T^2 + a_3T^3 + a_4T^4$, where T is the temperature in °C.

Table 4-28. Solid Reactions.

| Solid | Reaction | *log $K^{eq}$ (Sources) | | Source | |
|---|---|---|---|---|---|
| | | DS-1 | DS-2 | DS-1 | DS-2 |
| Spent Fuel<br>$UO_2$ | $UO_2 + 2\ H^+ + 0.5\ O_2(g) = UO_2^{++} + H_2O$ | $a_0$= 0.3118E+02<br>$a_1$=-0.1516E+00<br>$a_2$= 0.4863E-03<br>$a_3$=-0.1077E-05<br>$a_4$= 0.1083E-08 | | EQ3/6<br>(Uraninite) | |
| Uranophane<br>$Ca(UO_2)_2(SiO_3)_2(OH)_2$ | Uranophane + 6 $H^+$ = $Ca^{++}$ + 2 $SiO_2$(aq) + 2 $UO_2^{++}$ + 4 $H_2O$ | $a_0$= 17.2869 | 9.42 | EQ3/6 | Nguyen et al. 1992 |
| Schoepite<br>$UO_3{:}2H_2O$ | (Schoepite) + 2 $H^+$ = $UO_2^{++}$ 3 $H_2O$ | $a_0$= 0.5656E+01<br>$a_1$=-0.3578E-01<br>$a_2$= 0.1328E-03<br>$a_3$=-0.3213E-06<br>$a_4$= 0.3379E-09 | | EQ3/6 | |
| Soddyite<br>$(UO_2)_2(SiO_4){:}2H_2O$ | Soddyite + 4 $H^+$ = $SiO_2$(aq) + 2 $UO_2^{++}$ + 4 $H_2O$ | $a_0$= 0.3939 | 5.74 | EQ3/6 | Nguyen et al. 1992 |
| Na-Boltwoodite<br>$NaH_3OUO_2SiO_4{:}H_2O$ | Na-Boltwoodite + 3 $H^+$ = $Na^+$ + $SiO_2$(aq) + $UO_2^{++}$ + 4$H_2O$ | $a_0$= 14.5844 | 5.82 | EQ3/6 | Nguyen et al. 1992 |

* See the footnote of Table 1 for the explanation of polynomial coefficeints.

Table 4-29. Rate Constants of Solid Dissolution.

| | Spent Fuel | Schoepite | | Soddyite | | Uranophane | *Na-boltwoodite |
|---|---|---|---|---|---|---|---|
| | | DS-1 | DS-2 | DS-1 | DS-2 | | |
| $k_0$ (mol/m$^2$-sec) | 0.00137 | 3.89E+3 | 6.3E+6 | 6.8E+8 | 3.91E+25 | 5.56E+35 | 2.0E+12 |
| $E_a$ (J/mol) | 29697 | 0 | 0 | 0 | 0 | 0 | 0 |
| $k_1$ (m/sec) | 3.555E-8 | 0.253 | 416.94 | 8.93E+4 | 5.12E+21 | 1.25E+32 | 1.94E+8 |
| $\ln k_1$ | -17.1537 | -1.374 | 6.033 | 11.4 | 49.989 | 73.905 | 19.08 |

- The rate constant for Na-boltwoodite is estimated based on the uranophane data.

Table 4-30. Equilibrium Reactions Considered in the Stage-2 Simulations and Their Equilibrium Constants as Polynomial Functions of Temperature.

| Aqueous Equilibrium Reactions | * log $K^{eq}$ |
|---|---|
| $H_2O = H^+ + OH^-$ | -0.1494E+02<br>0.4171E-01<br>-0.1917E-03<br>0.4950E-06<br>-0.6159E-09 |
| $CO_2(aq) + H_2O = H^+ + HCO_3^-$ | -0.6576E+01<br>0.1198E-01<br>-0.1362E-03<br>0.4131E-06<br>-0.5483E-09 |
| $HCO_3^- = H^+ + CO_3^{--}$ | 0.1062E+02<br>-0.1397E-01<br>0.1143E-03<br>-0.3352E-06<br>0.4687E-09 |
| $HSiO_3^- + H^+ = SiO_2(aq) + H_2O$ | 0.1033E+02<br>-0.1707E-01<br>0.4438E-04<br>0.3611E-07<br>-0.9495E-10 |
| $CaCO_3(aq) + H^+ = Ca^{++} + HCO_3^-$ | 0.7500E+01<br>-0.2156E-01<br>0.7888E-04<br>-0.1821E-06<br>0.8651E-10 |
| $CaHCO_3^+ = Ca^{++} + HCO_3^-$ | -0.1091E+01<br>0.3525E-02<br>-0.9368E-04<br>0.3085E-06<br>-0.4615E-09 |
| $NaCO_3^- + H^+ = Na^+ + HCO_3^-$ | 0.9810E+01<br>-0.2859E-02<br>0.1433E-03<br>-0.3573E-06<br>0.3362E-09 |
| $NaHCO_3(aq) = Na^+ + HCO_3^-$ | -0.3675E+00<br>0.8192E-02<br>-0.9257E-06<br>-0.4679E-07<br>0.2168E-09 |
| $NaCl = Na^+ + Cl^-$ | 0.8298E+00<br>-0.1559E-02<br>-0.2947E-04<br>0.1183E-06<br>-0.2367E-09 |
| $NaHSiO_3(aq) + H^+ = Na^+ + SiO_2(aq) + H_2O$ | 0.8425E+01<br>-0.5331E-02<br>-0.2584E-04<br>0.2532E-06<br>-0.4395E-09 |

Table 4-30. (continued).

| Aqueous Equilibrium Reactions | * log $K^{eq}$ |
|---|---|
| $UO_2(CO_3)_3^{---} + 3H^+ = UO_2^{++} + 3\ HCO_3^-$ | 0.9493E+01<br>-0.4015E-03<br>-0.5581E-04<br>0.1200E-06<br>-0.2995E-09 |
| $UO_2(CO_3)_2^- + 2H^+ = UO_2^{++} + 2\ HCO_3^-$ | 0.4492E+01<br>-0.3047E-01<br>0.4683E-04<br>-0.7901E-07<br>-0.7331E-10 |
| $UO_2(CO_3)\ (aq) + H^+ = UO_2^{++} + HCO_3^-$ | 0.9531E+00<br>-0.1163E-01<br>-0.3975E-08<br>0.8229E-07<br>-0.3169E-09 |
| $UO_2(OH)_3^- + 3H^+ = UO_2^{++} + 3H_2O$ | 19.2227 |
| $UO_2(OH)_2\ (aq) + 2H^+ = UO_2^{++} + 2H_2O$ | 10.3155 |
| $UO_2(OH)^+ + H^+ = UO_2^{++} + H_2O$ | 0.5910E+01<br>-0.3035E-01<br>0.1067E-03<br>-0.2529E-06<br>0.2606E-09 |
| $Np(OH)_{4(aq)} + H^+ = Np(OH)_3^+ + H_2O$ | 3.8000 |
| $Np(OH)_5^- + H^+ = Np(OH)_{4(aq)} + H_2O$ | 4.7000 |
| $NpO_2^{++} + 4\ H_2O = Np(OH)_5^- + 3H^+ + 0.5O_2(aq)$ | -24.0615 |
| $NpO_2(OH)^+ + H^+ = NpO_2^{++} + H_2O$ | 5.2000 |
| $NpO_2(CO_3)_2^- + 2H^+ = NpO_2^{++} + 2\ HCO_3^-$ | 6.6576 |
| $NpO_2(CO_3)_3^{---} + 3H^+ = NpO_2^{++} + 3\ HCO_3^-$ | 10.5864 |
| $NpO_2(OH)\ (aq) + H^+ = NpO_2^+ + H_2O$ | 8.9000 |
| $NpO_2(CO_3)^- + H^+ = NpO_2^+ + HCO_3^-$ | 5.7288 |
| $NpO_2(CO_3)_2^{--} + 2H^+ = NpO_2^+ + 2\ HCO_3^-$ | 13.6576 |
| $NpO_2^+ + 3.5\ H_2O = Np(OH)_5^- + 2H^+ + 0.25O_2(aq)$ | -24.1683 |
| $NpO_2(CO_3)_3^{---} + 3H^+ = NpO_2^+ + 3\ HCO_3^-$ | 22.4864 |
| **Gaseous-Aqueous Equilibrium Reactions** | |
| $CO_2(g) + H_2O = H^+ + HCO_3^-$ | -0.7676E+01<br>-0.4984E-02<br>-0.2707E-04<br>0.1083E-06<br>-0.2044E-09 |
| $O_2(g) = O_2(aq)$ | 2.660<br>0.1142E-1<br>-0.9291E-4<br>0.2735E-6<br>-0.3402E-9 |

- See the footnote of Table 1 for the explanation of polynomial coefficeints.

Table 4-31. Inventory and U:Np Ratio.

| | Grams/MTIHM | Moles/MTIHM |
|---|---|---|
| $^{237}Np$ | 4.18E+2 | 1.764 |
| $^{241}Pu$ | 7.097E+2 | 2.945 |
| $^{241}Am$ | 4.701E+2 | 1.951 |
| U | 9.598E+5 | 4032.20 |
| Lumped $^{237}Np$ | | 6.66 |
| U:$^{237}Np$ | 4032.2 : 6.66 = | 1 : 0.0016 |

Table 4-32. Four Cases of Simulation from the Possible Combinations of Scenarios and Conditions.

| Conditions | Initial Amount of Schoepite (Cladding Failure) | Simulations |
|---|---|---|
| Condition-1 | 4.13% (11% ) | Case-1 |
| (Period 5) | 0.38% (1% ) | Case-2 |
| Condition-2 | 4.13% (11%) | Case-3 |
| (Period-6) | 0.38% (1% ) | Case-4 |

Table 4-33. Aqueous Solubilities (M) of Sodium and Potassium Salts at 100°C. Values Converted to Molal Concentrations from Solubilities Listed in the Handbook of Chemistry and Physics (Weast 1981), Unless Otherwise Indicated.

| Salt | Na | K |
|---|---|---|
| MCl | 6.7 | 7.6 |
| $M_2CO_3$ | 4.3 | 11.3 |
| MF | 1.2* | 25.8** |
| $M_2SO_4$ | 3.0 | 1.4 |
| $M_2SiO_3$ | s, d | s |
| $M_2Si_2O_5$ | s | nr |
| $MNO_3$ | 21.2 | 24.5 |

Key:

M = Na or K

nr = not reported

v = very

s = soluble

d = decomposes

* (Dean 1992 p. 5.20)

** at 80 ° C (Dean 1992 p. 5.17)

Table 4-34. Equilibrium Relative Humidity for Saturated Aqueous Solutions of Sodium and Potassium Salts at 100°C. Values Computed from Vapor Pressure Lowering Data Reported in the Handbook of Chemistry and Physics (Weast 1981) Unless Otherwise Indicated.

| Salt | Na | K |
|---|---|---|
| MCl | 76.8% | 80.0% |
| M2CO3 | 85.4% | nr |
| MF | nr | nr |
| M2SO4 | 90.3% | 96%** |
| M2SiO3 | nr | nr |
| M2Si2O5 | nr | nr |
| MNO3 | 65.5%* | < 81% |

Key:

M = Na or K

nr = not reported

< = less than (i.e., aqueous solution contains 10 g/L of salt and is not saturated with respect to the salt)

* at 80 °C (Dean 1992, p. 11.6)

** at 60 °C (Dean 1992, p. 11.6)

Table 4-35. Water Compositional Constraints on Colloid Abundances. Data are from CRWMS M&O 1998b, Section 6.3.6.1.

| Well | log ([Ca]+[Mg]) | log ([Na]+[K]) | Ionic Strength | log [coll] |
|---|---|---|---|---|
| WEL6 | -4.2 | -1.8 | 0.016101 | 6.7 |
| GO532 | -4.1 | -2.2 | 0.006627 | 6.7 |
| LEU | -3.6 | -1.9 | 0.013594 | 6 |
| 12 | -4.1 | -2.6 | 0.002830 | 8.6 |
| 11 | -4 | -2.4 | 0.004381 | 7.3 |
| 13 | -4 | -2.5 | 0.003562 | 8.5 |
| 10 | -3.8 | -2.5 | 0.003796 | 7.2 |
| 9 | -3.8 | -2.4 | 0.004615 | 6.8 |
| ZUR | -3.4 | -1.9 | 0.014182 | 5 |
| GTS | -3.8 | -3.1 | 0.001428 | 5.9 |
| j13 | -3.5 | -2.7 | 0.003260 | 6.6 |
| BAG2 | -3.9 | -3.5 | 0.000820 | 6.9 |
| 2 | -3.6 | -3.3 | 0.001506 | 5.7 |
| BDS | -2.3 | -1.4 | 0.059858 | 5 |
| MF | -3.4 | -3 | 0.002592 | 7.5 |
| 12 | -3.7 | -3.6 | 0.001049 | 7.3 |
| 4 | -3.7 | -3.6 | 0.001049 | 5.6 |
| 6 | -3.8 | -4.2 | 0.000697 | 7.2 |
| CIL139 | -3.6 | -3.8 | 0.001163 | 7.8 |
| 1 | -3.5 | -3.7 | 0.001464 | 6.3 |
| 5 | -3.6 | -4.1 | 0.001084 | 7.2 |
| 7 | -3.6 | -4.2 | 0.001068 | 6.6 |
| 8 | -3.4 | -3.8 | 0.001751 | 6.5 |
| MZD | -3.4 | -3.9 | 0.001718 | 6.4 |
| 16 | -3.4 | -4.1 | 0.001672 | 6.3 |
| MARK | -2.8 | -3.5 | 0.006656 | 4.7 |

Table 4-36. Temperature Dependant ΔG Relationships from 0°C to 150 °C for Selected Redox Half Reactions of C, N, S, Fe, Mn, H, and O. Table from Jolley (1998a) (TBV-370).

| Redox half reaction | | ΔGr° (cal/mol) vs. T(°C) | | | | ΔGr° (kJ/mol) vs. T(°C) | | |
|---|---|---|---|---|---|---|---|---|
| **Carbon** | RXN # | B0 | B1 | B2 | r^2 | B0 | B1 | B2 |
| CO2 + H+ + 2e- = HCOO- | C1 | 9.69E+03 | 2.79E+01 | 2.91E-02 | 0.9999 | 4.06E+01 | 1.17E-01 | 1.22E-04 |
| CO2 + 4H+ + 4e- = CH2O + H2O | C2 | 1.90E+04 | 5.89E+00 | 6.23E-02 | 0.9999 | 7.95E+01 | 2.46E-02 | 2.61E-04 |
| CO2 + 6H+ + 6e- = CH3OH + H2O | C3 | -4.58E+03 | 5.46E+00 | -6.96E-02 | 0.9996 | -1.92E+01 | 2.28E-02 | -2.91E-04 |
| HCOO- + 3H+ + 2e- = CH2O + H2O | C4 | -8.48E+03 | 7.80E+00 | -2.91E-02 | 0.9999 | -3.55E+01 | 3.26E-02 | -1.22E-04 |
| CO2 + 8H+ + 8e- = CH4 + 2H2O | C5 | -2.74E+04 | 2.18E+00 | -1.19E-01 | 0.9995 | -1.15E+02 | 9.14E-03 | -4.97E-04 |
| CH2O + 2H+ + 2e- = CH3OH | C6 | 1.52E+05 | -6.32E+01 | -7.98E-02 | 0.9969 | 6.37E+02 | -2.65E-01 | -3.34E-04 |
| HCOO- + 7H+ + 6e- = CH4 + 2H2O | C7 | -3.70E+04 | -2.57E+01 | -1.48E-01 | 0.9998 | -1.55E+02 | -1.08E-01 | -6.19E-04 |
| CH2O + 4H+ + 4e- = CH4 + H2O | C8 | 1.26E+05 | -1.00E+02 | -7.35E-03 | 0.9988 | 5.28E+02 | -4.20E-01 | -3.08E-05 |
| CH3OH + 2H+ + 2e- = CH4 + H2O | C9 | -2.28E+04 | -3.26E+00 | -4.91E-02 | 0.9998 | -9.53E+01 | -1.37E-02 | -2.06E-04 |
| CO32- + 10H+ + 8e- = CH4 + 3H2O | C10 | -5.35E+04 | -9.51E+01 | -1.91E-01 | 0.9999 | -2.24E+02 | -3.98E-01 | -7.98E-04 |
| CO32- + 6H+ + 4e- = CH2O + 2H2O | C11 | -2.17E+04 | -5.07E+01 | -1.47E-01 | 0.9999 | -9.08E+01 | -2.12E-01 | -6.16E-04 |
| CO32- + 8H+ + 6e- = CH3OH + 2H2O | C12 | 1.98E+05 | -6.83E-01 | -1.20E-01 | 0.9986 | 8.27E+02 | -2.86E-03 | -5.04E-04 |
| CO32- + 3H+ + 2e- = HCOO- + H2O | C13 | -1.32E+04 | -4.36E+01 | -1.07E-01 | 0.9999 | -5.53E+01 | -1.83E-01 | -4.50E-04 |
| **Nitrogen** | | | | | | | | |
| N2 + 6H+ + 6e- = 2NH3 | N1 | -1.64E+04 | -2.87E+01 | 9.55E-03 | 0.9998 | -6.86E+01 | -1.20E-01 | 4.00E-05 |
| N2 + 8H+ + 6e- = 2NH4+ | N2 | -4.15E+04 | -3.27E+01 | 3.24E-02 | 0.9996 | -1.74E+02 | -1.37E-01 | 1.36E-04 |
| NO2- + 7H+ + 6e- = NH3 + 2H2O | N3 | -1.11E+05 | -2.46E+01 | -1.07E-01 | 0.9999 | -4.66E+02 | -1.03E-01 | -4.49E-04 |
| NO3- + 2H+ + 2e- = NO2- + H2O | N4 | -3.76E+04 | -1.02E+01 | -1.69E-02 | 0.9999 | -1.57E+02 | -4.27E-02 | -7.07E-05 |
| NO3- + 10H+ + 8e- = NH4+ + 3H2O | N5 | -1.62E+05 | -3.59E+01 | -1.18E-01 | 0.9999 | -6.76E+02 | -1.50E-01 | -4.94E-04 |
| NO2- + 8H+ + 6e- = NH4+ + 2H2O | N6 | -1.24E+05 | -2.58E+01 | -1.01E-01 | 0.9999 | -5.19E+02 | -1.08E-01 | -4.23E-04 |
| NO3- 6H+ + 5e- = 0.5N2 + 3H2O | N7 | -1.41E+05 | -2.03E+01 | -1.30E-01 | 0.9999 | -5.89E+02 | -8.48E-02 | -5.45E-04 |
| 2NO2- + 8H+ + 6e- = N2 + 4H2O | N8 | -2.06E+05 | -2.01E+01 | -2.26E-01 | 0.9998 | -8.64E+02 | -8.42E-02 | -9.48E-04 |
| NO3- + 9H+ + 8e- = NH3 + 3H2O | N9 | -1.49E+05 | -3.52E+01 | -1.20E-01 | 0.9999 | -6.24E+02 | -1.47E-01 | -5.02E-04 |
| **Oxygen** | | | | | | | | |
| O2 + 4H+ + 4e- = 2H2O | O1 | -1.14E+05 | 1.76E+01 | -4.16E-02 | 0.9999 | -4.76E+02 | 7.35E-02 | -1.74E-04 |
| **Sulfur** | | | | | | | | |
| S + H+ + 2e- = HS- | S1 | 3.11E+03 | -1.05E+01 | 3.69E-02 | 0.9999 | 1.30E+01 | -4.41E-02 | 1.54E-04 |
| S + 2H+ +2e- = H2S | S2 | -1.27E+05 | -2.69E+00 | -1.19E-01 | 0.9998 | -5.32E+02 | -1.12E-02 | -4.99E-04 |
| SO4-2 + 9H+ + 8e- = HS- + 4H2O | S3 | -4.41E+04 | -7.13E+01 | -1.53E-01 | 0.9999 | -1.85E+02 | -2.99E-01 | -6.38E-04 |
| SO4-2 + 10H+ + 8e- = H2S + 4H2O | S4 | -5.34E+04 | -8.10E+01 | -2.36E-01 | 0.9999 | -2.23E+02 | -3.39E-01 | -9.89E-04 |
| HSO4- + 7H+ + 6e- = S + 4H2O | S5 | -4.51E+04 | -3.87E+01 | -1.12E-01 | 0.9999 | -1.89E+02 | -1.62E-01 | -4.68E-04 |
| SO4-2 + 8H+ + 6e- = S + 4H2O | S6 | -4.72E+04 | -6.06E+01 | -1.92E-01 | 0.9999 | -1.98E+02 | -2.54E-01 | -8.05E-04 |
| SO2 + 4e- + 4H+ = S + 2H2O | S7 | -4.13E+04 | -3.72E+00 | 7.20E-03 | 0.9991 | -1.73E+02 | -1.56E-02 | 3.01E-05 |
| SO32- + 7H+ + 6e- = HS- + 3H2O | S8 | -4.92E+04 | -6.68E+01 | -1.39E-01 | 0.9999 | -2.06E+02 | -2.80E-01 | -5.83E-04 |
| 2SO4-2 + 10H+ + 8e- = S2O3-2 + 5H2O | S9 | -5.04E+04 | -7.91E+01 | -2.15E-01 | 0.9999 | -2.11E+02 | -3.31E-01 | -9.00E-04 |
| **Hydrogen** | | | | | | | | |
| H+ + e- = 0.5H2 | H1 | 3.87E+02 | -1.54E+01 | -4.99E-03 | 0.9999 | 1.62E+00 | -6.44E-02 | -2.09E-05 |
| **Iron** | | | | | | | | |
| Fe2O3 + 6H+ + 6e- = 2Fe + 3H2O | F1 | 9.14E+03 | -4.13E+01 | -4.65E-02 | 0.9999 | 3.83E+01 | -1.73E-01 | -1.95E-04 |
| Fe2+ + 2e- = Fe | F2 | 2.26E+04 | -3.08E+01 | -1.88E-02 | 0.9999 | 9.48E+01 | -1.29E-01 | -7.87E-05 |
| Fe3+ + e- = Fe2+ | F3 | -1.68E+04 | -3.93E+01 | -3.44E-02 | 0.9999 | -7.01E+01 | -1.64E-01 | -1.44E-04 |
| Fe3O4 + 8H+ + 8e- = 3Fe + 4H2O | F4 | 1.71E+04 | -5.04E+01 | -6.08E-02 | 0.9999 | 7.16E+01 | -2.11E-01 | -2.55E-04 |
| FeOOH + 3H+ + e- = Fe2+ + 2H2O | F5 | -1.49E+04 | -8.63E+01 | -3.02E-02 | 0.9999 | -6.23E+01 | -3.61E-01 | -1.26E-04 |
| **Manganese** | | | | | | | | |
| MnO2 + 4H+ + 2e- = Mn2+ + 2H2O | M1 | -5.90E+04 | 6.49E+01 | -2.42E-01 | 0.9168 | -2.47E+02 | 2.72E-01 | -1.01E-03 |
| Mn3O4 + 8H+ + 2e- = 3Mn2+ + 4H2O | M2 | -2.95E+04 | -7.07E+00 | 4.80E+00 | 0.9807 | -1.24E+02 | -2.96E-02 | 2.01E-02 |

Table 4-37. Standard Default Input Parameters Used in MING Calculations.

| Default MING Input Parameters | Value | Source |
|---|---|---|
| Temperature Cut off | 120° | See section 4.2.5.2.4 |
| Humidity Cut off | 0.95 | See section 4.2.5.2.4 |
| Tunnel Diameter | 5.1 m | Repository design |
| Tunnel length | 1 m | Standard unit of length |
| Porosity | 0.2 | Assumed |
| Gas Buttons ($N_2$, $CO_2$, $O_2$) | On | See section 4.2.5.2.4 |
| Energy Cut off | 15 kJ | Grogan and McKinley (1991) |

Table 4-38. Reactant Compositions Used in rhe Energy Calculations for Each Material Used in the 21 PWR Case Calculations.

| Material Name | Reactant Compositions |
|---|---|
| Aluminum 6061 (TS) | Fe, $Mn^{2+}$ |
| C Steel ASTM A516 (CAM) | $CH_2O$, Fe, S, $Mn^{2+}$ |
| Neutronit A978 (BM) | $CH_2O$, Fe |
| 21 PWR Waste | $NO_3^-$, $CO_3^{2-}$, S, $Mn^{2+}$, Fe |
| Alloy C-22 ASTM B 575 (CRM) | Fe, $Mn^{2+}$, S, $CH_2O$ |
| Conductor Bar fittings | $CH_2O$, Fe |
| Type V Concrete | $CH_2O$, $Fe^{2+}$, SO42-, $Mn^{2+}$ |
| Gantry Rail | $CH_2O$, Fe, S, $Mn^{2+}$ |
| Rail Fittings | $CH_2O$, Fe, S |
| Water Reducer | $CH_2O$, $CH_3OH$, $NO_3^-$, $SO_3^{2-}$, $H_2S$ |
| Steel Fiber (ASTM A36) | $CH_2O$, Fe S |
| Superplasticizer | $CH_2O$, $SO_3^{2-}$ |
| Commo Cable | $CH_2O$ |

Table 4-39. Input Tracking.

| Near-Field Geochemical Environment Input Tracking Table 4-39 | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Name** | **Scale** | **Material** | **Property** | **Parameter Description** | **Model** | **Distribution Type** | **Units** | **Mean** | **Source** | **Q Status of Source** |
| **Incoming Gas (NFGE-1a)** | | | | | | | | | | |
| Temperature Constraints | drift | | | Temperatures for each period (A-F) | NFGE-1A | single value(s), variable per period | degrees Celsius | See Table 4-41 | See Section 4.5.1.1 | TBV |
| Abstracted Air Mass-Fraction | drift | | | Abstracted Air Mass-Fractions for each Period (A-F) | NFGE-1A | single value | fraction | see Table 4-8 | see Section 4.4.2.1 | TBV |
| Air Fluxes into the drift | drift | | | Air Fluxes into the drift as a function of time | NFGE-1A | single value | kg/m2-sec | output of 2-D TH model for cross section 233,400 | see Chapter 3 | TBV |
| $CO_2$ fraction in Air Period A 0 to 200 years | drift | | | carbon dioxide fraction in air | NFGE-1A | single value(s), variable per gas per period | parts/million | 100,000 | See Section 4.4.2.1 | TBV |
| $CO_2$ fraction in Air Period B to F 200 to 100,000 years | drift | | | carbon dioxide fraction in air | NFGE-1A | single value(s), variable per gas per period | parts/million | 1,000 | See Section 4.4.2.1 | TBV |
| $O_2$ fraction in Air Period A to F 0 to 100,000 years | drift | | | oxygen fraction in air | NFGE-1A | single value(s), variable per gas per period | parts/million | 200,000 | See Section 4.4.2.1 | TBV |
| $N_2$ fraction in Air Period A 0 to 200 years | drift | | | nitrogen fraction in air | NFGE-1A | single value(s), variable per gas per period | parts/million | 700,000 | See Section 4.4.2.1 | TBV |
| $N_2$ fraction in Air Period B to F 200 to 100,000 years | drift | | | nitrogen fraction in air | NFGE-1A | single value(s), variable per gas per period | parts/million | 800,000 | See Section 4.4.2.1 | TBV |
| **Incoming Water (NFGE-1B)** | | | | | | | | | | |
| Temperature Constraints | drift | | | Temperatures for each period (A-F) | NFGE-1B | single value(s), variable per period | degrees Celsius | See Table 4-41 | See Section 4.5.1.1 | TBV |
| Gas Composition and Budget, Periods A-F | drift | | | oxygen & carbon dioxide fugacity | NFGE-1B | single value(s), variable per gas per period | Parts/million | See Table 4-41 | See Section 4.5.1.1 | TBV |

Table 4-39. (continued).

| Near-Field Geochemical Environment Input Tracking Table 4-39 | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Name** | **Scale** | **Material** | **Property** | **Parameter Description** | **Model** | **Distribution Type** | **Units** | **Mean** | **Source** | **Q Status of Source** |
| Starting Water Compositions | N/A | | | Ambient Fracture water composition | NFGE-1B | Single values | Mg/l | See Table 4-2 | See Section 4.2.3.1.2 | TBV |
| **Water-Solids Chemistry—Corrosion products (NFGE-3A)** | | | | | | | | | | |
| Gas Composition and Budget, Periods A-F | Drift | | | oxygen & carbon dioxide fugacity | NFGE-3A | single value(s), variable per gas per period | parts/million | See Table 4-41 | See Section 4.5.1.1 | TBV |
| Water Compositions | N/A | | | Incoming water compositions into the drift | NFGE-3A | Single values | Mg/l | See Table 4-42 | See Section 4.5.1.2 | TBV |
| Temperature Constraints | drift | | | Temperatures for each period (A-F) | NFGE-3A | single value(s), variable per period | degrees Celsius | See Table 4-41 | See Section 4.5.1.1 | TBV |
| **Water-Solids Chemistry—Concrete (NFGE-3B)** | | | | | | | | | | |
| Gas Composition and Budget, Periods A-F | drift | | | oxygen & carbon dioxide fugacity | NFGE-3B | single value(s), variable per gas per period | parts/million | See Table 4-41 | See Section 4.5.1.1 | TBV |
| Scaled Gas Budget, Periods A-F | 1meter of drift | | | oxygen & carbon dioxide moles | NFGE-3B | single value(s), variable per gas per period | moles | See Table 4-22 | See Section 4.4.3.2.2.2 | TBV |
| Water Compositions | N/A | | | Incoming water compositions into the drift | NFGE-3B | Single values | Mg/l | See Table 4-42 | See Section 4.5.1.2 | TBV |
| Temperature Constraints | drift | | | Temperatures for each period (A-F) | NFGE-3B | single value(s), variable per period | degrees Celsius | See Table 4-41 | See Section 4.5.1.1 | TBV |
| Bulk Chemical Composition of Concrete | 1meter of drift | | | oxide weight percent composition of concrete components | NFGE-3B | single value(s) | weight percent | See Table 4-10 | QAP-3-12 1998a and CRWMS M&O 1997b. | TBV |
| Volume of Concrete Components per meter drift | 1meter of drift | | | Component masses per component | NFGE-3B | single value(s) | Cubic meter | 4.35 | See Section 4.3.1 and Figure 4-13 | TBV |
| Scaled Mass of Concrete Components per meter drift | 1meter of drift | | | Component masses per component | NFGE-3B | single value(s) | kilograms | See Table 4-11 | See Section 4.4.3.2.2.1 | TBV |

Table 4-39. (continued).

| Near-Field Geochemical Environment Input Tracking Table 4-39 | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Name** | **Scale** | **Material** | **Property** | **Parameter Description** | **Model** | **Distribution Type** | **Units** | **Mean** | **Source** | **Q Status of Source** |
| Concrete Component Mineralogy moles | 1meter of drift | | | component mineralogic masses | NFGE-3B | single value(s) | moles | See Table 4-12 | See Section 4.4.3.2.2.1 | TBV |
| Cement Mineral Thermochemical Data | NA | | | thermochemical data for cement phase minerals | NFGE-3B | single value(s) | NA | See Section 4.4.3.2.2.2 | Hardin et al 1998, Section 7, and Clodic, L., and A. Meike. 1997. | TBV |
| **Water-Solids Chemistry—Spent Fuel (nfge-3C)** | | | | | | | | | | |
| Rate constant for uranophane | Waste package | | | intrinsic value on how fast uranophane dissolves/precipitates | NFGE-3C | Single value | mol/m^2-sec | 5.56E+35 | Chapter 4.4, derived from Casas et al. 1994 | TBV |
| Rate constant for spent fuel | waste package | | | intrinsic value on how fast spent fuel dissolves/precipitates | NFGE-3C | single value | mol/m^2-sec | 0.00137 | Chapter 4.4, derived from Gray et al. 1992 | TBV |
| Rate constant for soddyite | waste package | | | intrinsic value on how fast soddyite dissolves/precipitates | NFGE-3C | single value | mol/m^2-sec | 3.91E+25 | Chapter 4.4, derived from Perez et al. 1997 | TBV |
| Rate constant for schoepite | waste package | | | intrinsic value on how fast schoepite dissolves/precipitates | NFGE-3C | single value | mol/m^2-sec | 6.30E+06 | Chapter 4.4, derived from Bruno et al. 1995 | TBV |
| Equilibrium constant | waste package | | | intrinsic value on how stable a species is | NFGE-3C | polynomail functions | N/A | See Tables 4-29 and 4-31 | Chapter 4.4, fitted from Wolery 1992 | TBV |
| Equilibrium constant | waste package | | | intrinsic value on how stable spent fuel | NFGE-3C | polynomial function | N/A | See Table 4-27 | Chapter 4.4, fitted from Wolery 1992 | TBV |
| Equilibrium constant | waste package | | | intrinsic value on how stable schoepite is | NFGE-3C | polynomial function | N/A | See Table 4-27 | Chapter 4.4, fitted from Wolery 1992 | TBV |

Table 4-39. (continued).

| Near-Field Geochemical Environment Input Tracking Table 4-39 | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Name** | **Scale** | **Material** | **Property** | **Parameter Description** | **Model** | **Distribution Type** | **Units** | **Mean** | **Source** | **Q Status of Source** |
| Equilibrium constant | waste package | | | intrinsic value on how stable a mineral is | NFGE-3C | single value | N/A | log K = 9.42, 5.82,5.74 (for uranophane, soddyitem, and Na-boltwoodite) | Nguyen et al. 1992 | TBV |
| **Water-solids chemistry—Precipitates/Salts (NFGE-3D)** | | | | | | | | | | |
| Temperature for Boiling Period A | Drift | | | temperature | NFGE-3D | single value | Celcius | 95 | Chapter 4.5 - abstracted 2-D TH results | TBV |
| Temperature for Boiling Period B | Drift | | | temperature | NFGE-3D | single value | Celcius | 95 | Chapter 4.5 - abstracted 2-D TH results | TBV |
| Temperature for Boiling Period C | Drift | | | temperature | NFGE-3D | single value | Celcius | 95 | Chapter 4.5 - abstracted 2-D TH results | TBV |
| Reflux Water Composition, Boiling Period A | Drift | | | aqueous concentration | NFGE-3D | array of values | molal | see Table 4-42 | Chapter 4.5 - abstracted 2-D TH results | TBV |
| Reflux Water Composition, Boiling Period B | Drift | | | aqueous concentration | NFGE-3D | array of values | molal | see Table 4-42 | Chapter 4.5 - abstracted 2-D TH results | TBV |
| Reflux Water Composition, Boiling Period C | Drift | | | aqueous concentration | NFGE-3D | array of values | molal | see Table 4-42 | Chapter 4.5 - abstracted 2-D TH results | TBV |
| Partial Pressure O2 for Boiling Period A | Drift | | | partial pressure O2 | NFGE-3D | single value | log atm | -3.7 | Chapter 4.5 - abstracted 2-D TH results | TBV |
| Partial Pressure O2 for Boiling Period B | Drift | | | partial pressure O2 | NFGE-3D | single value | log atm | -7.7 | Chapter 4.5 - abstracted 2-D TH results | TBV |
| Partial Pressure O2 for Boiling Period C | Drift | | | partial pressure O2 | NFGE-3D | single value | log atm | -2.7 | Chapter 4.5 - abstracted 2-D TH results | TBV |

Table 4-39. (continued).

| Near-Field Geochemical Environment Input Tracking Table 4-39 | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Name** | **Scale** | **Material** | **Property** | **Parameter Description** | **Model** | **Distribution Type** | **Units** | **Mean** | **Source** | **Q Status of Source** |
| Partial Pressure CO2 for Boiling Period A | Drift | | | partial pressure CO2 | NFGE-3D | single value | log atm | -4.0 | Chapter 4.5 - abstracted 2-D TH results | TBV |
| Partial Pressure CO2 for Boiling Period B | Drift | | | partial pressure CO2 | NFGE-3D | single value | log atm | -10.0 | Chapter 4.5 - abstracted 2-D TH results | TBV |
| Partial Pressure CO2 for Boiling Period C | Drift | | | partial pressure CO2 | NFGE-3D | single value | log atm | -5.0 | Chapter 4.5 - abstracted 2-D TH results | TBV |
| Seepage Flux for 0 to 5000 yrs | Drift | | | seepage flux | NFGE-3D | single value | kg/yr per waste package | 23.2 | Pa UZ Flow/TH Component models; Average seepage flux in region-6 (CC), 0-5000 yrs, from preliminary draft chapter on UZ flow (accdg to Vinod, 5/98) | TBV |
| Maximum Relative Humidity for KNO3 | Drift | | | maximum relative humidity for KNO3 | NFGE-3D | single value | volume percent | 50 | Approximate value for model based on data and information in Weast (1981, p. E-1, E-44); Kinsman (1976); Dean (1992, p. 11.6) | TBV |
| Maximum Relative Humidity for Na2SO4 | Drift | | | maximum relative humidity for KNO4 | NFGE-3D | single value | volume percent | 90 | Approximate value for model based on data and information in Weast (1981, p. E-1, E-44); Kinsman (1976); Dean (1992, p. 11.6) | TBV |

Table 4-39. (continued).

| Near-Field Geochemical Environment Input Tracking Table 4-39 | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Name | Scale | Material | Property | Parameter Description | Model | Distribution Type | Units | Mean | Source | Q Status of Source |
| Maximum Relative Humidity for Na2Si2O5 | Drift | | | maximum relative humidity for KNO5 | NFGE-3D | single value | volume percent | 80 | Approximate value for model based on data and information in Weast (1981, p. E-1, E-44); Kinsman (1976); Dean (1992, p. 11.6) | TBV |
| Maximum Relative Humidity for Na2SiO3 | Drift | | | maximum relative humidity for KNO6 | NFGE-3D | single value | volume percent | 80 | Approximate value for model based on data and information in Weast (1981, p. E-1, E-44); Kinsman (1976); Dean (1992, p. 11.6) | TBV |
| Maximum Relative Humidity for NaHCO3 | Drift | | | maximum relative humidity for KNO7 | NFGE-3D | single value | volume percent | 80 | Approximate value for model based on data and information in Weast (1981, p. E-1, E-44); Kinsman (1976); Dean (1992, p. 11.6) | TBV |
| Maximum Relative Humidity for Na2CO3 | Drift | | | maximum relative humidity for KNO8 | NFGE-3D | single value | volume percent | 80 | Approximate value for model based on data and information in Weast (1981, p. E-1, E-44); Kinsman (1976); Dean (1992, p. 11.6) | TBV |
| Maximum Relative Humidity for NaCl | Drift | | | maximum relative humidity for KNO9 | NFGE-3D | single value | volume percent | 80 | Approximate value for model based on data and information in Weast (1981, p. E-1, E-44); Kinsman (1976); Dean (1992, p. 11.6) | TBV |

Table 4-39. (continued).

| Near-Field Geochemical Environment Input Tracking Table 4-39 | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Name | Scale | Material | Property | Parameter Description | Model | Distribution Type | Units | Mean | Source | Q Status of Source |
| Maximum Relative Humidity for NaF | Drift | | | maximum relative humidity for KNO10 | NFGE-3D | single value | volume percent | 80 | Approximate value for model based on data and information in Weast (1981, p. E-1, E-44); Kinsman (1976); Dean (1992, p. 11.6) | TBV |
| Maximum Relative Humidity for NaNO3 | Drift | | | maximum relative humidity for KNO11 | NFGE-3D | single value | volume percent | 50 | Approximate value for model based on data and information in Weast (1981, p. E-1, E-44); Kinsman (1976); Dean (1992, p. 11.6) | TBV |
| Length of drift per waste package | Drift | | | length of drift per waste package | NFGE-3D | single value | meters | 13 | Chapter 3.0 | TBV |
| Diameter of drift | Drift | | | diameter of drift | NFGE-3D | single value | meters | 5.1 | Chapter 3.0 | TBV |
| Volume of drift occupied by waste package | Drift | | | fraction of drift space occupied by vapor phase | NFGE-3D | single value | volume percent | 75 | Section 4.6.2.2.3.3 | TBV |
| Water vapor pressure in drift at 160 years | Drift | | | water vapor pressure in drift at 160 years | NFGE-3D | single value | atm | 1 | Chapter 4.5 - abstracted 2-D TH results | TBV |
| Temperature in drift at 160 years | Drift | | | temperature in drift at 160 years | NFGE-3D | single value | Celcius | 113 | Approximate average temperature of vapor in drift, based on file: CC_noBF_j_12_04_averageSNF.xls, 12/97 PA property set, point load, 1X infiltration based on Flint infiltration map (7.8 mm/yr avg infiltration) | TBV |

Table 4-39. (continued).

| Near-Field Geochemical Environment Input Tracking Table 4-39 | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Name** | **Scale** | **Material** | **Property** | **Parameter Description** | **Model** | **Distribution Type** | **Units** | **Mean** | **Source** | **Q Status of Source** |
| **In-Drift Colloids (NFGE-4)** | | | | | | | | | | |
| Colloid concentrations in groundwaters | N/A | suspension | concentration | the number of colloid particles suspended in the solution | NFGE –4 | single values | particles per ml | See Table 4-35 | Section 4.4.3.3 | TBV |
| Ionic strength of colloid-bearing groundwaters | N/A | aqueous solution | ionic strength | the cumulative charge weighted concentrations of dissolved species | NFGE –4 | single values | molarity | See Table 4-35 | Section 4.4.3.3 | TBV |
| Microbial Communities (NFGE-5) | | | | | | | | | | |
| Temperature dependant Gibbs Free Energy relationships | N/A | | | Redox half reaction specific temperature relationships for Gibbs Free Energy | NFGE-5 | polynomial function | kJ/mol | See Table 4-36 | Jolley (1998a) | TBV (TBV-370) |
| MING V1.0 Default values | N/A | | | Default input parameters for model calculations (seven separate items) | NFGE-5 | Single values | Various | See Table 4-37 | See Table 4-37 | TBV |
| Reactant composition designators | N/A | | | Reactant compositions used in the energy calculation of limiting mass | NFGE-5 | Single values | none | See Table 4-38 | Section 4.43.4.2 | TBV |
| J-13 Water Compositions | N/A | | | Incoming water compositions into the drift | NFGE | Single values | $Kmol/m^3$ | See Table 4-58 | Harrar et al. 1990 | TBV |
| Gas flux | Drift | | | Cumulative gas flux into the drift over 1 million years | NFGE-5 | Single values | $Kg/m^2$ | See Table 4-59 | Section 4.6.2.3.3.1 | TBV |
| Repository Design Materials Compositions | Drift | Type V Concrete | | Elemental composition of Type V concrete | NFGE-5 | single values | Elemental Weight % | See Table 4-60 | Jolley (1998c) | TBV (TBV-372) |

Table 4-39. (continued).

| Near-Field Geochemical Environment Input Tracking Table 4-39 | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Name** | **Scale** | **Material** | **Property** | **Parameter Description** | **Model** | **Distribution Type** | **Units** | **Mean** | **Source** | **Q Status of Source** |
| Repository Design Materials Compositions | Drift | ASTM A36 Steel | | Elemental composition of Steel fiber | NFGE-5 | single values | Elemental Weight % | See Table 4-61 | Jolley (1998c) | TBV (TBV-372) |
| Repository Design Materials Compositions | Drift | Water Reducer | | Elemental composition of water reducer | NFGE-5 | single values | Elemental Weight % | See Table 4-62 | Jolley (1998c) | TBV (TBV-372) |
| Repository Design Materials Compositions | Drift | Superplasti cizer | | Elemental composition of Superplasticizer | NFGE-5 | single values | Elemental Weight % | See Table 4-63 | Jolley (1998c) | TBV (TBV-372) |
| Repository Design Materials Compositions | Drift | ASTM F432-95 Steel | | Elemental composition of Swellex rock bolt sets | NFGE-5 | single values | Elemental Weight % | See Table 4-64 | Jolley (1998c) | TBV (TBV-372) |
| Repository Design Materials Compositions | Drift | ASTM A706 Steel | | Elemental composition of Re-bar | NFGE-5 | single values | Elemental Weight % | See Table 4-65 | Jolley (1998c) | TBV (TBV-372) |
| Repository Design Materials Compositions | Drift | ASTM A36 Steel | | Elemental composition of wire mesh and rolled channel | NFGE-5 | single values | Elemental Weight % | See Table 4-66 | Jolley (1998c) | TBV (TBV-372) |
| Repository Design Materials Compositions | Drift | Unspecifie d Steel | | Elemental composition of Gantry Rail | NFGE-5 | single values | Elemental Weight % | See Table 4-67 | Jolley (1998c) | TBV (TBV-372) |
| Repository Design Materials Compositions | Drift | Unspecifie d Steel | | Elemental composition of Rail Fittings | NFGE-5 | single values | Elemental Weight % | See Table 4-68 | Jolley (1998c) | TBV (TBV-372) |
| Repository Design Materials Compositions | Drift | ASTM A36 Steel | | Elemental composition of Steel Set ground support | NFGE-5 | single values | Elemental Weight % | See Table 4-69 | Jolley (1998c) | TBV (TBV-372) |
| Repository Design Materials Compositions | Drift | ASTM A36 Steel | | Elemental composition of Conductor bar fittings | NFGE-5 | single values | Elemental Weight % | See Table 4-70 | Jolley (1998c) | TBV (TBV-372) |

Table 4-39. (continued).

| Near-Field Geochemical Environment Input Tracking Table 4-39 | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Name** | **Scale** | **Material** | **Property** | **Parameter Description** | **Model** | **Distribution Type** | **Units** | **Mean** | **Source** | **Q Status of Source** |
| Repository Design Materials Compositions | Drift | Various | | Elemental composition of Commo Cable | NFGE-5 | single values | Elemental Weight % | See Table 4-71 | Jolley (1998c) | TBV (TBV-372) |
| Repository Design Materials Compositions | Drift | Various | | Masses of materials for a one meter cast in place repository segment | NFGE-5 | single values | kg/meter of drift | See Table 4-72 | Jolley (1998c) | TBV (TBV-372) |
| Waste Package Design Materials Compositions | Waste package | 21PWR Waste | | Composition of waste in 21PWR fuel canister | NFGE-5 | single values | Elemental Weight % | See Table 4-73 | Jolley (1998d) | TBV (TBV-371) |
| Waste Package Design Materials Compositions | Drift | ASTM A36 Steel | | Composition of waste package supports | NFGE-5 | single values | Elemental Weight % | See Table 4-74 | Jolley (1998d) | TBV (TBV-371) |
| Waste Package Design Materials Compositions | Waste package | C-22 Alloy | | Composition of waste package corrosion resistant material (CRM) | NFGE-5 | single values | Elemental Weight % | See Table 4-75 | Jolley (1998d) | TBV (TBV-371) |
| Waste Package Design Materials Compositions | Waste package | ASTM A 516 Steel | | Composition of waste package corrosion allowance material (CAM) | NFGE-5 | single values | Elemental Weight % | See Table 4-76 | Jolley (1998d) | TBV (TBV-371) |
| Waste Package Design Materials Compositions | Waste package | Aluminum Type 6061 | | Composition of waste package thermal shunts | NFGE-5 | single values | Elemental Weight % | See Table 4-77 | Jolley (1998d) | TBV (TBV-371) |
| Waste Package Design Materials Compositions | Waste package | Neutronit A 987 | | Composition of waste package absorber plates | NFGE-5 | single values | Elemental Weight % | See Table 4-78 | Jolley (1998d) | TBV (TBV-371) |
| Waste Package Design Materials Compositions | Waste package | Various | | Masses of materials for a one lineal meter segment of a 21PWR waste canister | NFGE-5 | single values | Kg/meter of waste package | See Table 4-79 | Jolley (1998d) | TBV (TBV-371) |
| Waste package surface temperature history | Drift | | | Temperature of waste package surface over time | NFGE-5 | Single value | Deg C | See Table 4-80 | Chapter 3 | TBV |

Table 4-39. (continued).

| Near-Field Geochemical Environment Input Tracking Table 4-39 | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Name** | **Scale** | **Material** | **Property** | **Parameter Description** | **Model** | **Distribution Type** | **Units** | **Mean** | **Source** | **Q Status of Source** |
| Waste package surface relative humidity history | Drift | | | Relative humidity at the waste package surface over time | NFGE-5 | Single value | Deg C | See Table 4-80 | Chapter 3 | TBV |
| Infiltration rate into the drift over time | Drift | | | Infiltration into the over time | NFGE-5 | Single value | mm/yr | See Table 4-80 | Chapter 3 | TBV |
| Reactant Compositions | N/A | | | Reactant compositions required to determine appropriate breakdown of organic materials | NFGE-5 | Multiple Values | N/A | See Table 4-81 | Jolley (1998c) | TBV (TBV-369) |
| Breakdown Codes | N/A | | | Breakdown codes based on materials empirical formula required to determine appropriate breakdown of organic materials | NFGE-5 | Multiple Values | moles | See Table 4-81 | Jolley (1998c) | TBV (TBV-369) |
| Molecular Masses | N/A | | | Molecular masses based on material empirical formula required to determine appropriate breakdown of organic materials | NFGE-5 | Multiple Values | grams | See Table 4-81 | Jolley (1998c) | TBV (TBV-369) |
| Material lifetimes | N/A | Various | | Material lifetime inputs for determining fractional corrosion rate | NFGE-5 | Multiple values | years | See Table 4-82 | Section 4.6.2.3.3.1 | TBV |

Table 4-39. (continued).

| Near-Field Geochemical Environment Input Tracking Table 4-39 | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Name** | **Scale** | **Material** | **Property** | **Parameter Description** | **Model** | **Distribution Type** | **Units** | **Mean** | **Source** | **Q Status of Source** |
| Material layer designators | N/A | Various | | Layer designators for the sequential degradation of waste package and repository materials | NFGE-5 | Multiple Values | N/A | See Table 4-83 | Section 4.6.2.3.3.1 | TBV |

Table 4-40. Output Tracking.

| Near-Field Geochemical Environment Output Tracking Table 4-40 | | | | | | |
|---|---|---|---|---|---|---|
| **Figure/Table** | **Code and Version** | **Input Filename** | **Output Filename** | **Post-Processor** | **Output Filename (after post-processing)** | **Data Tracking Number** |
| Table 4-27 | Logkfit * | Data0.com.R22a | Datafit.txt | N/A | N/A | MO9807MWDEQ3/6.000 |
| Table 4-28 | Logkfit * | Data0.com.R22a and Ref. Nguyen et al. 1992 | Datafit.txt | N/A | N/A | MO9807MWDEQ3/6.000 |
| Table 4-29 | Hand Calculation | Gray et al. 1992<br>Casas et al. 1994<br>Bruno et al. 1995<br>Perez et al. 1997 | Notes in file | N/A | N/A | MO9807MWDEQ3/6.000 |
| Table 4-30 | Logkfit * | Data0.com.R22a | Datafit.txt | N/A | N/A | MO9807MWDEQ3/6.000 |
| Table 4-31 | RADDB CDB_R/V1.1 | Self-Contained | Print-out | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figure 4-18 | MS Excel; Office 97 | 2-DdatplusREV01.xls | same | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figure 4-19 | MS Excel; Office 97 | 2-DdatplusREV01.xls | same | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figure 4-20 | MS Excel; Office 97 | summarybasecaserev01.xls | same | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figure 4-25 | MS Excel; Office 97 | nobf_i_avgsnf.xls; summarybasecaserev01.xls | same | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figure 4-26 | MS Excel; Office 97 | nobf_i_avgsnf.xls; summarybasecaserev01.xls | same | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figure 4-30 | TBD | TBD | TBD | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figure 4-31 | TBD | TBD | TBD | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figure 4-32 | MS Excel; Office 97 | summarybasecaserev01.xls | same | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figure 4-33 | MS Excel; Office 97 | summarybasecaserev01.xls | same | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figure 4-34 | MS Excel; Office 97 | minggasfluxinputsrev01last.xls | same | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figure 4-35 | MS Excel; Office 97 | minggasfluxinputsrev01last.xls | same | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figure 4-36 | EQ3 and EQ6 v. 7.2b | J13evpr.3i<br>PeriodA.6i<br>PeriodB.6i<br>PeriodC.6i<br>PeriodD.3i<br>PeriodE.3i<br>PeriodF.3i | PeriodA.6o<br>PeriodB.6o<br>PeriodC.6o<br>PeriodD.3o<br>PeriodE.3o<br>PeriodF.3o | N/A | N/A | MO9807MWDEQ3/6.000 |

Table 4-40. (continued).

| Near-Field Geochemical Environment Output Tracking Table 4-40 | | | | | | |
|---|---|---|---|---|---|---|
| **Figure/Table** | **Code and Version** | **Input Filename** | **Output Filename** | **Post-Processor** | **Output Filename (after post-processing)** | **Data Tracking Number** |
| Figure 4-37 | EQ3 and EQ6 v. 7.2b | J13evpr.3l<br>PeriodA.6l<br>PeriodB.6l<br>PeriodC.6l<br>PeriodD.3l<br>PeriodE.3l<br>PeriodF.3l | PeriodA.6o<br>PeriodB.6o<br>PeriodC.6o<br>PeriodD.3o<br>PeriodE.3o<br>PeriodF.3o | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figure 4-38 | EQ3 v. 7.2b | PeriodA.3l<br>PeriodB.3l<br>PeriodC.3l<br>PeriodD.3l<br>PeriodE.3l<br>PeriodF.3l | PeriodA.3o<br>PeriodB.3o<br>PeriodC.3o<br>PeriodD.3o<br>PeriodE.3o<br>PeriodF.3o | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figure 4-39 | EQ3 v. 7.2b | PeriodA.3l<br>PeriodB.3l<br>PeriodC.3l<br>PeriodD.3l<br>PeriodE.3l<br>PeriodF.3l | PeriodA.3o<br>PeriodB.3o<br>PeriodC.3o<br>PeriodD.3o<br>PeriodE.3o<br>PeriodF.3o | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figure 4-40 | EQ3 v. 7.2b<br>Sigmaplot for windows v. 4.01 | PeriodA.3l<br>PeriodB.3l<br>PeriodC.3l<br>PeriodD.3l<br>PeriodE.3l<br>PeriodF.3l | PeriodA.3o<br>PeriodB.3o<br>PeriodC.3o<br>PeriodD.3o<br>PeriodE.3o<br>PeriodF.3o<br>phripdists.jnb | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figures 4-41 through 4-52 | EQ6 7.2b | PerAcon1.6l PerBcon1.6l<br>PerCcon1.6l PerDcon1.6l<br>PerEcon1.6l PerFcon1.6l | PerAcon1.6o<br>PerBcon1.6o<br>PerCcon1.6o<br>PerDcon1.6o<br>PerEcon1.6o<br>PerFcon1.6o | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figures 4-44 through 4-46 | EQ6 7.2b | PerAsen1.6l PerBsen1.6l<br>PerCsen1.6l PerDsen1.6l<br>PerEsen1.6l<br>PerFsen1.6l | PerAsen1.6o<br>PerBsen1.6o<br>PerCsen1.6o<br>PerDsen1.6o<br>PerEsen1.6o<br>PerFsen1.6o | N/A | N/A | MO9807MWDEQ3/6.000 |

Table 4-40. (continued).

| Near-Field Geochemical Environment Output Tracking Table 4-40 | | | | | | |
|---|---|---|---|---|---|---|
| **Figure/Table** | **Code and Version** | **Input Filename** | **Output Filename** | **Post-Processor** | **Output Filename (after post-processing)** | **Data Tracking Number** |
| Figures 4-44 through 4-46 | EQ6 7.2b | PerAsen2.6l PerBsen2.6l<br>PerCsen2.6l PerDsen2.6l<br>PerEsen2.6l<br>PerFsen2.6l | PerAsen2.6o<br>PerBsen2.6o<br>PerCsen2.6o<br>PerDsen2.6o<br>PerEsen2.6o<br>PerFsen2.6o | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figures 4-47 through 4-49 | EQ6 7.2b | PerAsen7.6l PerBsen7.6l<br>PerCsen7.6l PerDsen7.6l<br>PerEsen7.6l<br>PerFsen7.6l | PerAsen7.6o<br>PerBsen7.6o<br>PerCsen7.6o<br>PerDsen7.6o<br>PerEsen7.6o<br>PerFsen7.6o | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figures 4-47 through 4-49 | EQ6 7.2b | PerAsen8.6l PerBsen8.6l<br>PerCsen8.6l PerDsen8.6l<br>PerEsen8.6l PerFsen8.6l | PerAsen8.6o<br>PerBsen8.6o<br>PerCsen8.6o<br>PerDsen8.6o<br>PerEsen8.6o<br>PerFsen8.6o | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figures 4-50 through 4-52 | EQ6 7.2b | PerAsen5.6l PerBsen5.6l<br>PerCsen5.6l PerDsen5.6l<br>PerEsen5.6l PerFsen5.6l | PerAsen5.6o<br>PerBsen5.6o<br>PerCsen5.6o<br>PerDsen5.6o<br>PerEsen5.6o<br>PerFsen5.6o | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figures 4-50 through 4-52 | EQ6 7.2b | PerAsen6.6l PerBsen6.6l<br>PerCsen6.6l PerDsen6.6l<br>PerEsen6.6l PerFsen6.6l | PerAsen6.6o<br>PerBsen6.6o<br>PerCsen6.6o<br>PerDsen6.6o<br>PerEsen6.6o<br>PerFsen6.6o | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figure 4-53 | EQ6 7.2b | PerAcon1.6l PerBcon1.6l<br>PerCcon1.6l PerDcon1.6l<br>PerEcon1.6l PerFcon1.6l | PerAcon1.6o<br>PerBcon1.6o<br>PerCcon1.6o<br>PerDcon1.6o<br>PerEcon1.6o<br>PerFcon1.6o | N/A | N/A | MO9807MWDEQ3/6.000 |

Table 4-40. (continued).

| Near-Field Geochemical Environment Output Tracking Table 4-40 | | | | | | |
|---|---|---|---|---|---|---|
| **Figure/Table** | **Code and Version** | **Input Filename** | **Output Filename** | **Post-Processor** | **Output Filename (after post-processing)** | **Data Tracking Number** |
| Figure 4-54 | EQ6 7.2b | PerAsen1.6l PerBsen1.6l PerCsen1.6l PerDsen1.6l PerEsen1.6l PerFsen1.6l | PerAsen1.6o PerBsen1.6o PerCsen1.6o PerDsen1.6o PerEsen1.6o PerFsen1.6o | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figure 4-55 | AREST-CT V1.2 | Csfb013.actin Sptfl01.time | Csfb013.out2h,csfb013.out2b | pntinfo | Csfb013.p_201 | MO9807MWDEQ3/6.000 |
| Figure 4-56 | AREST-CT V1.2 | Csfb013.actin Csfb003.actin Csfb012.actin Csfb022.actin Sptfl01.time | Csfb013.out2h,csfb013.out2b Csfb003.out2h,csfb003.out2b Csfb012.out2h,csfb012.out2b Csfb022.out2h,csfb022.out2b | pntinfo | Csfb013.p_201 Csfb003.p_201 Csfb012.p_201 Csfb022.p_201 | MO9807MWDEQ3/6.000 |
| Figure 4-57a | AREST-CT V1.2 | csfnf01.actin sptfl02.time | csfnf01.out2h, csfnf01.out2b | cold4pc | UO200000D.nf1 | MO9807MWDEQ3/6.000 |
| Figure 4-57b | AREST-CT V1.2 | csfnf01.actin sptfl02.time | csfnf01.out2h, csfnf01.out2b | cold4pc | UO200000V.nf1 | MO9807MWDEQ3/6.000 |
| Figure 4-58a | AREST-CT V1.2 | csfnf01.actin sptfl02.time | csfnf01.out2h, csfnf01.out2b | cold4pc | SchoeplV.nf1 | MO9807MWDEQ3/6.000 |
| Figure 4-58b | AREST-CT V1.2 | csfnf01.actin sptfl02.time | csfnf01.out2h, csfnf01.out2b | cold4pc | UranophV.nf1 | MO9807MWDEQ3/6.000 |
| Figure 4-59 | AREST-CT V1.2 | csfnf01.actin sptfl02.time | csfnf01.out2h, csfnf01.out2b | cold4pc | SoddyltV.nf1 | MO9807MWDEQ3/6.000 |
| Figure 4-61 | AREST-CT V1.2 | corr201.actin, sptfl02.time | corr201.out2h,corr201.out2b | pntinfo | csfnf01.p_201 | MO9807MWDEQ3/6.000 |
| Figure 4-62 | AREST-CT V1.2 | corr201.actin, sptfl02.time | corr201.out2h,corr201.out2b | cold4pc | SchoeplV.c21 | MO9807MWDEQ3/6.000 |
| Figure 4-63 | AREST-CT V1.2 | corr201.actin, sptfl02.time | corr201.out2h,corr201.out2b | cold4pc | UranophV.c21 | MO9807MWDEQ3/6.000 |
| Figure 4-64 | AREST-CT V1.2 | corr201.actin, sptfl02.time | corr201.out2h,corr201.out2b | cold4pc | U(total).c21 | MO9807MWDEQ3/6.000 |
| Figure 4-65 | AREST-CT V1.2 | corr201.actin, sptfl02.time | corr201.out2h,corr201.out2b | cold4pc | pH.c21 | MO9807MWDEQ3/6.000 |

Table 4-40. (continued).

| Near-Field Geochemical Environment Output Tracking Table 4-40 | | | | | | |
|---|---|---|---|---|---|---|
| **Figure/Table** | **Code and Version** | **Input Filename** | **Output Filename** | **Post-Processor** | **Output Filename (after post-processing)** | **Data Tracking Number** |
| Figure 4-66 | AREST-CT V1.2 | corr201.actin, sptfl02.time | corr201.out2h,corr201.out2b | cold4pc | CO2(tota.c21 | MO9807MWDEQ3/6.000 |
| Figure 4-67 | AREST-CT V1.2 | corr201.actin, sptfl02.time | corr201.out2h,corr201.out2b | cold4pc | I(streng.c21 | MO9807MWDEQ3/6.000 |
| Figure 4-68 | EQ6 Ver 7.2b | fba.6i | fba.6o | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figure 4-69 | EQ6 Ver 7.2b | fbb.6i | fbb.6o | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figure 4-70 | EQ6 Ver 7.2b | fbc.6i | fbc.6o | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figure 4-71 | EQ6 Ver 7.2b | fba.6i | fba.6o | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figure 4-72 | EQ6 Ver 7.2b | fbb.6i | fbb.6o | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figure 4-73 | EQ6 Ver 7.2b | fbc.6i | fbc.6o | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figure 4-74 | Spreadsheet calculations | fba4.xls fbb4.xls fbc4.xls | fba4.xls fbb4.xls fbc4.xls | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figure 4-75 | Spreadsheet calculations | fba4.xls fbb4.xls fbc4.xls | fba4.xls fbb4.xls fbc4.xls | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figure 4-76 | Spreadsheet calculations | fba4.xls fbb4.xls fbc4.xls | fba4.xls fbb4.xls fbc4.xls | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figure 4-77 | Spreadsheet calculations | fba4.xls fbb4.xls fbc4.xls | fba4.xls fbb4.xls fbc4.xls | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figure 4-78 | MING V1.0 | Inputs contained in output file | Baseline Emma.mdb | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figure 4-79 | MING V1.0 | Inputs contained in output file | Ambient LTA inf b1mil.mdb | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figure 4-80 | MING V1.0 | Inputs contained in output file | Ambient LTA inf b10mil.mdb | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figure 4-81 | MING V1.0 | Inputs contained in output file | Ambient PDD b1mil.mdb | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figure 4-82 | MING V1.0 | Inputs contained in output file | Ambient PDD b1mil.mdb | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figure 4-83 | MING V1.0 | Inputs contained in output file | 21PWR Reference case.mdb | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figure 4-84 | MING V1.0 | Inputs contained in output file | 21PWR Reference case with J-13 @ 100000 yr.mdb | N/A | N/A | MO9807MWDEQ3/6.000 |

Table 4-40. (continued).

| Near-Field Geochemical Environment Output Tracking Table 4-40 | | | | | | |
|---|---|---|---|---|---|---|
| **Figure/Table** | **Code and Version** | **Input Filename** | **Output Filename** | **Post-Processor** | **Output Filename (after post-processing)** | **Data Tracking Number** |
| Figure 4-86 | MING V1.0 | Inputs contained in output file | 21PWR 5_50_10.mdb | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figure 4-87 | MING V1.0 | Inputs contained in output file | 21PWR 5_50_100.mdb | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figure 4-88 | MING V1.0 | Inputs contained in output file | 21PWR 10_250_10.mdb | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figure 4-89 | MING V1.0 | Inputs contained in output file | 21PWR 10_250_100.mdb | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figure 4-91 | EQ3 and EQ6 v. 7.2b | J13evpr.3i<br>PeriodA.6i<br>PeriodB.6i<br>PeriodC.6i<br>PeriodD.3i<br>PeriodE.3i<br>PeriodF.3i<br>PeriodA.3i<br>PeriodB.3i<br>PeriodC.3i<br>PeriodD.3i<br>PeriodE.3i<br>PeriodF.3i<br>PerAcon1.6i PerBcon1.6i<br>PerCcon1.6i PerDcon1.6i<br>PerEcon1.6i PerFcon1.6i | PeriodA.6o<br>PeriodB.6o<br>PeriodC.6o<br>PeriodD.3o<br>PeriodE.3o<br>PeriodF.3o<br>PeriodA.oi<br>PeriodB.3o<br>PeriodC.3o<br>PeriodD.3o<br>PeriodE.3o<br>PeriodF.3o<br>PerAcon1.6o<br>PerBcon1.6o<br>PerCcon1.6o<br>PerDcon1.6o<br>PerEcon1.6o<br>PerFcon1.6o | N/A | N/A | MO9807MWDEQ3/6.000 |

Table 4-40. (continued).

| Near-Field Geochemical Environment Output Tracking Table 4-40 | | | | | | |
|---|---|---|---|---|---|---|
| **Figure/Table** | **Code and Version** | **Input Filename** | **Output Filename** | **Post-Processor** | **Output Filename (after post-processing)** | **Data Tracking Number** |
| Figure 4-92 | EQ3 and EQ6 v. 7.2b | J13evpr.3i<br>PeriodA.6i<br>PeriodB.6i<br>PeriodC.6i<br>PeriodD.3i<br>PeriodE.3i<br>PeriodF.3i<br>PeriodA.3i<br>PeriodB.3i<br>PeriodC.3i<br>PeriodD.3i<br>PeriodE.3i<br>PeriodF.3i<br>PerAcon1.6i PerBcon1.6i<br>PerCcon1.6i PerDcon1.6i<br>PerEcon1.6i PerFcon1.6i | PeriodA.6o<br>PeriodB.6o<br>PeriodC.6o<br>PeriodD.3o<br>PeriodE.3o<br>PeriodF.3o<br>PeriodA.oi<br>PeriodB.3o<br>PeriodC.3o<br>PeriodD.3o<br>PeriodE.3o<br>PeriodF.3o<br>PerAcon1.6o<br>PerBcon1.6o<br>PerCcon1.6o<br>PerDcon1.6o<br>PerEcon1.6o<br>PerFcon1.6o | N/A | N/A | MO9807MWDEQ3/6.000 |
| Figure 4-93 | EQ3 and EQ6 v. 7.2b | J13evpr.3i<br>PeriodA.6i<br>PeriodB.6i<br>PeriodC.6i<br>PeriodD.3i<br>PeriodE.3i<br>PeriodF.3i<br>PeriodA.3i<br>PeriodB.3i<br>PeriodC.3i<br>PeriodD.3i<br>PeriodE.3i<br>PeriodF.3i<br>PerAcon1.6i PerBcon1.6i<br>PerCcon1.6i PerDcon1.6i<br>PerEcon1.6i PerFcon1.6i | PeriodA.6o<br>PeriodB.6o<br>PeriodC.6o<br>PeriodD.3o<br>PeriodE.3o<br>PeriodF.3o<br>PeriodA.oi<br>PeriodB.3o<br>PeriodC.3o<br>PeriodD.3o<br>PeriodE.3o<br>PeriodF.3o<br>PerAcon1.6o<br>PerBcon1.6o<br>PerCcon1.6o<br>PerDcon1.6o<br>PerEcon1.6o<br>PerFcon1.6o | N/A | N/A | MO9807MWDEQ3/6.000 |

* The work of fitting equilibrium constants in EQ3/6 database into polynomial functions of temperature was done at Pacific Northwest National Laboratory while Yueting Chen worked there from 1994-1997.

Table 4-41. Abstracted Time Periods, Temperatures, Gas Fugacities and Cumulative Gas Fluxes (per Meter of Drift) Used for the Near-Field Geochemical Environment Component (See Text for Discussion).

| **Boiling Regime** | | | | | | |
|---|---|---|---|---|---|---|
| **Abstracted Period** | **Time Years** | **Temperature °C** | **$CO_2$ Fugacity ppmv** | **$CO_2$ Σgas flux Moles/Meter** | **$O_2$ fugacity ppmv** | **$O_2$ Σgas flux Moles/Meter** |
| A | 0-200 | 95 | $1 \times 10^{2}$ | 180 | $2 \times 10^{2}$ | 510 |
| B | 200-1,000 | 95 | $1 \times 10^{-4}$ | 190 | $2 \times 10^{-2}$ | 1,000 |
| C | 1,000-2,000 | 95 | $1 \times 10^{1}$ | 270 | $2 \times 10^{3}$ | 25,000 |
| **Cooling Regime** | | | | | | |
| Abstracted Period | Time Years | Temperature °C | $CO_2$ Fugacity ppmv | $CO_2$ Σgas flux Moles/Meter | $O_2$ fugacity ppmv | $O_2$ Σgas flux Moles/Meter |
| D | 2,000-4,000 | 70 | $1 \times 10^{2}$ | 810 | $2 \times 10^{4}$ | 170,000 |
| E | 4,000-10,000 | 70 | $1 \times 10^{3}$ | 2,100 | $2 \times 10^{5}$ | 530,000 |
| F | 10,000-100,000 | 30 | $1 \times 10^{3}$ | 4,500 | $2 \times 10^{5}$ | 1,200,000 |

ppmv = parts per million by volume

Table 4-42. Calculated Incoming Water Compositions for the Potential Drifts.

| Parameter* | Boiling Period A | Boiling Period B | Boiling Period C | Cooling Period D | Cooling Period E | Cooling Period F |
|---|---|---|---|---|---|---|
| Time (yr) | 0-200 | 200-1,000 | 1,000-2,000 | 2,000-4,000 | 4,000-10,000 | 10,000-100,000 |
| Temp. (°C) | 95 | 95 | 95 | 70 | 70 | 30 |
| log $fCO_2$ | -4.0 | -10.0 | -5.0 | -4.0 | -3.0 | -3.0 |
| log $fO_2$ | -3.7 | -7.7 | -2.7 | -1.7 | -0.7 | -0.7 |
| pH | 9.72 | 10.2 | 10 | 8.94 | 8.2 | 8.12 |
| $Al^{3+}$ (molal) | 5.40E-07 | 2.99E-06 | 7.12E-07 | 6.06E-07 | 1.52E-07 | 4.89E-09 |
| $CO_3^{2-}$ (molal) | 5.06E-03 | 2.79E-08 | 1.24E-03 | 7.60E-04 | 1.46E-03 | 2.09E-03 |
| $Ca^{2+}$ (molal) | 7.87E-06 | 2.62E-06 | 1.01E-05 | 4.27E-05 | 9.44E-05 | 3.18E-04 |
| $Cl^-$ (molal) | 2.03E-03 | 2.03E-03 | 2.03E-03 | 2.01E-04 | 2.01E-04 | 2.01E-04 |
| $F^-$ (molal) | 1.16E-03 | 1.16E-03 | 1.16E-03 | 1.14E-04 | 1.14E-04 | 1.14E-04 |
| $Fe^{2+}$ (molal) | 4.08E-16 | 3.31E-17 | 2.24E-17 | 1.74E-15 | 1.74E-15 | 2.17E-14 |
| $K^+$ (molal) | 1.30E-03 | 1.30E-03 | 1.30E-03 | 1.29E-04 | 1.29E-04 | 1.29E-04 |
| $Mg^{2+}$ (molal) | 2.36E-10 | 5.79E-12 | 9.96E-12 | 5.58E-09 | 1.47E-07 | 1.66E-05 |
| $Na^+$ (molal) | 2.01E-02 | 2.01E-02 | 2.01E-02 | 1.99E-03 | 1.99E-03 | 1.99E-03 |
| $SO_4^{2-}$ (molal) | 1.93E-03 | 1.93E-03 | 1.93E-03 | 1.91E-04 | 1.91E-04 | 1.91E-04 |
| $SiO_2^{\circ}$ (molal) | 5.09E-03 | 6.13E-03 | 7.89E-03 | 1.79E-03 | 1.36E-03 | 4.42E-04 |

*-Parameter represents total dissolved concentration of that constituent, unless otherwise noted. Values of pH given in pH units.

Table 4-43. Calculated in-Drift Water Compositions Reaction with Corrosion Products (Goethite).

| Parameter* | Boiling Period A | Boiling Period B | Boiling Period C | Cooling Period D | Cooling Period E | Cooling Period F |
|---|---|---|---|---|---|---|
| Time (yr) | 0-200 | 200-1,000 | 1,000-2,000 | 2,000-4,000 | 4,000-10,000 | 10,000-100,000 |
| Temp. (°C) | 95 | 95 | 95 | 70 | 70 | 30 |
| log $fCO_2$ | -4.0 | -10.0 | -5.0 | -4.0 | -3.0 | -3.0 |
| log $fO_2$ | -3.7 | -7.7 | -2.7 | -1.7 | -0.7 | -0.7 |
| pH | 9.72 | 10.2 | 9.98 | 8.94 | 8.25 | 8.12 |
| $Al^{3+}$ (molal) | 5.41E-07 | 2.98E-06 | 7.12E-07 | 6.06E-07 | 1.52E-07 | 4.89E-09 |
| $CO_3^{2-}$ (molal) | 5.05E-03 | 2.78E-08 | 1.24E-03 | 7.60E-04 | 1.46E-03 | 2.09E-03 |
| $Ca^{2+}$ (molal) | 7.88E-06 | 2.62E-06 | 1.01E-05 | 4.27E-05 | 9.44E-05 | 3.18E-04 |
| $Cl^-$ (molal) | 2.03E-03 | 2.03E-03 | 2.03E-03 | 2.01E-04 | 2.01E-04 | 2.01E-04 |
| $F^-$ (molal) | 1.15E-03 | 1.15E-03 | 1.15E-03 | 1.14E-04 | 1.14E-04 | 1.14E-04 |
| $Fe^{2+}$ (molal) | 8.00E-14 | 1.77E-13 | 1.20E-13 | 1.64E-13 | 1.40E-13 | 2.39E-12 |
| $K^+$ (molal) | 1.29E-03 | 1.30E-03 | 1.29E-03 | 1.29E-04 | 1.29E-04 | 1.29E-04 |
| $Mg^{2+}$ (molal) | 2.36E-10 | 5.76E-12 | 9.96E-12 | 5.58E-09 | 1.47E-07 | 1.66E-05 |
| $Na^+$ (molal) | 2.01E-02 | 2.01E-02 | 2.01E-02 | 1.99E-03 | 1.99E-03 | 1.99E-03 |
| $SO_4^{2-}$ (molal) | 1.93E-03 | 1.93E-03 | 1.93E-03 | 1.91E-04 | 1.91E-04 | 1.91E-04 |
| $SiO_2°$ (molal) | 5.09E-03 | 6.13E-03 | 7.89E-03 | 1.79E-03 | 1.36E-03 | 4.42E-04 |

*-Parameter represents total dissolved concentration of that constituent, unless otherwise noted. Values of pH given in pH units.

Table 4-44. Input Parameters to the Repository Integrated Program Code for Base-Case Representation of the NFGE Chemical Parameters Used in the EBS Cells.

| Conversion of normal distributions for water composition parameters [log(conc)] to log normal distributions of concentrations [except for pH values and $logfO_2$ values] | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Normal distributions | | Molality units | | | | | |
| Period | Times (years) | pH | Std. dev. | Log $(CO_3^{2-})_{tot}$ | Std. dev. | Log(I) | Std. dev. | $LogfO_2$ | Std. dev. |
| A | 0-200 | 9.7 | 0.3 | -2.3 | 0.3 | -1.6 | 0.3 | -3.7 | 0.2 |
| B | 200-1,000 | 10.2 | 0.3 | -7.6 | 0.3 | -1.8 | 0.3 | -7.7 | 0.2 |
| C | 1,000-2,000 | 10 | 0.3 | -2.9 | 0.3 | -1.7 | 0.3 | -2.7 | 0.2 |
| D | 2,000-4,000 | 8.9 | 0.3 | -3.1 | 0.3 | -2.5 | 0.3 | -1.7 | 0.2 |
| E | 4,000-10,000 | 8.2 | 0.3 | -2.8 | 0.3 | -2.3 | 0.3 | -0.7 | 0.2 |
| F | 10,000-100,000 | 8.1 | 0.3 | -2.7 | 0.3 | -2.2 | 0.3 | -0.7 | 0.2 |
| ambient | 100,000-1,000,000 | 7.4 | 0.3 | -2.6 | 0.3 | -2.2 | 0.3 | -0.7 | 0.2 |
| | | | | | | | | | |
| | | log normal distributions | | | | | | | |
| | | | | molality units | | | | | |
| Period | times (years) | | | $(CO_3^{2-})_{tot}$ | std. dev. | I | std. dev. | | |
| A | 0-200 | | | 5.6E-03 | 2.7E-03 | 2.8E-02 | 1.3E-02 | | |
| B | 200-1,000 | | | 2.8E-08 | 1.3E-08 | 1.8E-02 | 8.4E-03 | | |
| C | 1,000-2,000 | | | 1.4E-03 | 6.7E-04 | 2.2E-02 | 1.1E-02 | | |
| D | 2,000-4,000 | | | 8.8E-04 | 4.2E-04 | 3.5E-03 | 1.7E-03 | | |
| E | 4,000-10,000 | | | 1.8E-03 | 8.4E-04 | 5.6E-03 | 2.7E-03 | | |
| F | 10,000-100,000 | | | 2.2E-03 | 1.1E-03 | 7.0E-03 | 3.4E-03 | | |
| ambient | 100,000-1,000,000 | | | 2.8E-03 | 1.3E-03 | 7.0E-03 | 3.4E-03 | | |

Table 4-45. Baseline Sensitivity Resultant Fluids Composition After Reaction with Concrete.

| Parameter | Period A | Period B | Period C | Period D | Period E | Period F |
|---|---|---|---|---|---|---|
| Input File | PerAcon1.6i | PerBcon1.6i | PerCcon1.6i | PerDcon1.6i | PerEcon1.6i | PerFcon1.6i |
| Output File | PerAcon1.6o | PerBcon1.6o | PerCcon1.6o | PerDcon1.6o | PerEcon1.6o | PerFcon1.6o |
| Code/version | EQ6/V7.2b | EQ6/V7.2b | EQ6/V7.2b | EQ6/V7.2b | EQ6/V7.2b | EQ6/V7.2b |
| PH | 10.5 | 10.5 | 10.5 | 11.0 | 11.0 | 7.46 |
| Total Al, m | 4.95E-03 | 4.96E-03 | 4.95E-03 | 4.45E-07 | 4.42E-07 | 2.82E-09 |
| Total CO3--, m | 7.67E-06 | 9.14E-07 | 7.67E-06 | 8.33E-06 | 8.32E-06 | 5.67E-04 |
| Total Ca, m | 5.40E-03 | 5.39E-03 | 5.40E-03 | 1.04E-02 | 1.04E-02 | 1.56E-02 |
| Total Cl, m | 1.59E-03 | 1.60E-03 | 1.59E-03 | 1.86E-04 | 1.82E-04 | 1.72E-04 |
| Total F, m | 3.36E-04 | 3.37E-04 | 3.36E-04 | 1.05E-04 | 1.03E-04 | 9.73E-05 |
| Total Fe, m | 5.35E-26 | 5.35E-25 | 3.01E-26 | 3.40E-32 | 1.35E-31 | 2.45E-22 |
| Total K, m | 1.52E-02 | 1.52E-02 | 1.52E-02 | 1.67E-02 | 1.64E-02 | 9.82E-05 |
| Total Mg, m | 3.45E-08 | 3.45E-08 | 3.45E-08 | 5.47E-10 | 5.48E-10 | 1.24E-03 |
| Total Na, m | 2.05E-02 | 2.05E-02 | 2.05E-02 | 7.38E-03 | 7.23E-03 | 6.81E-03 |
| Total S, m | 1.03E-02 | 1.03E-02 | 1.03E-02 | 1.24E-02 | 1.23E-02 | 1.99E-02 |
| Total $SiO_2$, m | 2.05E-08 | 2.05E-08 | 2.05E-08 | 7.30E-06 | 7.26E-06 | 1.26E-04 |

Table 4-46. Sensitivity to Reactant Relative Reaction Rates: rk1 = 0.2X.

| Parameter | Period A | Period B | Period C | Period D | Period E | Period F |
|---|---|---|---|---|---|---|
| Input File | PerAsen1.6i | PerBsen1.6i | PerCsen1.6i | PerDsen1.6i | PerEsen1.6i | PerFsen1.6i |
| Output File | PerAsen1.6o | PerBsen1.6o | PerCsen1.6o | PerDsen1.6o | PerEsen1.6o | PerFsen1.6o |
| Code/version | EQ6/V7.2b | EQ6/V7.2b | EQ6/V7.2b | EQ6/V7.2b | EQ6/V7.2b | EQ6/V7.2b |
| PH | 10.4 | 10.4 | 10.4 | 10.9 | 10.9 | 7.44 |
| Total Al, m | 4.04E-03 | 4.04E-03 | 4.04E-03 | 3.61E-07 | 3.61E-07 | 2.72E-09 |
| Total CO3--, m | 7.33E-06 | 8.73E-07 | 7.33E-06 | 8.02E-06 | 8.02E-06 | 5.50E-04 |
| Total Ca, m | 6.72E-03 | 6.71E-03 | 6.72E-03 | 1.32E-02 | 1.32E-02 | 1.62E-02 |
| Total Cl, m | 1.68E-03 | 1.68E-03 | 1.67E-03 | 1.98E-04 | 1.97E-04 | 1.94E-04 |
| Total F, m | 2.77E-04 | 2.77E-04 | 2.77E-04 | 1.12E-04 | 1.12E-04 | 1.10E-04 |
| Total Fe, m | 5.90E-26 | 5.90E-25 | 3.32E-26 | 2.22E-31 | 1.25E-31 | 2.61E-22 |
| Total K, m | 4.05E-03 | 4.05E-03 | 4.05E-03 | 3.67E-03 | 3.65E-03 | 1.01E-04 |
| Total Mg, m | 3.78E-08 | 3.78E-08 | 3.78E-08 | 6.29E-10 | 6.29E-10 | 1.28E-03 |
| Total Na, m | 1.76E-02 | 1.76E-02 | 1.76E-02 | 3.14E-03 | 3.13E-03 | 3.08E-03 |
| Total S, m | 6.80E-03 | 6.80E-03 | 6.80E-03 | 8.45E-03 | 8.44E-03 | 1.86E-02 |
| Total $SiO_2$, m | 1.65E-08 | 1.65E-08 | 1.65E-08 | 5.65E-06 | 5.64E-06 | 1.26E-04 |

Table 4-47. Sensitivity to Reactant Relative Reaction Rates: rk1 = 5X.

| Parameter | Period A | Period B | Period C | Period D | Period E | Period F |
|---|---|---|---|---|---|---|
| Input File | PerAsen2.6i | PerBsen2.6i | PerCsen2.6i | PerDsen2.6i | PerEsen2.6i | PerFsen2.6i |
| Output File | PerAsen2.6o | PerBsen2.6o | PerCsen2.6o | PerDsen2.6o | PerEsen2.6o | PerFsen2.6o |
| Code/version | EQ6/V7.2b | EQ6/V7.2b | EQ6/V7.2b | EQ6/V7.2b | EQ6/V7.2b | EQ6/V7.2b |
| PH | 10.7 | 10.7 | 10.7 | 11.2 | 11.2 | 7.49 |
| Total Al, m | 7.66E-03 | 7.67E-03 | 7.65E-03 | 6.98E-07 | 6.78E-07 | 3.08E-09 |
| Total CO3--, m | 9.18E-06 | 1.10E-06 | 9.18E-06 | 9.85E-06 | 9.69E-06 | 6.11E-04 |
| Total Ca, m | 3.83E-03 | 3.81E-03 | 3.83E-03 | 7.09E-03 | 7.22E-03 | 1.44E-02 |
| Total Cl, m | 1.29E-03 | 1.29E-03 | 1.28E-03 | 1.42E-04 | 1.32E-04 | 1.08E-04 |
| Total F, m | 5.14E-04 | 5.15E-04 | 5.13E-04 | 8.07E-05 | 7.50E-05 | 6.12E-05 |
| Total Fe, m | 4.86E-26 | 4.86E-25 | 2.73E-26 | 3.15E-31 | 1.74E-31 | 2.11E-22 |
| Total K, m | 5.79E-02 | 5.82E-02 | 5.78E-02 | 6.37E-02 | 5.92E-02 | 9.27E-05 |
| Total Mg, m | 3.04E-08 | 3.04E-08 | 3.04E-08 | 4.52E-10 | 4.56E-10 | 1.17E-03 |
| Total Na, m | 3.18E-02 | 3.19E-02 | 3.17E-02 | 2.26E-02 | 2.10E-02 | 1.71E-02 |
| Total S, m | 2.91E-02 | 2.93E-02 | 2.90E-02 | 3.44E-02 | 3.20E-02 | 2.38E-02 |
| Total $SiO_2$, m | 3.33E-08 | 3.34E-08 | 3.32E-08 | 1.32E-05 | 1.26E-05 | 1.26E-04 |

Table 4-48. Sensitivity to Reactant Relative Reaction Rates: rk1=Constant for All Reactants =1.0.

| Parameter | Period A | Period B | Period C | Period D | Period E | Period F |
|---|---|---|---|---|---|---|
| Input File | PerAsen7.6l | PerBsen7.6l | PerCsen7.6i | PerDsen7.6i | PerEsen7.6i | PerFsen7.6i |
| Output File | PerAsen7.6o | PerBsen7.6o | PerCsen7.6o | PerDsen7.6o | PerEsen7.6o | PerFsen7.6o |
| Code/version | EQ6/V7.2b | EQ6/V7.2b | EQ6/V7.2b | EQ6/V7.2b | EQ6/V7.2b | EQ6/V7.2b |
| pH | 7.89 | 7.89 | 7.80 | 8.14 | 8.14 | 7.81 |
| Total Al, m | 1.13E-06 | 1.13E-06 | 8.13E-07 | 3.88E-07 | 3.88E-07 | 6.95E-09 |
| Total CO3--, m | 5.53E-05 | 5.53E-11 | 4.43E-06 | 1.53E-04 | 2.17E-04 | 1.38E-03 |
| Total Ca, m | 2.71E-03 | 2.71E-03 | 2.80E-03 | 5.28E-03 | 5.28E-03 | 8.95E-03 |
| Total Cl, m | 1.06E-03 | 1.06E-03 | 1.05E-03 | 1.16E-04 | 1.16E-04 | 1.21E-04 |
| Total F, m | 6.04E-04 | 6.03E-04 | 5.98E-04 | 6.59E-05 | 6.60E-05 | 6.89E-05 |
| Total Fe, m | 4.07E-09 | 4.07E-09 | 1.23E-21 | 6.35E-23 | 3.58E-23 | 7.71E-23 |
| Total K, m | 6.51E-04 | 6.51E-04 | 5.41E-04 | 1.86E-04 | 1.86E-04 | 8.41E-05 |
| Total Mg, m | 1.98E-05 | 1.98E-05 | 2.30E-05 | 3.48E-05 | 3.48E-05 | 8.24E-04 |
| Total Na, m | 1.71E-01 | 1.71E-01 | 1.18E-01 | 1.49E-01 | 1.49E-01 | 5.40E-01 |
| Total S, m | 8.75E-02 | 8.75E-02 | 6.12E-02 | 7.97E-02 | 7.97E-02 | 2.79E-01 |
| Total $SiO_2$, m | 5.74E-04 | 5.74E-04 | 6.68E-04 | 3.63E-04 | 3.63E-04 | 1.39E-04 |

Table 4-49. Sensitivity to Reactant Relative Reaction Rates: rk1= Constant for All Reactants = 0.1.

| Parameter | Period A | Period B | Period C | Period D | Period E | Period F |
|---|---|---|---|---|---|---|
| Input File | PerAsen8.6i | PerBsen8.6i | PerCsen8.6i | PerDsen8.6i | PerEsen8.6i | PerFsen8.6i |
| Output File | PerAsen8.6o | PerBsen8.6o | PerCsen8.6o | PerDsen8.6o | PerEsen8.6o | PerFsen8.6o |
| Code/version | EQ6/V7.2b | EQ6/V7.2b | EQ6/V7.2b | EQ6/V7.2b | EQ6/V7.2b | EQ6/V7.2b |
| pH | 8.23 | 7.88 | 7.80 | 8.14 | 8.04 | 7.71 |
| Total Al, m | 2.29E-06 | 9.54E-07 | 8.11E-07 | 3.88E-07 | 2.61E-07 | 5.58E-09 |
| Total CO3--, m | 1.11E-04 | 5.16E-11 | 4.42E-06 | 1.53E-04 | 2.13E-04 | 1.04E-03 |
| Total Ca, m | 3.74E-04 | 1.78E-03 | 2.81E-03 | 5.28E-03 | 5.57E-03 | 1.01E-02 |
| Total Cl, m | 1.60E-03 | 1.60E-03 | 1.60E-03 | 1.88E-04 | 1.88E-04 | 1.89E-04 |
| Total F, m | 9.10E-04 | 8.84E-04 | 7.54E-04 | 1.06E-04 | 1.06E-04 | 1.07E-04 |
| Total Fe, m | 8.47E-10 | 3.66E-09 | 1.24E-21 | 6.35E-23 | 5.09E-23 | 1.05E-22 |
| Total K, m | 2.46E-04 | 4.33E-04 | 5.42E-04 | 1.86E-04 | 1.51E-04 | 7.15E-05 |
| Total Mg, m | 2.54E-06 | 1.43E-05 | 2.30E-05 | 3.48E-05 | 3.38E-05 | 8.95E-04 |
| Total Na, m | 6.81E-02 | 9.57E-02 | 1.18E-01 | 1.49E-01 | 9.53E-02 | 1.90E-01 |
| Total S, m | 3.31E-02 | 4.86E-02 | 6.10E-02 | 7.97E-02 | 5.30E-02 | 1.05E-01 |
| Total $SiO_2$, m | 6.16E-04 | 6.75E-04 | 6.68E-04 | 3.63E-04 | 4.36E-04 | 1.30E-04 |

Table 4-50. Input/Output Files for Sensitivity to Phase Suppression: Additional Phases Relative to Baseline (epidote, epidote-ord, fremolite amd diopside).

| Parameter | Period A | Period B | Period C | Period D | Period E | Period F |
|---|---|---|---|---|---|---|
| Input File | PerAsen5.6i | PerBsen5.6i | PerCsen5.6i | PerDsen5.6i | PerEsen5.6i | PerFsen5.6i |
| Output File | PerAsen5.6o | PerBsen5.6o | PerCsen5.6o | PerDsen5.6o | PerEsen5.6o | PerFsen5.6o |
| Code/version | EQ6/V7.2b | EQ6/V7.2b | EQ6/V7.2b | EQ6/V7.2b | EQ6/V7.2b | EQ6/V7.2b |

Table 4-51. Results of Sensitivity to Phase Suppression: Additional Phases Relative to Baseline (epidote, epidote-ord, fremolite amd diopside).

| pH | 10.5 | 10.5 | 10.5 | 11.0 | 11.0 | 7.46 |
|---|---|---|---|---|---|---|
| Total Al, m | 4.95E-03 | 4.96E-03 | 4.95E-03 | 4.44E-07 | 4.42E-07 | 2.82E-09 |
| Total CO3--, m | 7.67E-06 | 9.14E-07 | 7.67E-06 | 8.33E-06 | 8.32E-06 | 5.67E-04 |
| Total Ca, m | 5.40E-03 | 5.39E-03 | 5.40E-03 | 1.04E-02 | 1.04E-02 | 1.56E-02 |
| Total Cl, m | 1.59E-03 | 1.60E-03 | 1.59E-03 | 1.86E-04 | 1.82E-04 | 1.72E-04 |
| Total F, m | 3.36E-04 | 3.37E-04 | 3.36E-04 | 1.05E-04 | 1.03E-04 | 9.73E-05 |
| Total Fe, m | 5.35E-26 | 5.35E-25 | 3.01E-26 | 2.41E-31 | 1.35E-31 | 2.45E-22 |
| Total K, m | 1.52E-02 | 1.52E-02 | 1.52E-02 | 1.67E-02 | 1.64E-02 | 9.82E-05 |
| Total Mg, m | 3.45E-08 | 3.45E-08 | 3.45E-08 | 1.32E-09 | 1.33E-09 | 1.24E-03 |
| Total Na, m | 2.05E-02 | 2.05E-02 | 2.05E-02 | 7.37E-03 | 7.22E-03 | 6.81E-03 |
| Total S, m | 1.03E-02 | 1.03E-02 | 1.03E-02 | 1.24E-02 | 1.22E-02 | 1.99E-02 |
| Total $SiO_2$, m | 2.05E-08 | 2.05E-08 | 2.05E-08 | 7.30E-06 | 7.25E-06 | 1.26E-04 |

Table 4-52. Input/Output Files for Sensitivity to Phase Suppression: No Phases Suppressed.

| Parameter | Period A | Period B | Period C | Period D | Period E | Period F |
|---|---|---|---|---|---|---|
| Input File | PerAsen6.6i | PerBsen6.6i | PerCsen6.6i | PerDsen6.6i | PerEsen6.6i | PerFsen6.6i |
| Output File | PerAsen6.6o | PerBsen6.6o | PerCsen6.6o | PerDsen6.6o | PerEsen6.6o | PerFsen6.6o |
| Code/version | EQ6/V7.2b | EQ6/V7.2b | EQ6/V7.2b | EQ6/V7.2b | EQ6/V7.2b | EQ6/V7.2b |

Table 4-53. Results of Sensitivity to Phase Suppression: No Phases Suppressed.

| | | | | | | |
|---|---|---|---|---|---|---|
| PH | 10.5 | 10.5 | 10.5 | 11.0 | 11.0 | 7.46 |
| Total Al, m | 4.95E-03 | 4.96E-03 | 4.95E-03 | 5.24E-06 | 5.22E-06 | 2.82E-09 |
| Total CO3--, m | 7.67E-06 | 9.14E-07 | 7.67E-06 | 8.33E-06 | 8.32E-06 | 5.67E-04 |
| Total Ca, m | 5.40E-03 | 5.39E-03 | 5.40E-03 | 1.04E-02 | 1.04E-02 | 1.56E-02 |
| Total Cl, m | 1.59E-03 | 1.60E-03 | 1.59E-03 | 1.85E-04 | 1.82E-04 | 1.72E-04 |
| Total F, m | 3.36E-04 | 3.37E-04 | 3.36E-04 | 1.05E-04 | 1.03E-04 | 9.73E-05 |
| Total Fe, m | 5.35E-26 | 5.35E-25 | 3.01E-26 | 2.85E-30 | 1.60E-30 | 2.45E-22 |
| Total K, m | 1.52E-02 | 1.52E-02 | 1.52E-02 | 1.67E-02 | 1.64E-02 | 9.82E-05 |
| Total Mg, m | 3.45E-08 | 3.45E-08 | 3.45E-08 | 6.87E-09 | 6.89E-09 | 1.24E-03 |
| Total Na, m | 2.05E-02 | 2.05E-02 | 2.05E-02 | 7.36E-03 | 7.21E-03 | 6.81E-03 |
| Total S, m | 1.03E-02 | 1.03E-02 | 1.03E-02 | 1.24E-02 | 1.22E-02 | 1.99E-02 |
| Total $SiO_2$, m | 2.05E-08 | 2.05E-08 | 2.05E-08 | 1.41E-06 | 1.40E-06 | 1.26E-04 |

Table 4-54. Composition (m) of Reflux Water After EQ6 Evaporation to an Ionic Strength of 1 Molal.

| Component | Period A (0-200 yrs) | Period B (200-1000 yrs) | Period C (1000-2000 yrs) |
|---|---|---|---|
| pH | 10.4 | 11.7 | 10.8 |
| Al | 4.40E-08 | 6.11E-05 | 2.73E-07 |
| Ca | 6.85E-06 | 4.52E-08 | 6.96E-06 |
| Cl | 9.71E-02 | 1.12E-01 | 9.56E-02 |
| F | 5.53E-02 | 6.37E-02 | 5.45E-02 |
| Fe | 8.08E-16 | 1.19E-15 | 1.50E-16 |
| C | 2.22E-01 | 9.93E-05 | 1.29E-01 |
| K | 6.20E-02 | 7.16E-02 | 6.11E-02 |
| Mg | 1.64E-11 | 1.43E-13 | 3.39E-12 |
| Na | 9.61E-01 | 1.11E+00 | 9.45E-01 |
| S | 9.24E-02 | 1.06E-01 | 9.09E-02 |
| Si | 2.44E-01 | 3.37E-01 | 3.72E-01 |

Table 4-55. Normative Salt Distributions (m) for the Modeled Reflux Water During the Boiling Periods. These Values Assume Complete Vaporization of Water.

| Salt | Period A (0-200 yrs) | Period B (200-1000 yrs) | Period C (1000-2000 yrs) |
|---|---|---|---|
| $CaCO_3$ | 7.87E-06 | 2.62E-06 | 1.01E-05 |
| $Na_2SO_4$ | 1.93E-03 | 1.93E-03 | 1.93E-03 |
| $Na_2Si_2O_5$ | 2.55E-03 | 0.00E+00 | 2.76E-03 |
| $Na_2SiO_3$ | 0.00E+00 | 6.13E-03 | 2.37E-03 |
| $NaHCO_3$ | 2.28E-03 | 0.00E+00 | 0.00E+00 |
| $Na_2CO_3$ | 2.77E-03 | 0.00E+00 | 1.23E-03 |
| NaCl | 2.03E-03 | 2.03E-03 | 2.03E-03 |
| NaF | 1.16E-03 | 1.16E-03 | 1.16E-03 |
| $KNO_3$ | 1.30E-03 | 1.30E-03 | 1.30E-03 |
| $NaNO_3$ | 1.24E-04 | 1.21E-04 | 1.23E-04 |

Table 4-56. Comparison of the Swiss Model Results Using EMMA with that of the Same Swiss Model Parameters Used in MING. Table taken from Ehrhorn and Jolley (1998).

| Time Period (a) | Maximum Energy (kj/a) | | Maximum Biomass (g/a) | |
|---|---|---|---|---|
| | EMMA | MING | EMMA | MING |
| 0-270 | 50.6 | 50.6 | 0.79 | 0.791 |
| 271-3,030 | 8.3 | 8.14 | 0.13 | 0.127 |
| 3,031-10,000 | 2.5E-01 | 2.53E-01 | 4.0E-03 | 3.97E-03 |
| 10,001+ | 2.5E-01 | 2.53E-01 | 4.0E-03 | 3.97E-03 |

Table 4-57. Determination of an Equivalent Abundance of Microbes Measured at the Exploratory Studies Facility (ESF) with One Lineal Meter of Repository Drift. Data taken from Jolley (1998b) (TBV-373).

| Microbial Abundance | ESF Low Value | Reiner Mesa | ESF High Value |
|---|---|---|---|
| Number of cells per gram of crushed tuff | 3.20E+04 | 1.0E+04 | 3.20E+05 |
| Number of cells per linear meter of repository | 1.50E+12 | 4.7E+11 | 1.50E+13 |
| Average microbial mass (g) | 1.50E-13 | 1.50E-13 | 1.50E-13 |
| Mass (g) of cells per lineal meter of repository | 2.25E-01 | 7.05E-02 | 2.25E+00 |

Table 4-58. J-13 Water Compositions Used in MING Calculations. Data from Harrar et al. (1990) and converted to Kmol/m$^3$.

| Groundwater Constituent | Concentration (Kmol/m$^3$) |
|---|---|
| $Na^+$ | 1.99E-03 |
| Si | 1.02E-03 |
| $Ca^{2+}$ | 3.25E-04 |
| $K^+$ | 1.28E-04 |
| $Mg^{2+}$ | 8.38E-05 |
| $Li^+$ | 6.90E-06 |
| $HCO^{3-}$ | 2.12E-03 |
| $O_2$ | 1.75E-04 |
| $F^-$ | 1.15E-04 |
| $Cl^-$ | 2.03E-04 |
| $NO^{3-}$ | 1.42E-04 |
| $SO4^{2-}$ | 1.92E-04 |
| B | 1.22E-05 |
| Al | 1.80E-06 |
| $Mn^{2+}$ | 8.00E-07 |
| $Fe^{2+}$ | 5.80E-07 |
| $Sr^{2+}$ | 6.00E-07 |
| $PO4^{3-}$ | 3.80E-06 |
| DOC ($CH_2O$) | 3.30E-05 |
| Ph | 7.4 |

Table 4-59. Cumulative Gas Flux Values (kg/m2) Used in the Ambient Case MING Calculations. Values were Derived by Taking the 100,000 Year Cumulative Flux Value (Figure 4-34) and Assuming that Value was at or Very Near Ambient Conditions.

| Year | $CO_2$ | $O_2$ | $N_2$ | $CH_4$ |
|---|---|---|---|---|
| 1 | 2.00E-5 | 4.64E-3 | 1.85E-2 | 0 |
| 50 | 1.00E-3 | 2.32E-1 | 9.25E-1 | 0 |
| 200 | 4.00E-3 | 9.28E-1 | 3.70E-0 | 0 |
| 3,000 | 6.00E-2 | 1.39E+1 | 5.55E+1 | 0 |
| 5,000 | 1.00E-1 | 2.32E+1 | 9.25E+1 | 0 |
| 27,560 | 5.55E-1 | 1.27E+2 | 5.10E+2 | 0 |
| 28,000 | 5.60E-1 | 1.30E+2 | 5.17E+2 | 0 |
| 50,000 | 1.00E-0 | 2.32E+2 | 9.25E+2 | 0 |
| 100,001 | 2.00E-0 | 4.64E+2 | 1.85E+3 | 0 |
| 1,000,000 | 2.00E+1 | 4.64E+3 | 1.85E+4 | 0 |

Table 4-60. Elemental Composition of Type 5 Concrete Used in the 21 PWR MING Calculations. Data from Jolley (1998c) (TBV-372).

| Element | Wt % |
|---|---|
| Si | 30.27 |
| Al | 5.10 |
| Fe | 0.85 |
| Ca | 8.03 |
| Mg | 0.25 |
| Ti | 0.04 |
| Na | 2.25 |
| K | 2.03 |
| P | 0.01 |
| Mn | 0.03 |
| S | 0.12 |
| C | 0.03 |
| H | 0.38 |
| O | 50.78 |

Table 4-61. Elemental Composition of Steel Fiber, ASTM A36 Steel Used in the 21 PWR MING Calculations. Data from Jolley (1998c) (TBV-372).

| Element | Wt % |
|---|---|
| C | 0.26 |
| P | 0.04 |
| S | 0.05 |
| Si | 0.4 |
| Fe | 99.25 |

Table 4-62. Elemental Composition of Water Reducer Used in the 21 PWR MING Calculations. Data from Jolley (1998c) (TBV-372).

| Element | Wt % |
|---|---|
| C | 23.5 |
| H | 8.7 |
| Na | 6.64 |
| S | 5.01 |
| O | 54.46 |
| Cl | 0.06 |
| N | 0.81 |
| Ca | 0.78 |

Table 4-63. Elemental Composition of Superplasticizer Used in the 21 PWR MING Calculations. Data from Jolley (1998c) (TBV-372).

| Element | Wt % |
|---|---|
| C | 16.12 |
| H | 8.03 |
| S | 4.28 |
| O | 66.16 |
| Cl | 0.04 |
| Ca | 0.54 |

Table 4-64. Elemental Composition of Swellex Rock Bolt Sets, (ASTM F432-95 Steel) Used in the 21 PWR MING Calculations. Data from Jolley (1998c) (TBV-372).

| Element | Wt % |
|---|---|
| C | 0.79 |
| P | 0.058 |
| S | 0.13 |
| Fe | 99.022 |

Table 4-65. Elemental Composition of Rebar, (ASTM A 706 Steel) Used in the 21 PWR MING Calculations. Data from Jolley (1998c) (TBV-372).

| Element | Wt % |
|---|---|
| C | 0.3 |
| Mn | 1.5 |
| P | 0.035 |
| S | 0.045 |
| Si | 0.5 |
| Fe | 97.62 |

Table 4-66. Elemental Composition of Wire Mesh & Rolled Channel, (ASTM A36 Steel) Used in the 21 PWR MING Calculations. Data from Jolley (1998c) (TBV-372).

| Element | Wt % |
|---|---|
| C | 0.26 |
| P | 0.04 |
| S | 0.05 |
| Si | 0.4 |
| Fe | 99.25 |

Table 4-67. Elemental Composition of Gantry Rail, (Unspecified Steel) Used in the 21 PWR MING Calculations. Data from Jolley (1998c) (TBV-372).

| Element | Wt % |
|---|---|
| C | 0.67 |
| Mn | 1 |
| P | 0.04 |
| Si | 0.05 |
| S | 0.25 |
| Fe | 97.99 |

Table 4-68. Elemental Composition of Rail Fittings, (Unspecified Steel and Copper) Used in the 21 PWR MING Calculations. Data from Jolley (1998c) (TBV-372).

| Element | Wt % |
|---|---|
| C | 0.195 |
| P | 0.03 |
| S | 0.0375 |
| Si | 0.3 |
| Cu | 25 |
| Fe | 74.44 |

Table 4-69. Elemental Composition of Steel Set Ground Support, (ASTM A36 Steel) Used in the 21 PWR MING Calculations. Data from Jolley (1998c) (TBV-372).

| Element | Wt % |
|---|---|
| C | 0.26 |
| P | 0.04 |
| S | 0.05 |
| Si | 0.4 |
| Fe | 99.25 |

Table 4-70. Elemental Composition of Conductor Bar Fittings, (ASTM A36 Steel) Used in the 21 PWR MING Calculations. Data from Jolley (1998c) (TBV-372).

| Element | Wt % |
|---|---|
| C | 0.26 |
| P | 0.04 |
| S | 0.05 |
| Si | 0.4 |
| Fe | 99.25 |

Table 4-71. Elemental Composition of Commo Cable Used in the 21 PWR MING Calculations. Data from Jolley (1998c) (TBV-372).

| Element | WT % |
|---|---|
| Cu | 50 |
| C | 27 |
| H | 3 |
| Cl | 20 |

Table 4-72. Masses of Materials for a One-Meter CIP Concrete Repository Segment Used in the 21 PWR MING Calculations. Data from Jolley (1998c) (TBV-372).

| Material | Quantity kg/m |
|---|---|
| Type 5 concrete | 10,426.44 |
| Water reducer | 12.43 |
| Superplacticizer | 30.51 |
| Gantry Rail | 89.3 |
| Rail fittings | 8.9 |
| Conductor Bar Fittings | 0.2 |
| Commo cable | 0.79 |
| Rock Bolts | 12.2 |
| Wire Mesh | 233.9 |
| Steel Sets | 372.1 |

Table 4-73. Normalized Elemental Composition of 21 PWR Waste Used in the 21 PWR MING Calculations. Data from Jolley (1998d) (TBV-371).

| Element | % composition |
|---|---|
| C | 0.59 |
| N | 0.38 |
| P | 0.66 |
| S | 0.07 |
| Mn | 2.54 |
| Fe | 95.73 |

Table 4-74. Elemental Composition of Waste Package Supports (ASTM A 36 Steel) Used in the 21 PWR MING Calculations. Data from Jolley (1998d) (TBV-371).

| Element | % composition |
|---|---|
| C | 0.26 |
| P | 0.04 |
| S | 0.05 |
| Si | 0.4 |
| Fe | 99.25 |

Table 4-75. Elemental Composition of C-22 Alloy (ASTM B 575 [CRM]) Used in the 21 PWR MING Calculations. Data from Jolley (1998d) (TBV-371).

| Element | % composition |
|---|---|
| Mo | 14.5 |
| Cr | 22.5 |
| Fe | 6 |
| W | 3.5 |
| Co | 2.5 |
| C | 0.015 |
| Si | 0.08 |
| Mn | 0.5 |
| V | 0.35 |
| P | 0.02 |
| S | 0.02 |
| Ni | 50.015 |

Table 4-76. Elemental Composition of Carbon Steel ASTM A 516 (CAM) Used in the 21 PWR MING Calculations. Data from Jolley (1998d) (TBV-371).

| Element | % composition |
|---|---|
| C | 0.31 |
| Mn | 1.3 |
| P | 0.035 |
| S | 0.035 |
| Si | 0.045 |
| Fe | 98.275 |

Table 4-77. Elemental Composition of Aluminum, Type 6061 (Thermal Shunt) Used in the 21 PWR MING Calculations. Data from Jolley (1998d) (TBV-371).

| Element | % composition |
|---|---|
| Si | 0.8 |
| Fe | 0.7 |
| Cu | 0.4 |
| Mn | 0.15 |
| Mg | 1.2 |
| Cr | 0.35 |
| Z | 0.25 |
| Ti | 0.15 |
| other | 0.15 |
| Al | 95.85 |

Table 4-78. Elemental Composition of Neutronit A 978 (Absorber Plates) Used in the 21 PWR MING Calculations. Data from Jolley (1998d) (TBV-371).

| Element | % composition |
|---|---|
| C | 0.04 |
| Cr | 18.5 |
| Ni | 13 |
| Mo | 2.2 |
| Co | 0.2 |
| B | 1.74 |
| Fe | 66.06 |

Table 4-79. Masses of Materials for a One-Meter Segment of a 21 PWR Waste Package Used in the 21 PWR MING Calculations. Data from Jolley (1998d) (TBV-371).

| Material | Quantity (kg/m wp) |
|---|---|
| ASTM A 516 (CAM) | 4,301.7 |
| ASTM B 575 (C-22) (CRM) | 820.19 |
| ASTM A 516 (Basket guides) | 1,028.49 |
| Aluminum, Type 6061 (Thermal shunts) | 54.9 |
| Neutronit A 978 (Basket plates) | 355.28 |
| 21 PWR Waste | 34.359 |

Table 4-80. Temperature, Relative Humidity and Infiltration Rate Histories Used in the 21PWR Calculations. Values are taken from Chapter 3.

| Time (Years) | Temperature (°C) | RH (Fraction) | Infiltration Rate (mm/yr) |
|---|---|---|---|
| 1 | 1.083E+02 | 3.159E-01 | 7.800E+00 |
| 5 | 1.229E+02 | 4.211E-01 | 7.800E+00 |
| 10 | 1.331E+02 | 4.981E-01 | 7.800E+00 |
| 15 | 1.452E+02 | 3.331E-01 | 7.800E+00 |
| 20 | 1.474E+02 | 2.681E-01 | 7.800E+00 |
| 30 | 1.453E+02 | 2.171E-01 | 7.800E+00 |
| 50 | 1.391E+02 | 2.586E-01 | 7.800E+00 |
| 75 | 1.293E+02 | 3.436E-01 | 7.800E+00 |
| 100 | 1.253E+02 | 3.893E-01 | 7.800E+00 |
| 101 | 1.252E+02 | 3.900E-01 | 7.800E+00 |
| 125 | 1.225E+02 | 4.259E-01 | 7.800E+00 |
| 150 | 1.180E+02 | 4.909E-01 | 7.800E+00 |
| 175 | 1.162E+02 | 5.227E-01 | 7.800E+00 |
| 200 | 1.141E+02 | 5.677E-01 | 7.800E+00 |
| 225 | 1.135E+02 | 5.828E-01 | 7.800E+00 |
| 250 | 1.128E+02 | 6.009E-01 | 7.800E+00 |
| 300 | 1.118E+02 | 6.209E-01 | 7.800E+00 |
| 400 | 1.105E+02 | 6.472E-01 | 7.800E+00 |
| 500 | 1.093E+02 | 6.713E-01 | 7.800E+00 |
| 600 | 1.079E+02 | 7.019E-01 | 7.800E+00 |
| 700 | 1.066E+02 | 7.307E-01 | 7.800E+00 |
| 800 | 1.048E+02 | 7.792E-01 | 7.800E+00 |
| 900 | 1.034E+02 | 8.230E-01 | 7.800E+00 |
| 1,000 | 1.023E+02 | 8.578E-01 | 7.800E+00 |
| 1,250 | 1.008E+02 | 8.994E-01 | 7.800E+00 |
| 1,500 | 9.953E+01 | 9.348E-01 | 7.800E+00 |
| 1,750 | 9.883E+01 | 9.507E-01 | 7.800E+00 |
| 2,000 | 9.825E+01 | 9.609E-01 | 7.800E+00 |
| 2,500 | 9.676E+01 | 9.667E-01 | 7.800E+00 |
| 3,000 | 9.514E+01 | 9.691E-01 | 7.800E+00 |
| 3,500 | 9.363E+01 | 9.696E-01 | 7.800E+00 |
| 4,000 | 9.211E+01 | 9.708E-01 | 7.800E+00 |

Table 4-80. (continued).

| Time (Years) | Temperature (°C) | RH (Fraction) | Infiltration Rate (mm/yr) |
|---|---|---|---|
| 4,500 | 9.061E+01 | 9.717E-01 | 7.800E+00 |
| 5,000 | 7.163E+01 | 9.680E-01 | 4.206E+01 |
| 6,000 | 6.419E+01 | 9.685E-01 | 4.206E+01 |
| 7,000 | 5.972E+01 | 9.681E-01 | 4.206E+01 |
| 8,000 | 5.634E+01 | 9.693E-01 | 4.206E+01 |
| 9,000 | 5.393E+01 | 9.688E-01 | 4.206E+01 |
| 10,000 | 5.213E+01 | 9.693E-01 | 4.206E+01 |
| 12,500 | 4.816E+01 | 9.711E-01 | 4.206E+01 |
| 15,000 | 4.441E+01 | 9.734E-01 | 4.206E+01 |
| 20,000 | 3.918E+01 | 9.760E-01 | 4.206E+01 |
| 25,000 | 3.489E+01 | 9.793E-01 | 4.206E+01 |
| 30,000 | 3.163E+01 | 9.813E-01 | 4.206E+01 |
| 40,000 | 2.749E+01 | 9.848E-01 | 4.206E+01 |
| 50,000 | 2.519E+01 | 9.871E-01 | 4.206E+01 |
| 63,000 | 2.303E+01 | 9.904E-01 | 4.206E+01 |
| 75,000 | 2.182E+01 | 9.916E-01 | 4.206E+01 |
| 100,000 | 2.035E+01 | 9.939E-01 | 4.206E+01 |
| 120,000 | 1.983E+01 | 9.945E-01 | 4.206E+01 |
| 140,000 | 1.937E+01 | 9.952E-01 | 4.206E+01 |
| 160,000 | 1.904E+01 | 9.957E-01 | 4.206E+01 |
| 180,000 | 1.883E+01 | 9.962E-01 | 4.206E+01 |
| 200,000 | 1.863E+01 | 9.965E-01 | 4.206E+01 |
| 300,000 | 1.819E+01 | 9.972E-01 | 4.206E+01 |
| 400,000 | 1.801E+01 | 9.975E-01 | 4.206E+01 |
| 500,000 | 1.791E+01 | 9.977E-01 | 4.206E+01 |
| 600,000 | 1.785E+01 | 9.978E-01 | 4.206E+01 |
| 700,000 | 1.781E+01 | 9.979E-01 | 4.206E+01 |
| 800,000 | 1.778E+01 | 9.979E-01 | 4.206E+01 |
| 900,000 | 1.776E+01 | 9.980E-01 | 4.206E+01 |
| 1,000,000 | 1.776E+01 | 9.980E-01 | 4.206E+01 |

Table 4-81. Reactant Compositions, Breakdown Codes and Molecular Masses for the release of Organic Materials. This input is documented in Jolley (1998e) (TBV 369).

| **Water Reducer** | *Reactant Composition* | *Breakdown Code* | *Molecular Mass* |
|---|---|---|---|
| | $NO_3^-$ | 1 | 1731.8 |
| | $CH_2O$ | 7.85 | |
| | $H_2S$ | 0.42 | |
| | $CH_3OH$ | 2.01 | |
| | $SO_3^{2-}$ | 2.29 | |
| **Superplasticizer** | *Reactant Composition* | *Breakdown Code* | *Molecular Mass* |
| | $CH_2O$ | 0.96 | 1990.9 |
| | $SO_3^{2-}$ | 1 | |
| **Wire Conductor** | *Reactant Composition* | *Breakdown Code* | *Molecular Mass* |
| | $CH_2O$ | 8.53 | 3264.5 |
| | $CH_3OH$ | 0.02 | |
| **Commo Cable** | *Reactant Composition* | *Breakdown Code* | *Molecular Mass* |
| | $CH_2O$ | 3.95 | 174.8 |

Table 4-82. MING Input Material Lifetimes for Each Calculated 21PWR Case.

| Material_Name | Case 5 | Case 6 | Case 7 | Case 8 | Case 9 | Case 10 |
|---|---|---|---|---|---|---|
| Aluminum 6061 (TS) | 8000 | 8000 | 8000 | 8000 | 8000 | 8000 |
| C Steel ASTM A516 (CAM) | 8000 | 8000 | 5000 | 5000 | 10000 | 10000 |
| Neutronit A978 (BM) | 5000 | 5000 | 5000 | 5000 | 5000 | 5000 |
| 21 PWR Waste | 1000 | 1000 | 1000 | 1000 | 1000 | 1000 |
| Alloy C-22 ASTM B 575 (CRM) | 100000 | 100000 | 50000 | 50000 | 250000 | 250000 |
| Conductor Bar fittings | 2500 | 2500 | 2500 | 2500 | 2500 | 2500 |
| Type V Concrete | 100000 | 100000 | 10000 | 100000 | 10000 | 100000 |
| Gantry Rail | 8000 | 8000 | 5000 | 5000 | 10000 | 10000 |
| Rail Fittings | 2500 | 2500 | 2500 | 2500 | 2500 | 2500 |
| Water Reducer | 100000 | 100000 | 10000 | 100000 | 10000 | 100000 |
| Steel Fiber (ASTM A36) | 100000 | 100000 | 10000 | 100000 | 10000 | 100000 |
| Superplasticizer | 100000 | 100000 | 10000 | 100000 | 10000 | 100000 |
| Commo Cable | 2500 | 2500 | 2500 | 2500 | 2500 | 2500 |
| Waste Package Supports | 8000 | 8000 | 5000 | 5000 | 10000 | 10000 |

Table 4-83. Material Layer Designators Used in MING for the Sequential Degradation of Waste Package and Repository Materials.

| Material Name | Layer |
|---|---|
| Aluminum 6061 (TS) | 2 |
| C Steel ASTM A516 (CAM) | 1 |
| Neutronit A978 (BM) | 2 |
| 21 PWR Waste | 2 |
| Alloy C-22 ASTM B 575 (CRM) | 2 |
| Conductor Bar fittings | 0 |
| Type V Concrete | 0 |
| Gantry Rail | 0 |
| Rail Fittings | 0 |
| Water Reducer | 0 |
| Steel Fiber (ASTM A36) | 0 |
| Superplasticizer | 0 |
| Commo Cable | 0 |

Table 4-84. Limiting Nutrient Results for each 21 PWR Case. RH (Relative Humidity) is not a Nutrient but Prohibits Microbial Growth. P and C are Phosphorous and Carbon Respectively.

| Case 5 | | Case 6 | | Case 7 | | Case 8 | | Case 9 | | Case 10 | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Year | Nutrient | Year | Nutrient | Year | Nutrient | Year | Nutrient | Year | Nutrient | Year | Nutrient |
| 1 | RH | 1 | RH | 1 | RH | 1 | RH | 1 | RH | 1 | RH |
| 1750 | C | 1750 | C | 1750 | C | 1750 | C | 1750 | C | 1750 | C |
| 3500 | P | 3500 | P | 6000 | P | 6000 | P | 11000 | P | 3500 | P |
| 6000 | C | 7000 | C | 8000 | C | 40000 | C | 50000 | C | 7000 | C |
| 9000 | P | 11000 | P | 10001 | P | | | | | 11000 | P |
| 40000 | C | 40000 | C | 50000 | C | | | | | 40000 | C |

Table 4-85. Summary Results of the Average Quantities of Biomass Produced for Each Given Design Material.

| Material | Biomass Produced (g/year/m) |
|---|---|
| Concrete | 1 |
| Mild Steel (CAM, Ground support, etc.) | 10 to 12 |
| C-22 Alloy | 0.1 to 0.01 |
| Groundwater (J-13) | 0.1 to 0.01 |

Table 4-86. Input Parameters to the RIP Code for Representation of the NFGE Chemical Parameters Used for the Concrete Sensitivity Study Case in the EBS Cells.

| RIP water and gas composition parameters | | | | | |
|---|---|---|---|---|---|
| | | Molality units | | | |
| Period | Times (years) | pH | $(CO_3^{2-})_{tot}$ | Ionic Strength | $fO_2$ |
| A | 0-200 | 10.5 | 7.7E-6 | 5.0E-4 | 2.0E-4 |
| B | 200-1,000 | 10.5 | 9.1E-7 | 5.0E-4 | 2.0E-8 |
| C | 1,000-2,000 | 10.5 | 7.7E-6 | 5.0E-4 | 2.0E-3 |
| D | 2,000-4,000 | 11.0 | 8.3E-6 | 5.8E-4 | 2.0E-2 |
| E | 4,000-10,000 | 11.0 | 8.3E-6 | 5.7E-4 | 2.0E-1 |
| F | 10,000-100,000 | 7.5 | 5.7E-4 | 6.4E-3 | 2.0E-1 |
| ambient | 100,000-1,000,000 | 7.4 | 2.5E-3 | 2.5E-3 | 2.0E-1 |

#### 4.2.1.3.2 Concrete

A number of analyses of cement pore fluids are shown in Table 4-3 where it can be seen that, relative to ambient fluids (Table 4-2) and even some of the thermally perturbed fluids (see Section 4.2.1.2 above), they tend to be concentrated in alkalis, calcium, aluminum, and sulfate, and have distinctly higher pH values. The stoichiometric ionic strength of these pore fluids is in the tenths-molal range. Dissolved silica can also be elevated in these pore fluids, although the one high aqueous silica value shown in Table 4-3 is thought to be a number of times higher than normal (Silsbee et al. 1986). Currently a representative cement-dominated fluid composition would have the general characteristics of the analyses shown in Table 4-3, with the calcium, the alkalis, sulfate, and high pH being the key aspects of such fluids. High aluminum concentrations are also considered to be important for calculations of fluid/rock reaction, but it is not clear if these reported values include any colloidal Al or not.

These cement pore-fluid compositions only represent a starting point because the evolution of solid phases in the cement/concrete subjected to the near-field environment is still uncertain. Carbonation of the calcium within cement is a reaction that occurs naturally and relatively rapidly within cement/concrete at the surface of the Earth (Reardon and Dewaele 1990; Haque and Al-Khaiat 1997). The carbonation process is potentially the key to understanding the effects of materials that result from the evolution of cement/concrete in the near-field. Carbonation of the calcium phases in the cement may alleviate much of the pH perturbations to the system, which are primarily due to portlandite ($Ca(OH)_2$) and calcium-silicate-hydrate gels (Reardon and Dewaele 1990). Direct access of $CO_2$ gas in the potential drifts may produce calcite in place of much of these phases. This process could also impact porosity/permeability in the near-field, but would tend to produce a more moderate water composition in equilibrium with the evolved cement/concrete.

The pH of groundwater equilibrated with young cement will, in general, be shifted to the extremely alkaline range of about 12-13, or greater (see Table 4-3). The constituents in the cement that are responsible for the highest pH values (>13) are the alkali metals, Na and K, and values of about 12.5 are set by portlandite after the alkalis are exhausted, and the CSH phases maintain the pH near 11 (Silsbee et al. 1986; Reardon 1990, 1992; Reardon and Dewaele 1990; Sagues et al. 1997). This pH range may not constitute a concern for accelerated waste package general corrosion because of the formation of passivation films (Pourbaix 1966), however, pitting corrosion may be accelerated (see Chapter 5 for a detailed discussion).

At these high pH conditions, dissolved elements controlled by hydroxide complexing will have increased aqueous concentrations (e.g., aluminum [Castet et al. 1992]). At pH values higher than about 10 (for ambient temperatures) the carbonate ion will dominate in solution, and many actinides could experience enhanced formation of very stable carbonate complexes for similar constraints on carbon dioxide pressure (Clark et al. 1995). In addition, at pH above 10, silica polymorphs become unstable because of a large (3 to 6 orders of magnitude) increase in the stability of dissolved silica species. Thus the potential for migrating alkaline plumes to change the porosity and permeability of the system through silicate alteration is magnified (Baes and Mesmer 1976; Eikenberg 1990; Eikenberg and Lichtner 1992; Glassley 1993).

Acidic pH values have also been observed as a result of microbial colonies feeding on organic admixtures within concretes (Meike 1995). As with steel/corrosion products, geochemical effects of cements may generate colloids that enhance radionuclide mobility, but cement/concrete may also act to retard radionuclides by sorbing dissolved species onto the immobile solids (Meike and Wittwer 1993; Hardin et al. 1998, Sections 6.4.3.7 and 6.4.4.4). Cementitious materials represent a concentrated source of Ca to the aqueous phase, which may control the distribution of calcite in the near field, and represents a major sink for carbon dioxide in this system.

#### 4.2.1.3.3 Microbial Activity

A workshop conducted to examine the potential effects of microbial activity in the potential geologic repository at Yucca Mountain resulted in the following hypotheses (Horn and Meike 1995).

- Microbes can compromise the integrity of waste packages (and other repository materials)
- Microbes can modify water chemistry outside the bounds predicted by abiotic chemical calculations
- Microbes can alter the rate of radionuclide transport from breached waste packages.

In addition to these three potential effects of microbial populations on a radioactive waste disposal system, some additional concerns have been previously raised: degradation of concrete support structures (Perfettini et al. 1991), production of gas within a repository (Bachofen 1991), and alteration of pH and redox conditions within a repository (Hersman 1997). These effects among others are depicted in Figure 4-6.

*Microbial Effects on Radionuclide Transport*—Radionuclide transport is a performance issue that is continually being investigated. Thus, the effects of microbial populations are of concern to repository performance. Microbial processes affecting radionuclide transport are varied and significant. The processes include but are not limited to, sorption/precipitation, complexation/ chelation, dissolution, oxidation/reduction reactions, and colloidal agglomeration. Additionally microorganisms create microenvironments of nutrient and chemical gradients that are capable of altering radionuclide solubilities. For a more detailed review of these processes, the reader is referred to Hersman (1996 and 1997).

Included below is a summary describing the environmental conditions required to sustain and proliferate microbial life. (This summary information has been used as input for the development of both the conceptual model and the software code for microbial growth discussed below). The following were used as general references and are the basis for the majority of the text written in this section unless otherwise indicated: Amy and Haldeman (1997) is the fifth in a series of Chemical Rubber Company Volumes on The Microbiology of Extreme and Unusual Environments that compiles papers covering microbiology in the deep crust; Banfield and Nealson (1997) is the Mineralogical Society of America Reviews in Mineralogy Volume on geomicrobiology; and Pederson and Karlsson (1995) is a Technical Report from the Swedish

Program that assesses the potential importance of microorganisms to performance assessment of a radioactive waste disposal site.

*Metabolism*—The metabolic pathway that a given microorganism will use depends on the energy source (light or chemical) (Amy and Haldeman 1997; Banfield and Nealson 1997; Pederson and Karlsson 1995). Thus, a microorganism is described as either a phototroph or chemotroph, respectively. Among the chemotrophs are those microorganisms that use organic carbon as an energy source (chemoorganotrophs) or those that use an inorganic energy source (chemolithotrophs). If an organism uses organic carbon as its source of carbon, it is referred to as a heterotroph, while if it fixes all of its carbon from $CO_2$, it is an autotroph. Combinations of these metabolic pathways can give great versatility to organisms in nutrient-limited environments. The types of organisms that exist in the potential Yucca Mountain repository environment (see Section 4.2.1.1.4) should primarily follow the chemotrophic metabolic pathway.

Bacterial groups are known to use many redox pairs to derive their energy. If chemical kinetic constraints exist such that the rate of a given chemical reaction is sufficiently slow, bacteria can compete; thus, almost any redox couple that yields energy could be exploited (Amy and Haldeman 1997; Banfield and Nealson 1997; Pederson and Karlsson 1995). The metabolic processes listed below usually define the types of redox processes and input of organic carbon that are available to provide energy and nutrients for growth. They are: aerobic respiration, nitrification and denitrification, methane oxidation, manganese and iron oxidation, sulfur oxidation, manganese and iron reduction, sulfate reduction, and methanogenesis (for a summary discussion on the metabolic processes listed above, see Keift and Phelps 1997; Pederson and Karlsson 1995; or Nealson and Stahl 1997). Microbes accumulate at redox interfaces because of the energy that is available to be harvested. Often the metabolic pathways listed above are used to describe the various types of organisms that are present in microbial ecology (i.e., a methanogen is a type of bacteria that uses the redox reactions specific to methanogenesis).

*Redox Conditions*—Bacteria that are able to grow in the presence of molecular oxygen, either in gaseous or dissolved form, are termed aerobes, whereas those that can grow without oxygen are anaerobes (Amy and Haldeman 1997; Banfield and Nealson 1997; Pederson and Karlsson 1995). Table 4-4 shows the terms used to describe the $O_2$ relations of bacteria. Thus, we see that different microbes can thrive at various redox conditions, including both the oxygenated environments that are at high redox potential and the reducing environments where the oxygen abundance is minimal.

*Temperature*—The temperature of the subsurface environment will greatly affect or limit the type of bacteria present, based on the optimum growth band of the microbe (Amy and Haldeman 1997; Banfield and Nealson 1997; Pederson and Karlsson 1995). There are 5 temperature classifications of bacteria: psychrophiles, facultative psychrophiles, mesophiles, thermophiles, and hyperthermophiles. Table 4-5 shows the ranges of temperatures that are acceptable to the 5 classes of bacteria. Therefore, during elevated temperatures in the Yucca Mountain repository the microbial population would be dominated by thermophiles and hyperthermophiles; later, as the repository cooled, the repository would be dominated by mesophiles.

*Radiation*—Bacteria are much more resistant to radiation than are most humans (Amy and Haldeman 1997; Banfield and Nealson 1997; Pederson and Karlsson 1995). The acute lethal dosage for many bacteria is approximately 5 to 1,000 Krad (Pederson and Karlsson 1995, p. 48-49). The medical sterilization threshold is about 2,500 Krad, and the limit of microbial activity for some species indigenous to the ESF was found to be 200 Krad (Pitonzo 1996). Levels of radiation thought to be present after emplacement at Yucca Mountain should be low enough to allow microbial growth and catalysis (Van Konynenburg 1996).

*Hydrostatic Pressure*—Although hydrostatic pressure is not thought to be a problem in the proposed Yucca Mountain repository, bacteria are able to withstand and flourish at the highest hydrostatic pressure on the planet (Amy and Haldeman 1997; Banfield and Nealson 1997; Pederson and Karlsson 1995). Ordinary bacteria that have not been challenged by high hydrostatic pressure during their evolution are, nevertheless, remarkably tolerant to such pressure.

*Water Activity*—Water availability seems to be the most limiting condition for microbial growth (Amy and Haldeman 1997; Banfield and Nealson 1997; Pederson and Karlsson 1995). Microbiologists normally use water activity ($a_w$) to quantify the amount of water available to bacteria. Water activity is normally defined by the ratio of the solution vapor pressure to the vapor pressure of pure water.

Most bacteria cannot exist when $a_w$ falls below about 0.90 and have trouble thriving when $a_w$ is less than 0.95. In order for bacteria to grow well, $a_w$ needs to be around 0.98 (Pederson and Karlsson 1995). Many fungi and yeast can thrive at lower $a_w$ levels (on the order of 0.7 to 0.85; Pederson and Karlsson 1995). Water activity in the potential repository will range from about 1 to values approaching zero because of the thermal perturbation. See Section 4.4.3.4.1.2 for some discussion of the expected response of microbes to such fluctuations in water activity.

*Deep Vadose-Zone Microorganisms*—By definition, vadose zones are unsaturated. However, this does not imply that the water found in the vadose zone limits the presence or growth of the microorganisms present. In fact, matric water potentials in most vadose zones are not sufficiently low to cause desiccation stress in microbes (Amy and Haldeman 1997; Banfield and Nealson 1997; Pederson and Karlsson 1995). The microbes found in these unsaturated environments seem to be desiccation resistant (Kieft et al. 1993).

*Influence of pH*—Bacteria grow over wide ranges of pH, but there are limits to their tolerance (Amy and Haldeman 1997; Banfield and Nealson 1997; Pederson and Karlsson 1995). Bacteria frequently change the pH of their own habitat by producing acidic or basic metabolic waste products. Some bacteria create their own habitats by the formation of biofilms. Each species of microbe has a pH growth range and growth optimum. Table 4-6 below shows the types of microbes and their pH relationships. In certain areas of the Yucca Mountain repository where the pH is dominated by the cement phases, the repository is favorable to alkalophiles and extreme alkalophiles. In other areas of the repository where other materials would be present, such as iron from waste packages, nutrophilies or acidophiles may thrive.

*Salinity*—Bacteria can be affected by changes in the osmotic concentration of their surroundings (Amy and Haldeman 1997; Banfield and Nealson 1997; Pederson and Karlsson 1995).

However, there are bacteria that have adapted to highly saline conditions and can grow in high levels of sodium chloride (2.8 to 6.8M; Pederson and Karlsson 1995). Many bacteria are osmotolerant and thrive in saline solutions with concentrations up to 3M (Pederson and Karlsson 1995).

*Nutrition*—About 95 percent of the microbial cell dry weight is made up of a few major elements: carbon, oxygen, hydrogen, nitrogen, sulfur, phosphorous, potassium, calcium, magnesium and iron (Amy and Haldeman 1997; Banfield and Nealson 1997; Pederson and Karlsson 1995). Besides these macro-elements, there exists the requirement of several trace elements, namely, manganese, zinc, cobalt, molybdenum, nickel and copper. These trace elements are needed in such low concentrations that they are not thought to be the limiting factors in microbial growth. The requirements for carbon, hydrogen, and oxygen are normally satisfied together, because they are the chief constituents the molecules that make up the carbon sources for microbes. One source for which this is not true is the autotroph utilization of $CO_2$ as its principal source of carbon as opposed to the heterotroph utilization of reduced organic carbon. However, the direct utilization of $CO_2$ is a very energy expensive process. It is far easier for most microbes to utilize the heterotropic metabolic pathway. Heterotrophs show a great range of flexibility with respect to carbon sources. Some bacteria will degrade almost any reduced carbon source, whereas others will only catabolize a few select carbon compounds.

In order to grow, microbes need to be able to incorporate nitrogen, phosphorous, and sulfur (Amy and Haldeman 1997; Banfield and Nealson 1997; Pederson and Karlsson 1995). Microbes usually employ inorganic sources of these elements. Nitrogen is often used by taking nitrate and reducing it to ammonia, which then can be incorporated via biosynthetic pathways. Some microbes are able to reduce and assimilate atmospheric nitrogen. However, this process is extremely sensitive to oxygen and requires a great deal of available energy. Almost all bacteria use inorganic phosphate as their phosphorous source and incorporate it directly. Most bacteria use sulfate as a source of sulfur and reduce it by assimilatory reduction. Sulfate is available in groundwater and is not usually a limiting nutrient, but quantities of phosphate and nitrogen can be small enough to limit the growth of microorganisms. However, in most conditions, the flux of energy will limit the amount of microbial growth possible. Table 4-7 shows the nutritional requirements for chemotrophs.

*Starvation-Survival*—Evidence that supports the concept that microbial populations can survive for millions of years in the subsurface has been recently presented (for a detailed explanation of starvation-survival, see Amy [1997] and Morita [1990]). The basic idea is termed starvation-survival and is defined as a state of metabolic arrest, which permits the organisms to survive for long periods without sufficient energy for growth and reproduction (Amy and Haldeman 1997; Banfield and Nealson 1997; Pederson and Karlsson 1995). This state is the normal state of most microorganisms in nature. Cells exist at this starvation level until there are energy producing substrates present for growth and reproduction (Morita 1990). Following such a growth period, cells can then return to the starvation state when the metabolic substrates are depleted.

#### 4.2.1.3.4 Waste Forms

Fluids reacting with spent fuel and glass wastes may not only acquire some radionuclide content, but may also have their major element composition perturbed from its initial state if the waste

form becomes the dominant control on water composition. Major changes in water composition as a result of reaction with the waste form may impact both the stability of phases controlling solubility-limited radionuclide concentrations and the transport properties of radionuclides through the EBS and the geosphere. There are both spent fuel and glass waste forms, which are very different in composition, and in terms of their reaction with fluids, each of these will constrain fluid compositions in different ways.

For both batch reaction studies and for flow-through studies of spent fuel dissolution, resultant fluid compositions are not very different from initial compositions used (Wilson 1990a, 1990b; Gray and Wilson 1995). However, for vapor/drip tests on spent fuel, compositional changes can be large for dissolved organic and inorganic carbon contents (Bates et al. 1995). These changes were largest for the vapor tests and low drip rate tests, whereas there was virtually no change to the carbon distribution in the high drip rate tests. For the tests that did change, the starting compositions of ~5 ppm organic and 20 ppm inorganic carbon were changed to about 11-26 ppm organic C and ~3 ppm inorganic C (Bates et al. 1995). In all the vapor/drip experiments, starting pH values of ~8.4 changed to about 7 after reaction (Bates et al. 1995). The recent work by Finn et al. (1997) suggests that radiolysis-generated hydrogen peroxide provides a highly oxidizing local environment on the surface of the waste form and that this condition leads to rapid oxidation of the spent fuel and release of radionuclides from the ε-phase. The ε-phase occurs primarily as inclusions within the spent-fuel grains and contains many transition-metal fission products such as Tc, Mo, Ru, Rh, and Pd (Finn et al. 1997).

In addition to changes in organic/inorganic carbon ratios similar to the test results on spent fuel, experiments with glass waste indicate that, depending on glass history, cation and anion (chloride, sulfate, and phosphate) concentrations can be highly increased over ambient fluid compositions (Bates et al. 1993). For tests on aged glass, pH increases to 11-11.5, and concentrations of $Cl^-$, $SO_4^{2-}$, and $HPO_4^{2-}$ are about 150-250 ppm, 5000-10,000 ppm, and 200-400 ppm, respectively, in a first course of reaction (Bates et al. 1993). In a second series of tests, the values are lower at 40–70 ppm, ~800 ppm, and 150–200 ppm, respectively (Bates et al. 1993). In either case, these values are relatively high for $Cl^-$ and $SO_4^{2-}$, and extremely high for $HPO_4^{2-}$ compared even to the evaporated fluids discussed above. Total organic carbon in these tests reaches about 20–30 ppm and consists mostly of oxalic acid and formic acid, two simple organic acids whose dissociated anions (oxalate and formate) can complex dissolved metals (Bates et al. 1993).

In all of the vapor/drip studies, secondary phases are prevalent and diverse, including Ti-oxides, Ca-silicates, and uranium silicate phases (Bates et al. 1993; 1995). Colloidal material also is commonly observed to result. An evaluation of primary alteration of spent fuel and subsequent reaction of the secondary phases is included in the sections below. A similar evaluation has been started for defense high-level waste (DHLW) but model development has not yet been completed. Spent fuel was the first priority because it represents the bulk of the radionuclide inventory (about 90 percent, see Chapter 6). However, about 35 percent of the waste packages (i.e., the volume of waste) is represented by the DHLW (see Chapters 5 and 6). Because of its marked effects on bulk water composition, future analyses could benefit from inclusion of this material in the NFGE models.

*Waste Form Colloids*—For waste form colloids, it has been shown that degradation colloids form from high-level waste glass and can comprise over 99 percent of the mobile Am and Pu (Bates et al. 1992), but their long-term stability is poorly understood. Studies by Feng et al. (1993) indicate that these types of colloids will agglomerate readily at high ionic strengths or low temperatures and settle out of the aqueous phase, but may resuspend if contacted by dilute fluids. Under acidic conditions, stable Pu(IV) radiocolloids can form, but these may not be stable at higher pH (Hobart et al. 1989; Triay et al. 1991). Small-scale laboratory experiments on the transport of radiocolloids of both Pu(IV) and Am(III) through tuff columns indicate that most of the material was retained in the rock, but a minor portion moved through the system faster than a conservative tracer (Thompson 1989). Measurements from the Nevada Test Site indicate that Pu that has transported 1.3 km in approximately 30 years is associated with colloids in the water samples (Thompson 1998 p. vii). For both DHLW glass and commercial spent nuclear fuel, model waste-form colloids are included in the TSPA-VA base-case analyses as discussed in more detail in Chapter 6 covering the waste forms. These colloid types are not discussed further in this chapter on the NFGE component of the TSPA-VA.

### 4.2.2 Consideration of Coupled Processes Effects

The general TSPA model architecture is based on the ability to decouple system behavior both spatially and by type of process, (i.e., it assumes weak feedback spatially and among processes). This assumption is least tenable when applied to the NFGE, which may be highly coupled in a nonlinear fashion, being influenced by thermal, hydrologic, and multicomponent chemistry. This is evident by the numerous model interconnections shown in Figures 4-3 and 4-4 and detailed in the discussion below. The potential effects of the coupling within the thermal-mechanical-hydro-chemical system are uncertain, but work is ongoing (both within the project and outside of it) to delineate the first-order couplings that should be addressed and to define the magnitude of the effects of representing inherently coupled processes by uncoupled, or loosely, coupled models (Manteufel et al. 1993; Chen et al. 1996a; Lichtner et al. 1996; Lichtner and Seth 1996; Wilder 1996; NRC 1997; Hardin et al. 1997; Hardin et al. 1998). The coupling of the NFGE models to other aspects within the NFGE and other TSPA-VA components is done either in a single direction via output/input feeds at the process-model level, or by one-way, direct-connection feeds within the TSPA analyses. The main first-order interactions considered in the analyses are discussed below.

The Project's focus on coupled processes has increased, and modeling efforts are attempting to constrain the magnitude of such effects as indicated in these paragraphs from the *Near-Field/Altered-Zone Models Report*[2] (Hardin et al. 1998, p. 2-1):

> Discussion of near-field and altered-zone (NF/AZ) performance in terms of coupled processes emphasizes differences between ambient conditions

[2] The term "near field" is defined more broadly, in general, as given in Hardin et al. (1998) as "The near field is the region in which response to repository-induced conditions is critical to EBS performance." In addition, Hardin et al. (1998) provide the definition of the altered zone as the region within which "...temperature is increased significantly by radioactive decay heating. The AZ extends beyond the near field and may extend throughout the unsaturated zone (UZ) above and below the repository horizon."

> prior to waste emplacement, and an environment affected by excavation, heating, and introduced materials. For this report, "coupled processes" refers to thermal-hydrologic-chemical-mechanical (THCM) processes (in any combination) having the potential to significantly degrade natural or engineered barriers; this encompasses all modes of potentially significant degradation of engineered barriers, even for those of the so-called "cold repository" (Halsey 1994). Coupled processes figure prominently in current discussion of repository performance (NRC 1997). The topic receives close attention because of uncertainty associated with the long-term changes in the host rock resulting from artificially imposed conditions, and the behavior of introduced materials. These uncertainties are poorly constrained by human experience or by the geologic record, so predictive models are relied upon to judge the effects. This Near-Field and Altered-Zone Environment Models Report is intended to summarize conceptual and numerical models that have been developed for predicting the effects of coupled processes in the NF/AZ surrounding a Yucca Mountain repository.

and from p. 2-2 of the same reference:

> Every physical or chemical process that is likely to occur in the repository can be considered as thermally coupled in some way. However, all thermally coupled processes are not relevant to performance, and the occurrence of thermally coupled processes does not generally imply conditions adverse to waste isolation. Depending on repository thermal loading, the NF/AZ may not reach temperatures sufficient to drive thermally coupled processes to produce significant effects. However, other types of coupled processes, such as the ambient temperature effects of alkaline leachate from Portland cement, are likely to be significant.

In addition, the Project has just concluded the *Near-Field/Altered Zone Coupled Effects Expert Elicitation* (CRWMS M&O 1998b) project that covers some of the aspects of coupled processes. The two main goals of that elicitation were (1) to quantify uncertainties associated with certain key issues in the Total System Performance Assessment and (2) to provide a perspective on modeling and data collection activities that may help to characterize and reduce uncertainties (CRWMS M&O 1998b p. 1-2). These experts were asked to address a number of couplings among the thermal, hydrologic, mechanical, and chemical processes that would occur in the region of a heated repository. In terms of thermal-hydro-chemical (THC) coupling, the experts focussed on changes to porosity and permeability in the fractures above the drifts and provided a range of possible changes for those properties (CRWMS M&O 1998b, pp. 3-10-3-12). Within the potential emplacement drifts, the THC coupling will be complicated further by the potential variety of introduced materials. As process models are better able to directly incorporate the coupling among various processes, the abstracted models used for performance assessment will likewise be able to capture more of the relevant potential impacts from such effects.

### 4.2.3 Conceptual Models for the Near-Field Geochemical Environment Component

The discussion above provides the background for the processes considered in model construction for the NFGE component of the TSPA-VA. In this section, the specific conceptual models are presented. The processes upon which the concepual models are based are described in the spatial context of both the mountain-scale system (Figures 4-7 and 4-8) and the drift-scale system (Figures 4-9 through -11). The implementations of these conceptual models are discussed in Section 4.4, and results for the analyses using these models are given in either Section 4.5 (TSPA-VA base-case results) or in Section 4.6 (sensitivity studies).

#### 4.2.3.1 Incoming Gas, Water, and Colloids

The NFGE component of TSPA-VA provides values for the time-varying compositions and fluxes of gas, water, and colloids entering the drift. Changes to these variables are driven primarily by the thermal changes to the system. Reactions between the gas, water, and minerals in the rock occur as the system is heated and pore water boils. These processes change the system by changing phase stabilities or increasing rates of reaction for existing phases. The time evolution of the system was divided into two thermal regimes: a boiling regime and a cooling regime. These two regimes are further subdivided based on large changes to the gas composition (mainly within the boiling regime) or the changing temperature of the cooling system (within the cooling regime). The time periods are defined to have constant chemical conditions so that the description of the NFGE evolution consists of a set of step changes in system conditions.

##### 4.2.3.1.1 Conceptual Model for Incoming Gas

In the conceptual model for incoming gas, gas composition is represented by the major gas constituents: steam ($H_2O$), oxygen ($O_2$), carbon dioxide ($CO_2$), and nitrogen ($N_2$). The primary sources of these gases and the mountain scale processes affecting their quantities are shown in Figure 4-7. Steam (or water vapor) is generated during the boiling period and affects the rate at which waste packages corrode. The other three gas constituents are components of air considered in this model.[3] Oxygen is included because of its role in metal oxidation. Carbon dioxide directly affects the pH of solutions (which affects waste-form dissolution) and can strongly affect actinide complexes (increasing their dissolved concentrations). Finally, nitrogen generally comprises most of the air component of the gas and may serve as a nutrient source for microbial activity. The thermally driven changes to the physical chemistry of the system and the perturbed flow of gas through the mountain and, in particular, through the drift form the bases for the conceptual processes included in the incoming gas model, in addition to the ambient gas composition and flow conditions.

Because gas is less soluble at higher temperature, heating drives dissolved gases out of the water and into the gas phase. Rapid gas movement in the fractures may transport those dissolved gas constituents away from the heated water they came from and towards cooler water (that is, down

[3] Air does not necessarily imply atmospheric composition of these gases but is the term for the gas ingredient "other than steam" in the thermal-hydrologic models (see Section 3.2).

the temperature gradient) where they can redissolve. This process tends to deplete the heated water and enrich the cooler water in these gas species. As the temperature of the mountain increases farther away from the repository, these gas species are remobilized and transported farther away from the drifts in a continual process of revaporization and redissolution. In the rock near the heat sources, temperatures will rise above the boiling point of water, generating abundant steam, causing an overall dilution of the air component.

The major source of both oxygen and nitrogen is the atmosphere, so dilution of these two constituents by steam (from boiling) is accounted for by a direct reduction in their atmospheric partial pressures. For carbon dioxide, the system is somewhat more complex. Measurements of gas compositions from various UZ boreholes demonstrate that UZ $CO_2$ gas concentrations are elevated above atmospheric $CO_2$ partial pressures (about 350 ppmv—parts-per-million by volume) by about a factor of three (CRWMS M&O 1998a, Section 6.2.7.2, pp. 6.2-40). The values of UZ pore-gas composition analyzed for the site indicate that the $CO_2$ content of pore gases tends to average about 1000 ppmv (CRWMS M&O 1998a, Section 5.3.4.2.4.6, pp. 5.3-173). These elevated values could be the result of mixing of $CO_2$-rich gases generated in the soil zone with the rest of the gas volume of the mountain (CRWMS M&O 1998a, Section 5.3.4.2.4.6, pp. 5.3-173).

Because the rock contains the mineral calcite ($CaCO_3$) and there is a nonnegligible amount of dissolved carbonate in the water, these phases may act as sources of carbon dioxide that must be accounted for in the assessment of the air composition diluted by steam (Hardin et al. 1998, Sections 5.7.1 and 6.2.1). However, because gas flow is much more rapid than water flow, the NFGE model assumes that the water composition will be primarily controlled by the gas composition diluted by steam for most of the thermal period. Nevertheless, there are indications from water compositions in the single-heater test that carbon dioxide could be released to the gas phase during the heating stage (Hardin et al. 1998, Sections 5.7.1, 6.2.1 and 6.6). Therefore, a brief period with an elevated level of carbon dioxide in the air, which is then diluted by steam, was included at the start of the model to represent these potential sources of carbon dioxide.

The incoming-gas model also assesses constraints on the fluxes of the gas constituents into the drift. These values are used in analyses that evaluate the potential for depletion of these constituents by reaction with the solids in the drift, and the potential effects on water–solids chemistry of those reactions and the potential microbial growth (discussed below). For each of the gas constituents in the model, the cumulative gaseous flux of that chemical component into the drift is given by the product of the cumulative gas phase flux and the fraction of that constituent in the gas for a given period. In the conceptual models for the gas and water/solids chemistry in the drift, the fluxes of these gas constituents that could be derived from their dissolved counterparts in the water flux were also included. For this model, the fluxes of the dissolved gas constituents were based on the percolation flux for the drift cross-section. This water flux is larger than that given by the seepage model, which only has a fraction of the percolation flux entering the drift. Because gaseous diffusion for carbon dioxide or oxygen gas species is relatively rapid at this scale, the gas composition may be buffered by water just outside the drift. Therefore, this larger water flux should represent a more realistic bound on the masses of these gas constituents available for reaction in the drift (see Section 4.4).

#### 4.2.3.1.2 Conceptual Model for Incoming Water

In the conceptual model for incoming water, water composition is represented by the major dissolved constituents and by some of the less abundant dissolved constituents that participate in some of the dominant mineral reactions within the system. The compositional components considered for the water in the model are pH, sodium ($Na^+$), potassium ($K^+$), calcium ($Ca^{2+}$), magnesium ($Mg^{2+}$), iron ($Fe^{2+}$, $Fe^{3+}$), aluminum ($Al^{3+}$), silica ($SiO_2$), chloride ($Cl^-$), fluoride ($F^-$), carbonate ($CO_3^{2-}$), and sulfate ($SO_4^{2-}$). These constituents represent the total masses of these components within the fluid, and each may be comprised of a number of different species in solution. In addition, the dissolved oxygen content is included as constrained by the oxygen fugacity (approximately the partial pressure), and this value is used to calculate the equilibrium oxidation potential (Eh) of the system. Figure 4-8 shows the major processes at the mountain scale affecting the concentrations of these constituents in the incoming water.

The composition of ambient water moving through fractures and entering the drift has been constrained by examination of the various fluid compositions observed both at the site and near Yucca Mountain (Section 4.2.1.1). Pore water in unsaturated tuffs appears to have higher concentrations of some constituents like sulfate and chloride (CRWMS M&O 1997a, Appendix 3 Table 1; Bodvarsson et al. 1997, Chapter 14; CRWMS M&O 1998a, Sections 6.2.5 and 6.2.8) compared to the water in the SZ tuffs (Figure 4-8, Inset A). However, the composition migrating through the UZ fractures into the drift is assumed to be that observed within the saturated-zone tuff aquifer (from well J-13, Figure 4-8, Insets B and C) as discussed in Section 4.2.1.1. This assumption is based on compositional similarities between the perched water bodies, fracture fluids collected at Ranier Mesa (a nearby mountain of unsaturated volcanic tuffs analogous to Yucca Mountain), and groundwater samples from the J-13 well (Hardin et al. 1998, Section 6.2 Table 6.2-1; see also Sections 4.2.1.1 and 4.4.2.2 of this chapter).

The processes that change ambient water composition are driven by heating of the system and are closely linked with the processes shown in Figure 4-7 for evolution of the gas composition entering the drift. In the conceptual model for the incoming water composition, the time-varying gas composition is imposed as an equilibrium constraint on the water composition at the temperature of the system because the gas transport is fast relative to the water flow (that is, the changes to gas composition from the dilution by steam generation are expected to be very large compared to the other compositional changes to the gas in the geosphere and therefore these perturbed gas compositions are imposed directly—see Chapter 3 and Section 4.4.2.1). Water composition is also changed by reaction with minerals in the tuff and in the fracture linings at various temperatures (Hardin et al. 1998, Section 5). In addition to the heated reaction of water, gas, and minerals, the thermal change is projected to be large enough to create a boiling zone around the drifts (see Chapter 3).

The boiling process will affect water chemistry in a number of ways (Figure 4-8, Inset D). First, the gas composition changes as discussed above (Figure 4-7, Inset C). Second, many of the dissolved mineral constituents become more concentrated as the water boils (Hardin et al. 1998, Section 6.2). Some of these constituents concentrate to the point where solids (such as calcite and silica) precipitate and further constrain the water composition (see Section 4.2.1.1 and Hardin et al. 1998, Section 6.2). When the water boils away completely, some of the precipitated phases are relatively soluble salts that will react later with water and steam to create

concentrated salt solutions. In addition, salt will cause water to condense from steam at a lower RH than salt-free systems, forming concentrated salt solutions earlier and at higher temperatures if salts are in the fractures. During the period of boiling, the reaction of water, gas, and minerals was calculated at 95°C (203°F), just below boiling (at the elevation of the proposed repository). As the system cools, the boiling front will migrate back into the drift, ending up at the surface of the waste package. The potential amount of salt buildup within a drift (as discussed below) was assumed to depend on the composition of the starting fluid and the cumulative flux of that fluid through the fractures.

#### 4.2.3.1.3 Conceptual Model for Incoming Colloids

The degree to which colloids will impact the performance of a potential repository at Yucca Mountain is currently uncertain. In general, the detailed quantitative constraints and models for colloid processes are not available, and it is therefore difficult to eliminate any of the potential colloid types from consideration or to develop a comprehensive Performance Assessment model of the effects of colloids (Ramsay 1988; McCarthy and Zachara 1989; Manaktala et al. 1995; Gauthier 1995; Triay et al. 1996; CRWMS M&O 1998a, Section 6.3.6). The state of knowledge concerning this issue is summarized by Triay et al. (1995; 1996), who proposed a strategy to assess the importance of colloids for a potential repository by focusing on three aspects: (1) the presence/abundance of colloids (based on colloid stability relations) at the potential repository source term; (2) the stability of the radionuclide colloids in the groundwater system away from the source; and (3) the ability/efficiency of these colloids to migrate through the unsaturated and saturated hydrogeologic system.

The models of the NFGE component of the TSPA-VA focus on constraints for this first aspect—colloid stability and colloid abundances/concentrations at the source term that are based on stability relations. Concentrations of colloids in water from Well J-13 have been measured and were used to identify the site natural colloids and place their concentrations into context with colloids from other sites around the world (CRWMS M&O 1998a, Section 6.3.6.1). The waste form degradation/mobilization component (Chapter 6) addresses the second aspect (including sorption of radionuclides to the colloids and transport through the EBS). The final aspect is handled by both the UZ radionuclide transport (Chapter 7) and the SZ flow and transport (Chapter 8) components.

The NFGE component contains a conceptual model for incoming colloids. Natural colloids are minute particles (from about $1 \times 10^{-8}$ m [100 angstroms] up to about $1 \times 10^{-5}$ m [$1 \times 10^{5}$ angstroms]), which may be transported by the groundwater. Radionuclides can attach to these colloids and be transported through the system at a different rate than their dissolved counterparts. The colloids entering the drift are assumed to be those found in the natural system for the ambient saturated-zone water. These natural colloids are a small mass of entrained particles composed of clays, silica, and iron oxyhydroxides (about 20 to 30 ng/ml—Triay et al. 1996 p. 9, Table I; CRWMS M&O 1998a Section 6.3.6.1).

The composition of the natural colloids appears to be dominated by the clays ( CRWMS M&O 1998a, Section 6.1.8.5, p. 6.1-174 to 6.1-178). Because the iron-oxyhydroxide colloids generated within the drift represent a much larger potential source than the incoming natural iron-oxyhydroxide colloids, the incoming colloids are represented by the clay component of the

natural colloids. The amounts of the clay and iron-oxyhydroxide colloids are constrained by the ionic strength of the fluid in the drift. This relation is based on colloid concentrations in groundwaters of various ionic strengths from around the world (CRWMS M&O 1998a Section 6.3.6.1; see Section 4.4.3.3 for detailed discussion). Because it is possible to constrain the stability of clay colloids and the magnitude of Pu sorption onto them (see Chapter 6), these colloids have been included as representative of natural colloids within the TSPA-VA analyses. The implementation of the model for colloid abundance and the results of that model are discussed in Sections 4.4 and 4.5, respectively.

The models of the incoming gas, water, and colloids provide time-dependent boundary conditions for the models of chemical reactions in the drift. The processes for incoming gas, water, and colloids in the NFGE component are shown at the drift scale as Inset A in Figures 4-9, -10, and -11. These figures delineate three generalized time frames for the physical-mechanical evolution of the materials in the drift, based in part on a more detailed description of this evolution (Hardin et al. 1998, Section 2.2).

#### 4.2.3.2 Evolution of the In-Drift Chemistry

Once the model compositions of gas, water, and colloids entering the drift have been established, the chemical processes within the drift can be considered. Within the drifts, the coupling of the physical-mechanical deterioration of the introduced design materials (Hardin et al. 1998, Section 2.2) plays a large role in the reaction of water and materials because of changes to the flow pathways. Representations of these processes (pathways for fluid migration through the drifts and reaction with materials along those pathways) at the drift scale are shown in Figures 4-9, -10, and -11. The major physical/mechanical aspects of the system that change are the location and integrity of the concrete that comprises the liner and other ground support (e.g., pier and invert), and the integrity of the waste package and its pedestal.

While the concrete liner is still intact during the first few hundred years, any water dripping onto the waste package would have already reacted with concrete (Figure 4-9). However, once the liner has collapsed, concrete-modified water is most likely to contact the waste package only where concrete blocks lie against the container (Figure 4-10 and -11, Inset B), or below that point. These pathways that include concrete may lead to alkaline fluids (Section 4.6.2.2.1) and aggressive pitting corrosion of the outer waste package (see Chapter 5). Once the concrete liner collapses, the most direct pathway would be for water to drip directly onto the waste package without reaction with concrete. All of the boiling occurs within Time Frames 1 and 2 (Figures 4-9 and 4-10), even for the center portions of the repository block. The system is at ambient temperatures by the end of Time Frame 3 (Figure 4-11).

##### 4.2.3.2.1 In-Drift Gas

The composition of the in-drift gas phase is assumed to be constant throughout the drift because of rapid migration of gas constituents at this scale, particularly for higher temperatures (Figures 4-9, -10, and -11). However, the mass of each gas constituent available to react with the water and materials in the drifts is limited by the flux of that gas into the drift. If for a given period the amount of gas needed for a reaction exceeds the amount available because of the gas flux, the water flowing close to the drift wall can de-gas dissolved volatile constituents to supply

the reactions taking place. However, once that reservoir of gas is exhausted, the concentration in the gas phase of the reacting gas constituent will decrease until a new equilibrium concentration is reached. This new level depends in a complex manner on reaction rates that change with compositional changes, but the capacity to use up a particular gas constituent in a given period can be assessed using mass balance relations. Steel (or iron) is the major material that will act as a sink for the oxygen in the system as it oxidizes to either hematite ($Fe_2O_3$) or goethite (FeO(OH) (or even to other metastable ferric hydroxides, [see Hardin et al. 1998, Section 6.4.3.1]). The cement phases (portlandite and calcium-silicate hydrates) in concrete are the major sinks for carbon dioxide, because reaction with calcium in the cement will lead to calcite precipitation. The degree to which these reactions may affect the gas composition is discussed in Section 4.4.3.1.

#### 4.2.3.2.2 In-Drift Water-Solids Chemistry

The model for the in-drift water-solids chemistry is comprised of a number of submodels. Some of these submodels are used quantitatively within the performance assessment analyses, and others are used for conceptual scenario development for other components and analyses. A flow chart depicting the detailed relations among the submodels of the in-drift water-solids chemistry portion of the NFGE is shown in Figure 4-12. Both the incoming water submodel and the in-drift gas model feed water composition and gas constraints directly into the water-solids chemistry submodels. As shown in Figure 4-12, the calculated fluid composition is provided by one submodel and used by another submodel that represents materials "downstream" in the conceptual flow pathway through the system (Figures 4-9, -10, and -11). The four features (submodels) of the water-solids chemistry model (corrosion products, concrete, spent fuel, and precipitates/salts) are described below, following some general conceptual discussion of reaction between water and solids in the drift.

For water that has entered the drift, model calculations were done to evaluate the reaction with the major solids in the drift, in particular with concrete and with the corrosion products of the steel (represented by iron oxyhydroxides-goethite). Constraints for the composition of water reacting with the waste form were derived from these models. These reactions between water and solids in the drift are assumed to occur at the conditions for gas fugacities and gas fluxes derived from the in-drift gas model. The reactions will proceed to equilibrium depending on the relative magnitude of gas sinks versus gas fluxes into the drift.

For reaction with repository design and waste package design materials in the repository, the in-drift water-solids chemistry model represents local equilibrium (water movement is slow compared to the reaction rates of the dripping water and reacting solids). This local equilibrium would correspond to reaction along permeable matrix pathways, perhaps with small fractures (Figures 4--9, -10, and -11, Insets B and C), but does not correspond to reaction along large, highly permeable fractures through the system. Fast flow along such pathways would result in less pronounced changes to fluid composition. For these analyses, two conceptual pathways for the incoming water were defined as described in the next sections.

#### 4.2.3.2.2.1 Corrosion Products

In the first pathway, water does not react with concrete, but drips directly onto the waste package through gaps in the liner during early time frames (Figure 4-9), or through the area from which the concrete liner has collapsed during later time frames (Figures 4-10 and -11). Because there will likely be water-flow pathways without concrete after the drift liner collapses (Hardin et al. 1998, Section 2.2), the water compositions calculated for this corrosion-products-only pathway are used as the base-case fluids. This leg of the pathway is represented by iron oxides, (goethite, FeO(OH)), because the bulk of water that gets into the waste must encounter corroded package material. The primary effect on water chemistry from this reaction is to the dissolved iron content of the fluid. The resulting water composition is used as the initial fluid composition for calculating the effects of reaction with spent fuel during the active alteration period and at later stages when secondary uranium phases are reacting.

#### 4.2.3.2.2.2 Concrete

The second pathway is the concrete conceptual pathway, which was not part of the base case, but considered as a sensitivity case. As shown in Figures 4-10 and 4-11, concrete adjacent to the waste package could provide concrete-modified fluid compositions through diffusive migration of alkaline components into the waste package. Such fluids could then affect the waste package corrosion and possibly change waste form behavior (Figure 4-10, Inset B). Along this conceptual pathway, water will react with corrosion products after reaction with concrete.

The concrete within the potential drifts will be comprised of tuff aggregate, sand, cement, and steel fibers (see Sections 4.3 and 4.4). Within the cement, there may be large amounts of organic admixtures (see Section 4.3), but these are only considered within the NFGE models as nutrient sources for microbes. The alkaline components of cement, in particular the calcium content, will represent a large compositional change to the system. The phases that produce high pH are primarily portlandite ($Ca(OH)_2$) and calcium-silicate-hydrate phases formed by reaction of the silica with portlandite in the cement (note; although the Na and K contents of the cement can cause more highly alkaline fluids than does Ca, their masses are much smaller and so have been ignored in this analysis—see Section 4.4.3.3.3 for details). Reaction of the incoming water with these constituents will continue to cause high pH in the resulting fluids until the cement phases are neutralized by carbonation via reaction with water and gas. Until the alkaline cement compounds are neutralized, water compositions may be mostly affected by reaction with the concrete. Reaction rates for this neutralization process are assumed to be relatively fast; however, availability of carbon dioxide will tend to constrain the time frame for this process (Reardon and Dewaele 1990; Haque and Al-Khaiat 1997). In addition, the cement contains sulfate phases that will tend to control the concentration of dissolved calcium, silica, and sulfate through different mineral equilibria than for the interaction of water with tuff.

#### 4.2.3.2.2.3 Spent Fuel

Once inside the waste package, water can react with exposed fuel. The effects of this reaction have been calculated with a model that couples the flow rate of water through the package with the kinetics of spent fuel dissolution and the formation of secondary phases. Because the base-case waste package failures occur primarily after the boiling period, "iron-oxide-reacted" water

was calculated to react with $UO_2$ at two different temperatures during the cooling period. The cladding and basket materials within the package were assumed to be inert. This reactive-transport model is not part of the base case, but its effects are examined in a waste form sensitivity study for attenuation of Np releases (see Chapter 6).

The spent fuel is conceptualized as a porous media with an initial porosity equal to the porosity inside a waste package. The water flux through the spent fuel is assumed to be the long-term average seepage flux through the drift (see Chapter 2), taken directly or modified for the breached area of the waste package (see Chapter 5). Flow rates through the spent fuel porous media depend on the evolution of porosity within the system. The water drips into the top of the waste package and then reacts with spent fuel along a 1.56-meter path, after which it leaves the waste package. The transport of dissolved constituents through the system includes advection, diffusion, and dispersion in the solution. The water composition at the outlet of the system is the primary focus of this submodel for the NFGE.

In the model, the waste form dissolves as oxidized uranyl (uranium) species with secondary uranium phases precipitating at the carbon-dioxide and oxygen-gas conditions determined for the cooling periods (from the in-drift gas model). Carbonate equilibria and calcite precipitation and dissolution are included in this submodel. The uranium solids considered for precipitation are four secondary uranyl (uranium) minerals: uranophane, sodium-boltwoodite, schoepite, and soddyite. These phases are commonly observed in alteration of uranium ore deposits and in laboratory tests of spent-fuel dissolution (Hardin et al. 1998, Section 6.5; CRWMS M&O 1998a, Section 6.3). In addition, after conversion of $UO_2$ to secondary phases, the dissolution of those secondary phases occurs more slowly because they are closer to equilibrium with the fluid entering the waste package. The effects on water composition of the secondary phases are evaluated to provide a bound on the magnitude of the entire suite of chemical changes.

#### 4.2.3.2.2.4 Precipitates/Salts

Mineral deposits will develop as refluxed water drips through fractures and possibly onto the waste packages throughout the boiling period. The degree of boiling and evaporation of the water will cause various minerals to saturate within the solution. These precipitating minerals will change with time as the water composition changes. The major purpose of this model is to assess the magnitude of mineral precipitation and salt formation, the length of time to redissolve the soluble salts, and the amount of concentrated salt solutions from these processes. Although the amount of salt precipitation was assessed in the NFGE component (see Sections 4.4 and 4.6), it was not directly used in the TSPA-VA analyses. The effect of salt on waste-package degradation was used only indirectly for evaluation of potential sensitivity analyses (see Chapter 5).

The precipitates that form as a result of the vaporization of refluxed water are a function of temperature, gas fugacities, and refluxed water composition. For example, the gas fugacity of carbon dioxide controls the precipitation of carbonates and pH. Complicating the problem is the fact that the fugacity itself is a function of the extent to which the system is open or closed. When refluxed water is nearly completely evaporated, more calcite precipitates in an open system compared to a closed system (Glassley 1994; Murphy and Pabalan 1994). Lichtner and Seth (1996) used a multiphase, multicomponent, nonisothermal reactive transport code to

simulate the evolution, vaporization, and condensation of groundwater through the vertical centerline of the repository during the boiling period. This type of code does not fix local gas fugacities, but evaluates them based on multiphase reactions. Their results predict that in the vicinity of the potential repository, pH increases to about 10 and chloride concentration increases to approximately 100 mg/L in the vicinity of the drift. Lichtner and Seth (1996) indicate that a 10-fold increase in J-13 fluid concentrations (for conservative elements) could be a reasonable water composition entering the drift through fractures during the boiling period. Quartz and calcite were predicted to dissolve where water condenses and precipitate where water evaporates (Lichtner and Seth 1996).

The model developed for the NFGE abstraction represents the temporal gas changes by using fixed fugacities for abstracted time periods with step changes in between. The boiling periods are the times of particular interest for the evaluation of precipitates/salts buildup and redissolution. The high waste package temperatures during the boiling period are expected to create dry conditions on the package that effectively prevent waste package corrosion. Corrosion of the waste package and dissolution of spent fuel are expected to begin only after temperatures are low enough to allow surface wetness (see Chapter 5). Although the refluxed water entering the drift during the boiling period may not remain long enough to initiate considerable corrosion, as it boils away it will deposit its dissolved, nonvolatile constituents as minerals. These phases may range from relatively insoluble minerals like silicates and carbonates to very soluble salts, and have the potential to change the interaction of water with the waste-package surface as well as to change the composition of that water.

Because salts are hygroscopic, that is they condense water from steam at relative humidities lower than 100 percent, they may cause water to occur on waste packages at earlier times than for salt free systems (Kinsman 1976). As the salts dissolve in such a fluid, the concentration of that solution will increase. How large of an effect this may be is the question that this model attempts to assess. Even if the salts are deposited in the fractures outside the tunnel, they likely will be redissolved and moved into the potential drift by these processes of redissolution. Relative humidities above the critical value for a salt will cause that salt to condense water from vapor and dissolve into a brine (Kinsman 1976). Thus, salts deposited in fractures cause the liquid to form that could move them into the drift. However, it is possible that salts are precipitated initially in the matrix and then isolated from fracture flow, or that brines forming in the fractures are imbibed into the matrix. The extent to which these processes occur is uncertain, but in this conceptual model all dissolved salts in the incoming water are taken to end up on the waste package surface.

After the boiling period ends, incoming water may serve to dissolve the previously deposited minerals and possibly flush brines out of the system, thereby affecting the composition of water in contact with the waste package. However, continued evaporation on the waste package surface may drive concentration of brines faster than this dilution process, resulting in concentrated fluids below boiling. Thus, predicting the salts and other minerals that precipitate on the waste package during the boiling period is important in predicting the chemistry of the water composition in contact with the waste package after the temperature drops low enough to allow surface wetness.

The conceptual model of the evolution of mineral deposits and waste package surface water composition assumes no interaction with concrete or waste package materials. Refluxed water drips onto the waste package throughout the boiling and cool-down periods at the seepage rate. Upon entry into the drift, the model temperature and abstracted initial composition of the refluxed water as a function of time are defined by the incoming-water model. The abstracted equilibrium partial pressures of oxygen and carbon dioxide as a function of time are given by the model for gases entering the drift. The flux of refluxed water (from the seepage model—Chapter 2) onto the average waste package will control the extent of accumulation of solids brine formation that occurs on the waste package.

In the conceptual model, the drips may occur over the entire waste package surface or may be concentrated at specific locations on the surface (i.e., no specific spatial distribution of the salts is given). During the boiling period, immediate vaporization on the waste package induces precipitation of all dissolved solids. The precipitating mineral assemblages change with the composition of incoming water. When the water can no longer boil to dryness, reflux water and, potentially, water vapor will dissolve previously deposited solids. This cooler period may allow for dripping of water and dissolved solids off the waste package if the rate of seepage exceeds the rate of vaporization.

#### 4.2.3.2.3 Colloids in the Drift

In addition to the natural colloids discussed above, colloids in the drift from introduced materials are another consideration in the evolution of the in-drift chemistry. The in-drift colloids are comprised of both the clay colloids entering the drift (Figures 4-9, -10, and -11, Inset A) and the iron-oxyhydroxide colloids produced within the drift from the steel components of the design materials (Figures 4-9, -10, and -11, Inset C). Because these colloids can sorb and may transport radionuclides, the amounts of these colloids affect the amounts of radionuclides that can be transported. The concentration of these colloids depends on the ionic strength of the solution; water with higher ionic strength causes colloids to coagulate and drop out of solution (Triay et al. 1996; CRWMS M&O 1998b, Section 6.3.6). The abundances of natural and introduced colloids that can interact with the waste form is the primary focus for the NFGE. Radionuclide sorption to natural and introduced colloid types, the model for waste-form colloids, and the transport of all colloids through the EBS are discussed in more detail in Chapter 6. The transport of colloids through the geosphere system is discussed in both Chapters 7 and 8.

#### 4.2.3.2.4 In-Drift Microbial Communities

In-drift microbial communities are also considered as part of the in-drift chemistry. Microbial activity exists at low levels in the host rock (see Section 4.2.1.1 above; Hardin et al. 1998, Section 7). Throughout the drift, microbes will use the nutrients and available energy from chemical oxidation and reduction reactions. The nutrients and energy are present because of system heating, fluid movement, and materials emplaced in the drifts. In the repository environment, many different microbes could grow and provide a plethora of potential chemical processes that may affect the bulk chemistry within the emplacement drifts (Hardin et al. 1998, Section 7). A large source of potential nutrients for microbes is the organic material in concrete ground supports. The waste-package materials represent reduced metals that can be oxidized to

provide energy for microbes to thrive, and the waste forms themselves contain both nutrient and energy sources for microbes.

A model was developed to assess the possible magnitude of such effects on the system's total chemistry by bounding the magnitude of development of microbial communities (Hardin et al. 1998, Section 7; see also Sections 4.4 and 4.6 below). This model uses constraints on the supply rates of the nutrients used to build an idealized microbial composition, comprised of carbon, nitrogen, sulfur, and potassium in addition to the water components. The rates of supply of these constituents are input as constant release rates for each introduced material in the system by specifying the mass and composition of the material and its degradation lifetime. The other major constraint evaluated is the energy available for microbes to grow based on the pH corrected, standard state free energy released from oxidation/reduction reactions. Other constraints on microbial growth are temperature and RH thresholds in the model that limit the start of microbial activity until the boiling period is over. Even though microbes could be sterilized out of the drifts during the highest temperature period, because they are present in the water-rock system they will return as water drips back into potential drifts. Microbes could also be sterilized in high radiation fields, but microbes would be reintroduced from the geosphere once the radiation field decays to lower levels. This model was not directly used in the base case, but provided first-order limits on potential microbial effects.

The microbial communities model is meant to quantify the growth of microbes and to identify the potential bulk chemical effects to the NFGE from the overall microbial community that would grow. Such growth would be a direct result of perturbing the ambient environment and adding potential nutrients (e.g., steel, concrete, and other repository materials) for bacterial catalysis and growth. The following paragraphs summarize the conceptual model for microbial activity in the near-field environment.

Microbes can thrive over a wide range of pH, under high hydrostatic pressures, in highly saline conditions, and in high radiation conditions that would normally be lethal to humans. Microbes live in nutrient starved environments and can be expected to continue to live even if the nutrient supply of introduced repository materials becomes exhausted. In these nutrient starved environments, some microbes even metabolize $CO_2$, $N_2$ and $CH_4$ directly from the gas phase via autotrophic behavior or methanogenic metabolic processes.

Microbes will alter their environment by creating biofilms. Biofilms make it possible for anaerobic microbes to live in aerobic conditions by isolating them from the normal atmospheric conditions in which they would not survive. Therefore, all microbial influenced redox mineral transformations are possible in a Yucca Mountain repository. Microbes will adhere to mineral surfaces where they are able to utilize available nutrients and energy; otherwise they can act as colloidal particles and move through the subsurface via advective-dispersive mechanisms.

Over time, the repository environment will have environmental conditions that will favor certain bacteria over others (i.e., thermophiles over mesophiles or acidophiles over neutrophiles). However, with the exception of the period in time where the temperature of the repository is >120°C and the water activity is <0.95, microbes should be able to grow and produce their metabolic byproducts.

Microbes will either attach (accumulate) themselves to surfaces in the near-field environment, thus affecting the chemical environment in the repository or they will be available to act as colloids, thus affecting radionuclide transport. In addition to these two aspects, Figure 4-6 depicts other impacts to the near field that are not discussed above. Because the microbial communities model has not been designed to include many of the effects depicted in Figure 4-6, other modeling and abstraction activities will be necessary in the future to assess further effects on the near-field geochemistry.

## 4.3 DESCRIPTION OF DESIGN INPUTS ON MATERIALS QUANTITIES AND COMPOSITIONS FOR THE NFGE

There are a number of substances that could have large effects on the water compositions in the potential emplacement drifts. During both site characterization activities and construction of a potential repository, a number of substances will be introduced into the site such that they become committed to remain in the system over geologic time. These may include a variety of compounds but there are three main categories that, as part of the waste package or as structural components, will potentially be abundant post-closure: steels, organic substances, and cementitious materials. In addition to the direct compositional effects of such introduced materials, the processes associated with microbiological activity within this environment may also be enhanced by the construction and characterization activities. Some of the potentially dominant effects of these major phases are briefly summarized here.

Steel, containing abundant Fe, may stabilize Fe-oxide or Fe-hydroxide solids in the near-field which could provide effective sorption sites for many dissolved species, and may be particularly effective in retarding generally nonsorbing elements such as Tc (Meijer 1990). In addition, as the Fe in steel will oxidize, it will provide a sink for oxygen in the system and may generate locally reducing conditions dependent upon the rate of oxygen supply from the vapor phase. This could lower solubility-limits on dissolved concentrations of many multivalent metals. Finally, colloid generation from steel may strongly sorb radionuclides and provide additional transport capabilities (Meike and Wittwer 1993).

The introduction of organic substances into the near-field may have an impact on performance through changes in the concentrations of organic acids and organic colloids which can increase waste package corrosion, increase radionuclide solubility-limits and transport properties, and enhance silicate mineral dissolution (Choppin 1992; Minai et al. 1992; Bennett et al. 1993; Meike and Wittwer 1993). Such organics may also promote microbial activity that could affect detrimentally the waste package corrosion (Meike 1995). In addition, organic substances can take part in oxidation/reduction reactions and may therefore contribute to generation of locally reducing conditions, possibly reducing metal solubilities.

Based on ease of construction and preclosure tunnel stability considerations, precast concrete is the primary option for ground support in the emplacement drifts of the potential Yucca Mountain repository. Using precast concrete lining segments for tunnel excavation and construction provides an efficient means of developing the vast lengths of emplacement drifts in the potential repository. Lining of the emplacement drifts with precast steel-reinforced concrete may enhance the stability of the emplacement drifts, possibly throughout the preclosure period. These linings may also help to assuage potential rock falls on the waste packages in the early post-closure

stages. However, the potential geochemical effects of the long-term evolution of cementitious materials in the potential repository drift environment may result in both beneficial and detrimental impacts to post-closure waste isolation capabilities of the system.

Only substances that are used for potential repository (including EBS) construction/operation/ closure that are left in the geologic environment post closure (either intentionally or inadvertently) are of concern for potential impacts to potential repository performance, unless the substance irreversibly alters the geologic environment prior to being removed from the site. In order to assess the potential effects to site geochemistry, and to evaluate the potential impacts to waste isolation resulting from usage of tracers, fluids, and materials (TFM, where materials specifically refers to solid substances) in a potential repository, the needed information consists of the following three parts: (a) the amount of the TFM to be committed to the tunnel (i.e., emplaced and expected to be left after closure); (b) the distribution of that TFM throughout the tunnels; and (c) the composition of each phase of the TFM. This information can be represented simply as the answers to these questions; how much, where is it, and what is it?

### 4.3.1 Inputs on Materials Masses, Locations, and Compositions

Requests were made to the waste package design organization and the subsurface repository design organization to obtain the appropriate information for the NFGE model analyses. Each organization responded using QAP-3-12 Design Input Transmittals to provide the requested information. The reader is directed to these three inputs for further information not summarized below (QAP-3-12 Design Input Transmittal 1998a, 1998b, and 1998c).

#### 4.3.1.1 Waste Package Design

The first QAP-3-12 Transmittal (1998b) provided the following information:

A. The quantities, waste package type (e.g., 21 PWR, 44 BWR etc.), and mass of each individual design component for each waste package (e.g., corrosion allowance material [CAM], corrosion resistant material [CRM], Basket Plates, Basket Tubes, Basket Guides, and Thermal Shunts).

B. Materials compositions (percent) for each of the individual design components.

C. The total mass of the supports and piers in the repository.

The second QAP-3-12 Transmittal (1998c) provided information on the length of the emplacement drift over which the supports and piers were to be positioned. It also included the spacing distance between each waste package support.

#### 4.3.1.2 Repository Design

The third QAP-3-12 Transmittal (1998a) provided the following information:

A. The material quantities per lineal meter of drift. These include masses or volumes for the following: bolts, channel, and mesh support; steel set support; precast and cast in

place concrete liners, floor slabs, turn outs, loading docks, and inverts; gantry rail and fittings; conductor bar and fittings; and communications cable.

B. Materials compositions (percent) for each of the individual design components.

C. Layout information on the locations of the drift segments.

### 4.3.2 Materials Used for Near-Field Geochemical Environment Component

Figure 4-13 shows the major materials that are used in the base case NFGE analyses. This figure does not include all of the detailed materials information provided by the design organizations; neither does it provide information on all of the materials analyzed in the sensitivity analyses. However, each of the sensitivity analyses will discuss in further detail the use of any design inputs not included in Figure 4-13.

## 4.4 APPROACH, BASES, AND IMPLEMENTATION OF MODEL ABSTRACTIONS FOR NEAR-FIELD GEOCHEMICAL ENVIRONMENT PROCESSES

This section contains descriptions of the methods and constraints used for implementation of the models for the NFGE component of the TSPA-VA. This includes the descriptions of the codes used (if any) or the calculations performed to arrive at the model results. The section begins with a short section on the general approach for the NFGE (i.e., there is not a single code that produces a set of results, rather a number of codes/calculations that are linked via outputs/inputs). This is followed by the approach, bases and implementation for each model.

Within these descriptions there is some overlap with discussion of conceptual models presented in Section 4.2 because many of the details described there provide the bases for the model implementation. This section provides details of what was done for each model—that is, how it was implemented and analyses were performed. The two sections below this one (Sections 4.5 and 4.6) contain discussions of the model results. Each of these model implementation sections provides some discussion of uncertainties within that particular model. There is also a general section on the major uncertainties at the end of Section 4.4.

The input, output, and bases for the models in the NFGE component are shown as the flow chart in Figure 4-14. The major input parameters come from the UZ flow and thermal-hydrology components and from the VA design. The primary outputs of the NFGE are water and gas compositions provided to the waste package and waste form components. Additional input for conceptual scenarios is provided to the criticality, waste form, and UZ transport component analyses. In the latter two cases, sensitivity studies were conducted based on scenario development in the NFGE (see Section 4.6). The bases for the conceptual models and parameter sets defining the NFGE models discussed in Section 4.2. are in five general categories: site measurements, site experiments, site analogues, laboratory experiments, and data analysis and compilation (Figure -14). The implementation for each of the NFGE models is discussed in this section. The connections among the NFGE models are shown in Figure 4-15.

### 4.4.1 General Approach to NFGE Model Development/Abstraction

The strategy taken in the models that follow was to begin incorporating the geochemical effects into the performance assessment one layer at a time. This permits the development of relatively idealized conceptual models in a short period of time. Such models allow the analyst to begin evaluating the system, to identify areas where models need to be enhanced or model assumptions challenged, and to delineate the connections that are needed for such models to be integrated into a total system performance assessment calculation. A number of the models discussed below are based, in part, on the process-level models presented in the *Near-Field/Altered-Zone Models Report* (Hardin et al. 1998). However, many of the models in the TSPA-VA NFGE component are a combination of abstracted models with some process-level components that performance assessment personnel and principal investigators within the scientific program have worked together to develop for the TSPA-VA. For example, there is no process-level model that calculates the evolving composition of gas around or within the potential drifts. Therefore abstracted air mass-fractions from process-level thermal-hydrology calculations are used in conjunction with descriptions of the composition of that air, based on both site measurements and logical arguments about how those values apply to the system throughout time. A brief overview of the NFGE models is given here, below which is the detailed implementation of the models.

The NFGE model for gas composition utilizes the ambient pore gas composition (differing from atmospheric in terms of carbon dioxide content) with the results of the thermal-hydrology calculations as the major drive to perturb these values due to the boiling of water. Part of the rationale for this is the rapidity with which gas movement appears to takes place in the mountain, particularly under a thermal perturbation. In addition this model tries to incorporate a first estimate at the early behavior of this heated system in terms of other sources of $CO_2$ in the near field. The changes in gas composition and fluxes are utilized to identify and abstract a number of periods for which gas compositions can be taken as approximately constant. Because most of the changes take place during the higher temperature due to boiling effects, these earlier times have a finer discretization than later time periods. The time that average drift-wall temperatures are above boiling is used to delineate the period during which large amounts of water will be vaporized in the rock mass.

These perturbed gas compositions are utilized within EQ3/6 calculations in which fluids are equilibrated at higher temperatures with these perturbed gas values. Two types of higher temperature regimes are recognized here: (a) a boiling regime and (b) a cool-down regime. Both of these regimes have multiple periods defined for them to account for differences in gas composition and in the temperature of equilibration for the cool-down regime. The major difference is that during the boiling regime fluids are not just equilibrated with the perturbed gas compositions, rather they also are calculated as having been 90 percent boiled, or 10 times concentrated for conservative elements. This fluid composition is then possibly in equilibrium with some additional phases that may have saturated during the concentration process. For each time period these calculated fluid compositions are taken to be the composition of fluid that can enter the drift and react with solid phases within it.

During the boiling period there is some indication that water may not even enter the drift, and even if it does it would be close to the boiling point and boil away relatively quickly. Even so,

these compositions are evaluated in order to track the possible fluid compositions at those times and to permit evaluation of reactions with materials at about the boiling temperature. However, it is likely that for this boiling period, the sensitivity analyses covering build-up of mineral precipitates will be more directly applicable. The submodel for precipitates/salt buildup followed by redissolution and brine generation is discussed below within the in-drift water-solids chemistry model.

For water that has entered the drift, model calculations are done to evaluate the reaction with the major solids in the drift, in particular concrete and the corrosion products of the steel (as represented by iron oxides). These reactions are done using the gas fugacities and mass fluxes derived from the incoming gas submodel in a manner that tries to assess the relative magnitude of these terms. This application was assessed both in simple mass-balance calculations and within the water-solids chemistry calculations. Effectively the calculations performed assume that for these reactions, the water and solids reactions move to some extent towards equilibrium (i.e., these are not fast flow paths). These models were used to evaluate the ability of the materials in the drift to deplete gas components supplied by fluxes into the drift. This was done by making the primary assumption that no gas reactions are limited by the rates of reaction, rather the mass flux of gas is utilized as the rate limiting step (i.e., carbon dioxide is made available to cement phases to carbonate them as readily as possible given the supply for that period of time). Water compositions were calculated for reaction with corrosion products alone (the base-case analyses), and for concrete and corrosion products (sensitivity analyses) because there will likely be water flow pathways without concrete along them after the drift liner collapses.

These reacted fluids may then enter the waste package and react with the spent fuel there at the same gas compositions. Again the calculated gas compositions are imposed on the spent fuel-water reaction because no barrier to gas flow into the package has been demonstrated. (Although it should be noted that water filled corrosion products would represent a gas diffusion barrier for as long as the corroded pathways could support water retention via capillary forces. No model of such a barrier has been developed for these analyses.) These spent fuel-water reaction calculations were done for sensitivity analyses to bound the length of time that some dissolved constituents may be dominated by this waste-form reaction. In addition, analyses were performed to assess the amount of change induced to the fluid from the secondary uranium phases that form and then dissolve over geologic time. As pointed out in Section 4.2.1.3.2, no models of the DHLW effects on water composition were finalized for the TSPA-VA analyses.

The ionic strength of fluids used for the base-case and sensitivity analyses at the TSPA level was used to assess the abundances of the natural and introduced colloids. The colloid model is relatively independent other than this particular link. For both waste forms, Fe-oxyhydroxy and clay colloids representing the introduced and ambient colloid populations were evaluated. As discussed in the waste form degradation/mobilization component (Chapter 6), a third colloid was included that is specific to each waste form (representing the waste form colloids).

Another aspect being addressed is the evolution of microbial communities within the drift. This is intended to be a bounding assessment on the masses of microbes produced. It uses an idealized approach, similar to that of McKinley et al. (1997). This approach uses abiotic processes to determine the rate at which nutrients become available to microorganisms, and then

assumes that the microorganisms convert those nutrients to the products instantaneously, using limiting guidelines of energy availability and the availability of all the required nutrients in the proper ratio. It may be possible that this model can identify additional constituents that need to be added to the abiotic NFGE gas-water-solid system.

Other than the colloid model, which is not thought to have any strong feedbacks to the other systems, there are many interactions between the other component models for interaction of gas, water, and solids that are being ignored for the base-case analyses by making initial assumptions about what the first-order effects might be in this system. For example, the major perturbation to the gas phase is taken to be the thermal pulse and resultant thermohydrology, even though there are source and sink terms for gas constituents that may need to be considered in order to adequately assess the system. As mentioned above and discussed below, some of these assumptions are assessed within the analyses. In any case, it is the first-order effects, (i.e., those that get the models beyond the previously assumed ambient geochemical conditions for all of time), that need to be incorporated so that the system model can be utilized in a more representative manner, assessed, critiqued, and subsequently refined. The major assumptions are discussed within the descriptions of each model.

For the model implementations below, a number of calculations are discussed that were produced using a variety of software programs and databases for some of the fundamental thermochemical data that form the foundation of such calculations. In some cases these codes are long established tools (e.g., the EQ3/6 code package, Wolery 1992a) and in others the tools are newly developed (MING, Ehrhorn and Jolley 1998). For some of the EQ3/6 calculations presented below, different versions of the code package were utilized (e.g., version 7.2b versus version 7.2c). However, for the calculated results incorporated into the TSPA-VA analyses, only version 7.2b of the EQ3/6 code package was used. This is a QA version of this code (EQ3/6-V7-REL-V7.2b.2599) that is under Configuration Management control and that was installed and tested on the analysts' computers following the Computer Software Qualification Procedure,QAP-SI-03.

Many of the thermochemical data utilized in the NFGE analyses were drawn from different versions of the GEMBOCHS database in the form of the data files associated with the EQ3/6 code package (Wolery 1992a, 1992b). Other data taken from the literature and developed into data sets for NFGE model analyses are described in detail within this document. This is the first time these NFGE models have been developed either for use in TSPA analyses or for assessing the magnitude of specific in-drift geochemical issues. Because of this and the coarse level of abstraction at which the results are used, this variety of tools and data sets is thought to have negligible effect on the qualitative nature of the results. Because all analyses presented within were not performed with qualified data sets, all results within this report are considered unqualified and are to be verified (TBV) for use in any quality-affecting activity. However, in future analyses that will be used in support of potential site licensing work, all analyses will draw upon a single qualified data set and utilize a single version of any qualified tool that is applied. Tracking of input data and output results is discussed further in Section 4.4.5.

### 4.4.2 Incoming Gas, Water, and Colloids

The submodels of incoming gas, water, and colloids in the NFGE component provide both the time-dependent boundary conditions for the gas, water, and colloids compositions and the cumulative fluxes of gas and water constituents entering the emplacement drift. Each of these is discussed in this section in terms of the methods used to implement the submodels and the bases for the constraints used within those implementations. For each of these, the analyses that were done for both the base-case and sensitivity studies are described in this section. Results of all the analyses are presented in Section 4.5 for the base-case and in Section 4.6 for the sensitivity analyses.

For all the models in the NFGE component, the abstracted evolution of system conditions is based on the thermal-hydrologic changes. However, because the total system analyses use time steps of 100 years, explicit coupling of the NFGE evolution with the time-dependent thermal changes only captures the coarse behavior of the system. The development of the abstracted periods used in the process-level calculations for the NFGE is discussed in the following paragraphs.

#### 4.4.2.1 Incoming Gas

The model implementation for incoming gas combines a model of the "air" composition in the mountain with the results of the thermal-hydrology calculations for gas flux. This combination determines changes to the air-mass fraction values caused by boiling water. The thermal-hydrology models evaluate a two-component gas phase (steam and air, see Chapter 3). The air portion represents the fraction of all noncondensable gas components (i.e., everything that is not steam), given by the air-mass fraction (which is 1 minus the steam fraction). The thermal-hydrologic results include the effects of boiling and gas flow on the mix of air and steam in the gas phase but none of the water-rock chemical interactions.

Constraints on the air-mass fractions within, and gas flux into, the potential emplacement drifts as functions of time were taken from the results of mountain-scale thermohydrologic (TH) analyses provided in Chapter 3. These results were generated from 2-dimensional (2-D) thermohydrologic calculations for a cross section at N233,400, or about the center of the potential repository block. Values of both the air-mass fraction and gas flux as functions of time were provided for both the center and edge portions of this cross-section and for a number of different infiltration scenarios (see Chapter 3 for details).

The infiltration scenarios were based on the present-day climate, designated I-dry, that has an average infiltration rate of 7.96 mm/year, and an estimated long-term average climate, designated I-LTA, that has an average infiltration rate of 45.3 mm/year for the N233,400 cross section (Chapter 2 and Chapter 3). These scenarios were also evaluated for extreme periods of dry or wet variability by using multipliers on the average values (factors of 3—see Chapter 3). The two nominal infiltration rates were also combined into a TSPA-VA base-case climate model (Chapter 2) which had an expected value of I-dry to 5,000 years, I-LTA from 5,000 to 95,000 years, and then I-dry to 100,000 years. It is this base-case set of results that was utilized for the NFGE analyses. The other cases where climates were drier did not result in substantially longer periods of perturbed gas compositions compared to these results for the center of the cross

section (less than a factor of two). The wetter climatic scenarios resulted in system responses that were similar to those for the edge portion of the base-case results, and should be bounded by the center response as discussed below.

The two-dimensional thermal-hydrology model at the mountain scale provides both the air mass fraction and the gas flux through the drifts as continuous functions of time to 100,000 years. After that time, the system is considered to have returned entirely to ambient conditions. These results were provided at the center and edge of a two-dimensional cross section running east to west through the middle of the repository (Chapter 3). Figures 4-16 and -17 show the 2-D mountain-scale thermal-hydrologic results for air mass fraction through time at both the center and edge of the potential repository.

The details of the boiling period can be seen in Figure 4-16 (5,000 years), whereas Figure 4-17 indicates that the air mass fraction is back to ambient by 100,000 years. It can be seen in Figure 4-16 that the thermal perturbation is much longer for the center portion than for the edge portion, and that the magnitude of changes to the air mass fraction are larger. This means that gas compositional changes driven by this process will be larger and longer lasting for the center portion. Because the magnitude and duration of the thermally induced changes are greatest for the central portion of the repository, the NFGE analyses were focused on this portion of the system. Any resultant effects in the edge areas will be bounded by those evaluated for the center of the potential repository.

The 2-D thermohydrology results provide both the horizontal and vertical instantaneous gas fluxes through the drifts as functions of time for the center and edge of the N233,400 cross section (Chapter 3). These values used with the corresponding air mass fractions were evaluated to determine the cumulative air flux into the potential emplacement drifts. This was done in order to utilize these values as one source of potential reactant within the drift in the thermochemical calculations discussed below. Using the cumulative flux of the air into the drift keeps track of the maximum reactant that could be supplied via this mechanism to the potential drift. The cumulative air flux to 5,000 years is shown in Figure 4-18 for both the center and edge portions. The flux of air back into the edge portion occurs much sooner than that for the edge portion, although by 5,000 years the cumulative air fluxes are nearly the same. In fact, as can be seen in Figure 4-19, the cumulative air fluxes are larger for the center portion of the system after about 10,000 years.

The air-mass-fraction variations and the changes in air fluxes were used to delineate a number of periods for which gas compositions can be approximated as constant values with step changes at the transition points. For each of these periods, constant average values for air mass fraction were abstracted from the more continuous thermohydrologic results resulting in a stepped representation that captures the major variations that occur. Because most of the variation is caused by boiling effects during the early, higher temperature conditions (boiling regime), these earlier times are divided at a finer scale than the later periods that represent below boiling conditions (cooling regime). Table 4-8 shows the abstracted air mass fractions and the times over which they apply for both the edge and center portions of the system. The abstracted values for the center of the potential repository are shown as step functions of time in Figures 4-20. This abstraction is a coarse representation of the continuous results shown in Figures 4-16 and 4-17, and were used for constraints on the chemical conditions during abstracted time periods.

The thermal-hydrologic results for gas flux into the drift were used with the air mass fractions to constrain the cumulative flux of air into the drift both continuously (Figures 4-18 and 4-19) and for the specifically defined periods. Combining these with the air composition defined for each period (as discussed below) allowed derivation of cumulative fluxes of each air constituent per meter of drift. The results of these analyses are presented in Section 4.5.1.1.

In general, the abstracted air mass fractions return to constant ambient values in only hundreds to a few thousand years after the boiling regime. Therefore, the air mass fractions do not provide a useful basis for delineating abstracted periods for calculating chemical interactions after that point (about 4,000 years in this case). For later times, variations in drift-wall temperature were used to develop an additional basis for abstracted periods that represent both the transition from boiling to cooling and the temperature decrease during the cooling regime. The time above boiling was defined based on the drift-wall temperature because, for gas-water-rock reactions, the water boiling in the host rock represents a fundamental difference in chemical processes. The two dimensional, thermal-hydrology model at the mountain scale uses a smeared heat source and provides temperatures in the rock a small distance from the drift wall (Chapter 3). The model does not give an accurate drift wall temperature history, including the transition time to below boiling conditions and therefore was not recommended for this purpose (Chapter 3). Instead, the drift-scale results of the multiscale (drift plus mountain scale) thermal-hydrologic models were used because they provided a more accurate thermal history of the drift wall.

The multiscale thermal-hydrologic calculations provided average thermal and RH evolutions at both the drift wall and the waste package surface for six repository regions (Chapter 3). These six regions were classified (Chapter 3) as center-like (Region central-central [CC]), edge-like (Region SW), and intermediate (the other four regions) to determine how to link their average thermal evolutions with the center and edge results from the two-dimensional, mountain-scale model. The results for Region CC, at both the present day (I-dry) and long-term average (I-LTA) infiltration conditions, corresponding to the representative commercial spent nuclear fuel waste package were provided to be combined with the center portion results from the 2-D mountain-scale thermal-hydrology models.

To represent the base-case climate scenario, the results for the I-dry case are used up to 5,000 years, whereas the I-LTA case is used from 5000 to 100,000 years. These combined results for the average drift-wall temperature history for Region CC are shown for 5,000 years and 100,000 years in Figures 4-21 and 4-22, respectively. The shift in infiltration rates at 5,000 years shows up clearly in Figure 4-22. It should be noted that at 95,000 years the thermal histories of both the infiltration cases are so close to ambient that not shifting back to the I-dry case introduces negligible uncertainty—particularly true for the abstracted representations of the cooling regime that are developed here. The corresponding RH conditions at the drift-wall are shown in Figures 4-23 and 4-24 for 5,000 and 100,000 years, respectively. These values can affect the point in time that salts deposited near the potential drift may redissolve and flow onto the waste package, or the point in time that microbes may be brought back into the system.

The time that average drift wall temperatures are above boiling is given by drift-scale results of the multiscale (drift plus mountain scale) thermal-hydrologic model for Region CC (Figure 4-21). To abstract periods of constant temperatures for calculating chemical reaction in this system, a set of temperature conditions were chosen in order to span the possible relevant

range. During the boiling regime, any reaction of gas with fracture water was assumed to occur at 95°C (just below the boiling temperature), approximating reflux water reacting just before reevaporation. The cooling regime was divided into temperatures of 70°C and 30°C to capture coarsely the intermediate- and lower-temperature conditions for reaction in the system. These constraints were utilized with the thermal history shown in Figures 4-21 and 4-22 to define the transition times.

The abstracted periods defined for the NFGE component based are shown together with this drift-wall thermal history in Figures 4-25 and 4-26 to 5,000 and 100,000 years respectively. These periods, as initially defined, overlapped somewhat with those based on the air-mass fraction but were not identical. These two sets of abstracted periods were synchronized by ensuring that the break between the boiling and cooling regimes corresponded to the end of the last boiling period as defined by air-mass fraction changes (this point is 2000 years for the center area of the repository). Because such a coarse level of representation is being used to capture the major aspects of this system affecting the chemistry, this adjustment should not affect the conclusions of these analyses. The abstracted temperatures capture a rough estimate of the cooling in the system (Figure 4-26), and allow evaluation of the possible chemical differences at various temperatures.

For the repository center, the time-period abstractions created three boiling periods which were defined as Period A (0–200 years), Period B (200–1,000 years), and Period C (1,000–2,000 years), and three cooling periods which were defined as Period D (2,000–4,000 years), Period E (4,000–10,000 years), and Period F (10,000–100,000 years). The boiling-regime periods are assigned the same temperatures, but they have various gas constraints (air mass fractions and air fluxes). The cooling-regime periods have different temperature and gas constraints (gas fugacities and cumulative fluxes) for some periods.

The incoming gas submodel also defines the air composition. The model air composition description is based on the ambient pore gas (which differs from atmospheric air in carbon-dioxide content—Section 4.2.1.1.1), with inclusion of a limited period of elevated carbon dioxide values for the early behavior of the heated system. This early change in carbon dioxide content may reflect primarily potential mineral sources of carbon dioxide in the rock (Section 4.2.3.1.1).

The model of air composition is implemented only as a logical model (there is not a code that calculates the values); the values are assigned directly for the specific periods in the system evolution. The oxygen and nitrogen values used are atmospheric, about 20 volume percent oxygen and 80 volume percent nitrogen, throughout all periods, except with the partial pressure of the nitrogen gas adjusted to 70 volume percent to offset the increased carbon dioxide in Period A. For carbon dioxide (as discussed in Sections 4.2.1.1.1 and 4.2.3.1.1) the ambient value is taken as 1,000 ppmv (parts-per-million by volume). A value of 100,000 ppmv, or 10 volume percent, is designated for the first 200 years (Period A) to reflect enhanced $CO_2$ in the gas possibly from either reaction of heated calcite and silica to form a calcium-silicate mineral, degassing of $CO_2$ from heated water, or release of carbon dioxide from the water-mineral interface (Section 4.2.3.1.1; Codell and Murphy 1992; Hardin et al. 1998, Section 5.7.1, 6.2.1, and 6.6). The abstracted air composition in terms of the carbon dioxide content through time to

10,000 years is shown in Figure 4-27. The initial transient period of enhanced carbon dioxide content shows up clearly.

Combining this abstracted air-composition model and the abstracted air mass fractions from the thermal-hydrology model results provides the incoming gas compositions within the NFGE that are presented in Section 4.5.1.1. This is done simply by multiplying the fraction of air in the gas phase by the fraction of the constituent in the air.

#### 4.4.2.2 Incoming Water

The model implementation for incoming water included process-level calculations using version 7.2b of the EQ3/6 geochemical modeling package (Wolery 1992a; 1992b; Wolery and Daveler 1992). (The calculations also used the supporting data0.com.R2 thermochemical datafile generated by GEMBOCHS.V2-JEWEL.SRC.R3 02-aug-1995 16:45:06 thermochemical database). The calculations implementations are discussed below and results of the analyses are given in Section 4.5.1.2. For each of the abstracted periods, the conditions for gas composition from the incoming gas model are used (Table 4-8 and Table 4-41), and the abstracted temperatures shown in Figures 4-25 and 4-26 (listed in Table 4-41) were used in calculations of incoming water compositions. For each period, calculations were performed for reaction and equilibration of the heated water with the minerals and the gas phase. The two types of temperature regimes, a boiling regime and a cooling regime, were again recognized here and had somewhat different implementations. The additional processes considered during boiling regime calculations required a different model implementation than the implementation for cooling regime calculations. The specific differences between these two implementations are detailed in the following paragraphs.

Despite some differences in the methods of calculation, the boiling and cooling regime implementations have many factors in common. Both of these implementations consider the same dissolved constituents in the aqueous phase: pH, sodium ($Na^+$), potassium ($K^+$), calcium ($Ca^{2+}$), magnesium ($Mg^{2+}$), iron ($Fe^{2+}$), aluminum ($Al^{3+}$), silica ($SiO_2$), chloride ($Cl^-$), fluoride ($F^-$) carbonate ($CO_3^{2-}$) and sulfate ($SO_4^{2-}$). These constituents comprise the total masses of these components within the fluid and may be represented by a number of different species in solution. In process-level calculations, initial concentrations for many of these constituents are taken from the average composition of the groundwater sampled at Well J-13 for the saturated-zone tuff aquifer (Harrar et al. 1990; Hardin et al. 1998, Section 6.2). In addition, the equilibrium oxidation potential of the system was constrained by the oxygen fugacity values as discussed and developed in Sections 4.2.3.1.1 and 4.4.2.1, and the total dissolved carbonate was set to equilibrium with the carbon dioxide fugacity (these values that result from the incoming gas model are listed in Table 4-41). The total $Ca^{2+}$ content of the solution was set by equilibrium with the mineral calcite, and the system pH was calculated by charge balance constraints.

##### 4.4.2.2.1 Cooling-Regime Implementation

Calculations for the two temperature regimes, differ in the mineralogical constraints on the fluid composition and in the calculation method for the final fluid composition. The cooling regime implementation is simpler; for each of the periods in the cooling regime, a single model calculation was performed using the EQ3nr code (Wolery 1992a; 1992b). In these calculations,

the average J-13 water composition was equilibrated with the gas phase and a set of minerals representing the tuff phases at the appropriate temperature conditions (Section 4.4.2.1 above and Table 4-41). In addition to the common constraints listed in the previous paragraph, the cooling regime calculations had dissolved silica set to equilibrium with alpha-cristobalite, $Al^{3+}$ set to equilibrium with calcium-montmorillonite, $Fe^{2+}$ set to equilibrium with calcium-nontronite, and $Mg^{2+}$ set to equilibrium with calcium-saponite. These mineral constraints represent the silica and clay minerals resulting from alteration of the primary phases in the tuff (Hardin et al. 1998, Section 5.1).

This implementation of the incoming water model composition for the cooling regime was based on the implementation of analyses that were performed for actinide solubilities in the waste-form studies (Chapter 6) and also presented within the models for the system from the scientific program (Hardin et al. 1998, Section 5.1). These analyses and a brief discussion of the constraints used are presented here and form the basis of the implementation presented above.

As part of the waste-form degradation and mobilization (WFD) activities (Chapter 6), a set of preliminary calculations was performed to begin the reevaluation of solubility-limited concentration distributions in J-13-like water compositions at a range of temperatures. These calculations were constrained at atmospheric oxygen fugacity (0.2 bar) and at the ambient carbon dioxide concentrations in the pore gas of the tuff (about 1000 ppm) as discussed above in Sections 4.2.1.1.1, 4.2.3.1.1, and 4.4.2.1). The solubility calculations were done for 31°, 60°, and 90°C for a variety of phases of the elements Np, Pu, and U and the preliminary results are given in Chapter 6. Because the focus of the NFGE is the bulk fluid chemistry, not the radionuclide content (although in some cases the radionuclide concentrations are greater than some of the trace constituents in the fluid), the constraints on radionuclide concentrations are not discussed further here, only the constraints on major element composition are presented.

It should be noted that the results for 90°C are not directly comparable to the NFGE 95°C cases because (1) the 90°C calculations performed to evaluate actinide solubilities were set to much higher values of carbon dioxide gas fugacity (log $fCO_2 = -3$), and (2) the NFGE 95°C cases include consideration of the effects of boiling. In any case, the calculations performed at 31°C and 60°C are at comparable conditions to those for the NFGE incoming water model at 30°C and 70°C. Specifically, the temperatures are close and the gas constraints were set to the same ambient gas compositions (corresponding to abstracted Periods E and F above, respectively).

Compared to the analyses done for the NFGE models discussed below, these calculations were performed with a different version of the EQ3/6 database ("com" = composite, R6 = Revision 6, generated by GEMBOCHS on 12/3/96) and a different version of the EQ3NR code (version 7.2c of the EQ3/6 code package). However, it is expected that any differences would result primarily from the differences in conceptual model constraints. As such, the conceptual model used in these analyses was followed as closely as possible. Compared to simply calculating the high-temperature results of heating J-13 water compositions in equilibrium soley with calcite and the gas phase, this alternate conceptual model assumes less equilibrium concerning the silica and feldspar phases than simply calculating the equilibria with J-13-like fluids at these conditions, and provides a simple way for extrapolative modeling of water compositions to the higher temperatures using EQ3NR.

The constraints for, and results of, these calculated water compositions at 31°, 60°, and 90°C are given in Table 4-9. These calculations were set so the water has a silica level close to that required by equilibrium with cristobalite (alpha). The actual J-13 water at 31°C seems to have a higher level; however, this assumption of equilibrium with cristobalite (alpha) is probably more realistic as the temperature is increased (Duffy 1993). In fact for lower temperature calculations, the silica concentration in the fluids should be set to values about twice what is given in these results to reflect the measured values at lower temperatures, which are supersaturated with respect to quartz via dissolution of volcanic glass (Duffy 1993).

The model water (Table 4-9) is also in equilibrium with calcite and set to be in equilibrium with some clay minerals, so as to not be greatly supersaturated with respect to any such phases. Furthermore, the conceptual model is such that the water should be undersaturated with unstable feldspars (e.g., sanidine, plagioclase), and supersaturated with respect to stable feldspars (e.g., albite, K-feldsar, maximum microcline). For more discussion of such conditions see CRWMS M&O (1998a, Section 5.1). As indicated in the discussion above on ambient gas compositions, the $fO_2$ was set at 0.2 bar, and the $fCO_2$ was set at $1.0 \times 10^{-3}$ bar (which ties in well with the assumption of calcite equilibrium). The pH and carbonate part of the model was set up by constraining the pH itself by the $fCO_2$, the $HCO_3^-$ by calcite equilibrium, and the $Ca^{++}$ by electrical balance. This was the key to doing all the temperature extrapolations in the context of EQ3NR and accounting for interaction with the tuff.

The effect of retrograde calcite solubility, as well as decreasing gas solubility at higher temperatures, can be observed in the resultant fluid compositions in Table 4-9. In addition, these model groundwater compositions are all significantly supersaturated with respect to Ca-clinoptilolite. The 60°C waters are also highly supersaturated with respect to stilbite and mesolite. Consideration of the formation of these latter phases may affect the groundwater composition, but such phases are not common in the tuff where one would expect to find them on the basis of thermodynamic calculations such as these. The general conceptual constraints illustrated in these calculations formed the bases for the implementation of the cooling regime calculations for the NFGE. The results of these analyses are given in Section 4.5.1.2.

#### 4.4.2.2.2 Boiling Regime Implementation

In the calculations for the boiling-regime fluids, the water is not simply equilibrated with the changed gas compositions and minerals in the tuff. Instead, to represent some of the effects of concentration via boiling, calculations were done to evaporate 90 percent of the water, allowing mineral phases to precipitate as the solution becomes more concentrated. Equilibrated water compositions were calculated using the strategy proposed in the near-field/altered-zone models report (Hardin et al. 1998, Section 6.2), modified with appropriate incoming-gas model compositions and temperatures for each of the three boiling regime periods shown in Figures 4-25 and -26 (gas composition results are shown in Table 4-41).

Equilibration of the initial J-13 water composition was calculated with EQ3nr at the appropriate temperature and gas conditions with dissolved silica set to alpha-cristobalite equilibrium, in addition to the common constraints listed earlier. This is provides an initial starting point for performing the reaction mass-transfer calculations of "boiling" using the EQ6 code. The evaporation of water was simulated with EQ6 at the same temperature and gas conditions using

the resulting fluid from the previous EQ3nr calculation. Quartz, tridymite, and talc were suppressed for these analyses, to reflect possible kinetic constraints in the system (Hardin et al. 1998, Sections 5.1 and 6.2). Conservative elements that are not precipitated in minerals have their final concentrations increased to 10 times the starting J-13 concentration. However, final concentrations of elements such as $Ca^{2+}$ are controlled by phases that precipitate during the evaporation and boiling process.

Results of the incoming water model are discussed in Section 4.5.1.2 and utilized as the starting composition by all the models for reaction within the potential drift environment. In the discussion below regarding implementation of these models, the starting fluid composition is that which results from the incoming water model unless specifically stated otherwise. This water composition represents the time-dependent boundary condition to the potential emplacement drifts for water that may flow in through fractures in the absence of the additional processes discussed below (see Section 4.6.2.2.3, in particular) that may alter that composition.

#### 4.4.2.3 Incoming Colloids

The incoming-colloids model is a qualitative assessment of the types of colloids that may enter the drift and general constraints on the amounts of those colloid types. This model provides those qualitative constraints to the in-drift colloids model, in the form of a potential source of clay colloids. The in-drift colloid model is the source of colloid abundances that are used by the other performance-assessment models. Therefore, the implementation of the model for incoming colloids (i.e., calculated abundances of clay colloids) was handled within the model for in-drift colloids discussed in Section 4.4.3.2. In brief, this entailed the use of site measurements on naturally occurring colloids in Yucca Mountain groundwaters (Triay et al. 1996, Table I, Sections 4.2.1.1 and 4.2.3.1.3 above) to show that a relation universally observed for colloids is relevant for the Yucca Mountain site (CRWMS M&O 1998a, Section 6.3.6, see also Section 4.4.3.3 for a discussion of the bases of the relation). This relation was implemented directly within the TSPA computer program RIP (Golder 1998, see Chapter 11 for background code discussion and code version) in the engineered-barrier-system cells (see Chapter 6 for details).

### 4.4.3 Evolution of In-drift Chemistry

The four NFGE component models that describe the interactions within the drift are discussed in this section in terms of the methods used to implement the models and the bases for the constraints used within those implementations. For each of the four in-drift models (gas, water-solids, colloids, and microbial communities) the analyses that were done for both the base-case and sensitivity studies are described in this section. Results of all the analyses are presented in Section 4.5 for the base-case and in Section 4.6 for the sensitivity analyses.

#### 4.4.3.1 In-Drift Gas

The model implementation for in-drift gas used the incoming gas compositions and fluxes directly to define in-drift gas constituents through time. There are two related major assumptions underlying this model. The first is that the in-drift gas composition is not affected substantially by reaction with the in-drift solids, and the second is that gas migration and mixing in the drift is

rapid enough to maintain a homogeneous gas composition throughout the environment. The second assumption is relatively robust because gaseous diffusion alone is rapid enough to ensure homogeneity on these scales. The first assumption precludes generation of local changes to the in-drift gas composition from reaction with materials that are abundant compared to the gas. However, this assumption was evaluated in sensitivity analyses and found to be reasonable for oxygen and carbon dioxide, the two major gas constituents of interest.

The first assumption was evaluated using mass-balance calculations. For these calculations, the in-drift materials were first assessed for their ability to act as either source or sinks of oxygen and carbon dioxide, and then relative masses for the sink and the source were compared. For oxygen, the major sink was taken to be oxidation of the iron content of the steels in both waste package and ground support materials. No major sources of oxygen from in-drift materials have been identified. The large mass of calcium in the concrete that would need to be carbonated to prevent extensive development of alkaline water in the drift was used for the mass-balance assessment for carbon dioxide. A simple mass-balance calculation was performed for each of these cases in which the cumulative flux of the constituent was compared with the mass that potentially could be removed by the material. Results of both the mass-balance and reaction-path analyses are presented in Section 4.6.2.

#### 4.4.3.2 In-Drift Water-Solids Chemistry

For model implementation of in-drift, water-solids chemistry, the incoming-water model composition is used as the starting composition for reaction. In most cases, the reaction of this initial fluid with in-drift materials, including spent fuel, was evaluated at the temperature and gas conditions of the appropriate abstracted period (Figures 4-25 and 26 and Table 4-41). As discussed in Section 4.2.3.2.2, a number of materials representing various conceptual flow pathways or processes were evaluated in these NFGE submodels. For inclusion in the base case TSPA-VA analyses, incoming water was equilibrated with waste package corrosion products represented by the iron-oxyhydroxide phase goethite (Hardin et al. 1998, Section 6.4.3.1). Materials evaluated in NFGE sensitivity analyses are concrete, spent fuel, and precipitates/salts, but only concrete modified water compositions were utilized directly within TSPA-VA-level sensitivity analyses as discussed below, and in Section 4.6.

##### 4.4.3.2.1 Corrosion Products

The model implementation for in-drift water reaction with corrosion products included process-level calculations using version 7.2b of the EQ3/6 geochemical modeling package (Wolery 1992a; 1992b; Wolery and Daveler 1992). (The calculations also used the supporting data0.com.R2 thermochemical data file generated by GEMBOCHS.V2-JEWEL.SRC.R3 02-aug-1995 16:45:06 thermochemical database). The calculation implementations are discussed below and results of the analyses are given in Section 4.5.2.2.2. For each of the abstracted periods, the conditions for gas composition from the incoming gas model are used (Table 4-14 and Table 4-41), and the abstracted temperatures shown in Figures 4-25 and 26 (listed in Table 4-41) were used in calculations of incoming water compositions.

These analyses were implemented using the EQ3nr code (Wolery 1992b) to simulate the equilibration of the incoming water composition (Section 4.4.2.2) with goethite, FeO(OH). This

oxidized-iron phase was used to represent the corrosion products of the iron in steel (Hardin et al. 1998, Section 6.4.3.1), although there are a couple of other possible Fe-oxide or oxyhydroxide phases that may also exist for periods of time (Hardin et al. 1998, Section 6.4.3.1). The calculations were done for each period at the appropriate temperature and gas composition as discussed in Section 4.4.2.1 (given in Table 4-41), with the initial dissolved concentrations specified as those from the incoming water composition except that the total dissolved iron constraint which was set to equilibrium with goethite. The output results are discussed in Section 4.5.2.2.1 and represent the base-case NFGE composition for water that may enter the waste package. The resulting water compositions are used in the TSPA-VA base-case analyses and provided to the spent-fuel submodel as shown in Figure 4-12.

#### 4.4.3.2.2 Concrete

The model calculations to evaluate the geochemical effects of concrete on the water composition were performed as reaction-path calculations using version 7.2b of the EQ6 code (Wolery 1992a; Wolery and Daveler 1992). (Also used was the thermochemical datafile data0.cemcomp.R28 generated by GEMBOCHS.V2-Jewel.src.R5 08-nov-1995 14:02:22, which was created specifically for analyses performed in a cementitious system—Hardin et al. 1998, Section 7.2). These calculations were performed as titration calculations where mineral constituents in the concrete progressively react with the incoming water compositions at the gas constraints and temperature conditions discussed in Section 4.4.2.1 (given in Table 4-41). The carbon dioxide and oxygen gas concentrations were specified initially but, as the reaction progressed, the gas composition could change in response to the water-mineral reactions. This flexibility was used to evaluate whether available carbon dioxide could neutralize concrete alkalinity (high pH).

Design information on the concrete compositions was used to define reactant materials for these analyses (see Section 4.3 and the specific subsections below). The concrete consists of cement, coarse and fine tuff aggregate, and steel fiber (iron) (Section 4.3; Hardin et al. 1998, Sections 6.3 and 7.2). (Although the cement potentially will contain a large amount of organic admixtures, these materials were not evaluated in terms of their effects on water chemistry because of the lack of current appropriate data and models. The organic materials were considered within the analyses of microbial communities growth as discussed below in Section 4.4.3.4.) The cement and tuff both consist of multiple phases. The mineral assemblage used for the cement is for a relatively young cement that has not undergone much chemical or thermal alteration. This mineral assemblage consists of ettringite, calcium-silicate hydrate, brucite, hydrogarnet, and portlandite, with the relative amounts calculated based on the oxide composition (Hardin et al. 1998, Sections 6.3 and 7.2). Both the coarse and fine aggregate are composed of Topopah Spring tuff and were represented by a normative modal mineral assemblage consisting predominantly of alkali feldspar, alpha-cristobalite and quartz (Hardin et al. 1998, Section 6.3). These minerals reacted with the incoming water composition at relative rates assigned to represent relatively fast dissolution of the cement phases and slower dissolution of the tuff aggregate phases and steel fiber.

Results of the analyses for water reaction with concrete are given in Section 4.6.2.2.1. Because the concrete liner is expected to collapse within the first few hundred years (see Sections 4.2 and 4.4; Hardin et al. 1998, Section 2.2), concrete-modified water is not used in the base case. The collapse of the concrete liner would remove it from much of the potential pathways of

dripping water above waste containers. However, because the collapsed concrete mass will still be available to react with water on the lower portion of the waste package for a long time, these water compositions are evaluated in a sensitivity study (Sections 4.6.3 and 4.7; also see Chapter 5 and 11). In addition, the possibility that these fluids could migrate through the UZ, causing large changes to radionuclide sorption, is examined in Chapter 7.

#### 4.4.3.2.2.1 Solids Definition

The first step in the analysis was defining the phases and their quantities that were used to represent the concrete (cement + aggregate). The composition of the concrete to be used for construction of the liner and invert material is presented in CRWMS M&O 1997b for 3.85 $m^3$ of concrete per meter of tunnel liner (Section 4.3). The masses of the concrete components used in the calculations were recalculated to include the concrete in the pier, which adds an additional 0.5 $m^3$ of concrete per meter of tunnel. Therefore, the component masses were scaled by the ratio of 4.35/3.85. Table 4-10 presents the mass of each concrete component and the weight percent and major oxides composing the component per linear meter of tunnel scaled to include the liner, invert and pier.

The water reduction admixture and superplasticizer are organic components and were not considered for this modeling study other than accounting for their mass in the other component mass balances.

Three steps were required to convert the oxide weight percent data to usable EQ6 input data:

A. Calculate the total mass of each constituent element for each component per meter of tunnel.

B. Calculate the total moles of each constituent element for each component per meter of tunnel.

C. Distribute the elements into phases for each component using normalization calculations.

In Table 4-11 and 4-12 the oxide weight percent data of the concrete components have been transformed into elemental mass and moles, respectively.

CRWMS M&O 1997b does not provide alkali (Na and K) concentration values for the cement analysis. However, that report states that the recommended total alkali concentration should not exceed 0.6 percent, and that if a reactive type of aggregate is used, the upper limit on total alkali should not exceed 0.4 percent, (CRWMS M&O 1997b, pp. 33 and 38). These values were given in the context of a discussion about aggregate and the potential for alkali-silica reaction in the concrete.

The alkali elements are potentially important in their effect on the early-time concrete reacted fluid chemistry. Berner (1990) and Neall (1994) state that sodium and potassium hydroxide can raise the early time pH up to 13.5. However, Neall also states that the entire alkali budget is expended in eight to twelve exchange cycles where typically 10,000 exchanges cycles are

required to completely dissolve a mass of cement. An exchange cycle in Berner's and Neall's methodology is a surrogate representation of time. Based on the relatively short duration that alkalis are expected to influence the reacted fluid chemistry, the small size of the alkali budget compared to the calcium budget, and coarse time discretization of the NFGE thermal/hydraulic regimes the alkali input was not considered for the TSPA-VA round of calculations.

**Cement Phase Normalization Calculations** - For the cement, coarse aggregate, and fine aggregate fractions it was necessary to perform normalization calculations to distribute the elements among selected mineral phases.

The mineral assemblage used for the TSPA-VA calculations represents a young cement mineral assemblage and was chosen based on discussions with A. Meike of Lawrence Livermore National Laboratory (Meike 1997; Hardin et al. 1998, Sections 6.3.3.1 and 7.1.2.1). This mineral assemblage is well supported in the literature (Berner 1990; Atkins 1992; Reardon 1992). The phases and their chemical formula are presented in Table 4-13.

The chemical symbol for each element or mineral phase in Table 4-13 represents the number of moles of that component, and C/S signifies the calcium oxide-silica ratio of the CSH phase. The number of moles of CSH were calculated by combining the total silica from the cement analysis with a fraction of that from the silica fume component of the concrete. Only a fraction (x) of the silica fume was allowed to react because it is assumed that reaction products, namely CSH, would tend to form and isolate the silica fume from further reaction. For this study 50 percent of the silica fume was allowed to react to form CSH, and the remainder was included in the fine aggregate element budget. Silica fume is composed primarily of silica, however, minor amounts of other elements are also present and were added to the cement mineral budget and the fine aggregate budget. The cement mineral normalization expressions, the total number of moles per meter tunnel, and phase relative reaction rates are presented in Table 4-14.

The implemented cement mineral phase assemblage for the TSPA-VA calculations was based on the assemblages given in Section 7.1.2.1 of Hardin et al. (1998) for Young cement. This differs slightly from that given in Section 6.3.3.1 of Hardin et al. (1998) and used by those investigators for similar analyses at different gas conditions. The difference is the substitution of gehlenite hydrate ($Ca_2Al_2SiO_7{:}8H_2O$) and hematite ($Fe_2O_3$) (Hardin et al. 1998, Section 6.3.3.1) for aluminum hydrogarnet ($Ca_3[Al(OH)_6]_2$) and iron hydrogarnet ($Ca_3[Fe(OH)_6]_2$) (Hardin et al. 1998, Section 7.1.2.1), respectively. Because this substitution is done in a way that represents the same bulk composition, it is expected that these changes to the reactant assemblage would have a minimal effect on the concrete reacted fluid chemistry, unless actual kinetic rates were being used for the phase dissolution. The results of the analyses presented in Hardin et al. (1998, Section 6.3.4) are consistent with the analyses presented here that are tied directly to the gas evolution through time in the potential in-drift environment (see Section 4.6.2.2.1). This indicates that the slightly different reactant assemblages did not make a noticeable difference in the results.

**Aggregate Phase Assemblage and Normalization Calculations** - Both the coarse and fine aggregate are composed of Topopah Springs tuff, and the choice of mineral phases is the same as that used in the EQ6 test input file "J13WTUFF.6I" which is provided with version 7.2b of the EQ3/6 geochemical modeling code package (Wolery 1992a, 1992b; Wolery and Daveler 1992).

The test input file "J13WTUFF.6I" is set up to simulate the hydrothermal alteration experiment of Topopah Springs tuff performed at LLNL and evaluated by Delany (1985).

There are two primary differences between the mineral assemblage used in "J13WTUFF.6I" and that used in the current exercise: (1) Three of the mineral phases are solid solutions (biotite, plagioclase, and K-Na Sanidine) which are not represented in the database constructed for the cement phases, therefore, these phases were represented as their pure end member phases; (2) The clay mineral Mg-beidellite ($Mg_{0.165}Al_{2.33}Si_{3.67}O_{10}(OH)_2$) used in the "J13WTUFF.6I" test input file is not included in the cement database, therefore, pyearophyllite ($Al_2Si_4O_{10}(OH)_2$) was used as a surrogate. Table 4-15 lists the aggregate phases and their chemical formula.

Normalization calculations were also performed for the aggregate fraction of the concrete. The expressions used to calculate the abundance of coarse aggregate phases are given in Table 4-16. The ratio of quartz to cristobalite-alpha in the reference input file "J13WTUFF.6I" is QTZ:CRIS-A = 0.45, using this ratio the number of moles of each phase was calculated for the EQ6 simulations.

The normalization expressions for the fine aggregate differ from those for the coarse in that they include the additional elements from the unreacted silica fume. Table 4-17 lists the normalization expressions for the fine aggregate phases. The excess elements from the silica fume not incorporated into the cement CSH phase were included in the fine aggregate element budget. They were included in the fine aggregate because of the higher relative reactivity of the silica fume and the fine aggregate compared to the coarse aggregate.

Table 4-18 presents the input values used in the EQ6 simulations. The relative reaction rates were chosen such that the reactivity values were much less than those used for the cement fraction, and to reflect the low reactivity of the coarse aggregate compared to the fine aggregate.

**Steel Reinforcing Fiber** - The final component of the concrete considered for modeling purposes is the steel reinforcing fiber. This phase was simply represented as metallic iron, and the number of moles calculated by dividing the mass of steel fiber by the atomic weight of iron (Fe moles = Mass Fe (g)/(55.847 g/mol). The EQ6 input value is tabulated in Table 4-18.

#### 4.4.3.2.2.2 Reaction-Path Calculations

**EQ3/6 Code Package and Cement Database** - All of the simulations described herein were performed with the EQ3/6 version 7.2b family of codes. EQ3/6, Version 7.2b (EQ3/6-V7-REL-V7.2b-PC), EQ3NR speciation-solubility code (EQ3/6-V7-EQ3NR-EXE-R139-P5), and EQ6 reaction-path code (EQ3/6-V7-EQ6-EXE-R137-P5), supported by the EQLIB library (EQ3/6-V7-EQLIB-LIB-R168-P5).

Clodic and Meike (1997) provide a description of the thermochemical database constructed for the cement phase calculations. The database "CEMCOMP.R28" was generated using GEMBOCHS.V2-Jewel.src.R5 on 08-nov-1995 at 14:02:22. Most of thermochemical data for cement phases included in the cement database was derived from the experimental data of Atkins (1992) and is limited to 25°C. Without enthalpy information and/or heat capacity functions it is

not possible to extrapolate these log K values to higher temperatures, this is both a limitation and source of uncertainty in the simulations.

**Input Setup for Baseline Concrete Calculations** - Input for EQ6 consisted of setting the EQ6 calculational mode, inputting the system information (temperature, gas reservoir information, and reactant information), and adding the appropriate EQ3NR pickup file. These files are generated as output files from EQ3NR calculations and provide the starting water composition to the EQ6 code (Wolery 1992b; Wolery and Daveler 1992). Appending the pickup file to the end of the EQ6 input file is a standard step in performing an EQ6 calculation (Wolery and Daveler 1992). Six starting solutions were used for the EQ6 simulations. The first three solutions (Periods A-C) represent 90 percent evaporated J-13 water (see Section 4.5.1.2), and the final three solutions represent J-13 water equilibrated with some of the tuff phases at elevated temperature with a variable oxygen and carbon dioxide fugacity (Periods D-F). These fluids represent the results of the incoming-water model (see Section 4.5.1.2) and the compositions are given in Table 4-42. The pickup files for the EQ6 calculations were generated from the EQ3NR input files listed in Table 4-19, which represent the values used for the TSPA-VA sensitivity calculations.

The concrete simulations were set up as a titration process (*nmodl1*=1) in EQ6. The maximum value of the reaction progress variable (*zi* or $\xi$) was set to 1 mole. At higher values of *zi* water is consumed in the formation of hydrous mineral phases which causes the ionic strength to increase beyond the applicability of the aqueous-ions activity-coefficient model.

**Thermal Hydrologic Regimes and Gas Reservoir Parameters** - The EQ3/6 simulations of the fluid entering the drift correspond to discrete periods of time for which the temperature and gas composition were utilized from the results of the incoming gas model (see Section 4.5.1.1). Table 4-20 presents the pertinent information related to the thermal/hydrologic regimes, and Table 4-21 lists the gas compositions corresponding to these periods.

For the purposes of EQ6 simulations the size of the gas reservoir for each period was scaled by the total moles of calcium reacted per total moles of Ca in one meter of liner. This step was necessary due to the limiting value of the reaction progress variable ($\xi_{max}$ = 1). The total moles of calcium reacted is equal to a phase's relative reaction rate multiplied by the stoichiometric coefficient of calcium in that phase times the maximum value of $\xi$. The sum of these terms for each calcium phase divided by the total calcium per meter tunnel is equal to the gas reservoir-scaling factor (GRSF). Because $\xi_{max}$ is the same for all reactants, it can be brought outside the summation and the resulting relation is

$$GRSF = \left( \frac{\xi_{max}}{Ca_{total}} \right) \times \sum_{i=1}^{n} v_i \times r_i \qquad (4\text{-}1)$$

where,

$\xi_{max}$ = maximum value of the reaction progress variable

$v_I$ = stoichiometric coefficient of Ca in phase *i*

$r_I$ = relative reaction rate of phase *i*

$Ca_{total}$ = total moles of calcium per 1 meter of tunnel.

The scaling factor and the scaled reservoir size used in the TSPA-VA calculations are presented in Table 4-22.

Oxygen and carbon dioxide were set up as fixed fugacity gases, rather than as reactants in the EQ6 simulations. This option was chosen because it is possible to specify the reservoir size, EQ6 variable *moffg*, for each gas phase, and maintain a constant fugacity, EQ6 variable *xlkffg*, for each gas until they are consumed by reaction(s) at which point the fugacity responds to the heterogeneous reactions in the system and can fluctuate. Table 4-23 lists the EQ3NR output for the incoming fluids used as input for the EQ6 simulations in the form of pickup files.

**Phase Suppression** - In an EQ6 calculation, the code evaluates the saturation state of phases given the speciation of the solution composition and then allows the most supersaturated phases to precipitate before going onto the next time step in the reactant dissolution process. In EQ6 modeling it is sometimes necessary for the modeler to indicate phases that are not allowed to form during a reaction path calculation. This can be done to represent kinetic constraints on the formation of that particular phase that are indicated from observational data, but for which there are not sufficient data to constraint the kinetic parameters quantitatively. Deciding which phases to suppress is based on knowledge of the system and by iteratively running the code to see which phases form and deciding if they are compatible with the conditions of the modeled system.

Those phases that are not allowed to form are suppressed in the EQ6 input file. This suppression effectively removes that phase from the system being modeled. Phase suppression is most easily handled in the EQ3NR input file via the *nxmod* option switch and specifying phases to suppress. The simplest method to suppress phases, for the purpose of EQ6 modeling, is to edit the EQ3NR pickup file portion of the EQ6 input deck. Wolery and Daveler (1992) recommend this procedure for adding and subtracting suppressed phases.

For the TSPA-VA baseline sensitivity calculations a total of six phases were suppressed. These included talc, tridymite, wollastonite, antigorite, magnetite, and maximum microcline. These phases were chosen based on their mode of occurrence in nature and their propensity to form during the EQ6 simulations. Tridymite is not contained within the CEMCOMP.R28 database. This is equivalent to having tridymite continuously suppressed (phases not in the database can never be considered for precipitation) and has the same effect on the outcome of the EQ6 run as explicitly suppressing it.

**Input Setup for Sensitivity-Studies Concrete Calculations** - A series of EQ6 simulations were performed to investigate the effect of key variables on the concrete reacted resultant fluid chemistry. The goal was to the bound variables which were highly uncertain from a conceptual and/or data stand point to make more defensible arguments for the chosen baseline values of these variables.

- Dissolution model and relative reaction rates of reactant phases
- EQ6 Phase Suppression.

**Concrete Dissolution and Relative Reaction Rates** - Concrete is a complex solid composed of multiple components each of which are composed of multiple mineral phases of variable chemical reactivity. The components of the proposed concrete (CRWMS M&O 1997b) to be used in the construction of the underground facility at Yucca Mountain, in order of decreasing mass, include: (1) Coarse aggregate; (2) fine aggregate; (3) cement; (4) silica fume; (5) steel fiber. The contrast in the reactivity of the mineral phases determines the temporal evolution of the concrete-reacted fluid chemistry. The cement fraction of the concrete is the most reactive component of the concrete, and Berner (1990) has described the relative kinetics for the dissolution of cement. The characteristics of the dissolution sequence are reflected in Table 4-24.

There have been several efforts by investigators of concrete chemistry to use geochemical models as a predictive tool for the evolution of pore water within cement (Reardon 1990, 1992) and the evolved chemistry of water reacted with mature cement (Atkins 1992; Berner 1990; Neall 1994). Berner and Neall both used mixtures of $SiO_2$ and $CaH_2SiO_4$, or $Ca(OH)_2$ and $CaH_2SiO_4$ with log K values dependent on Ca/Si of the solid to represent CSH, whereas Reardon describes CSH dissolution using a linear relation. To simulate the flow of water through the cement, both Berner and Neall employed a mixing tank approach, where a given mass of water is equilibrated with the cement phases, the equilibrated chemistry is then used to compute the input for the next water exchange cycle. This approach results in a continuum of fluid chemistry and solids evolution as a function of cycle number, which is a surrogate of time. It should be noted that neither Berner (1990) nor Neall (1994) include the aggregate fraction of the concrete in their modeling studies, rather only the cement fraction is considered as chemically reactive. This indicates very different reaction rates for the aggregate versus the cement portion of the concrete.

The approach used in the TSPA-VA is a "point" type of calculation, where the chemistry of the reacted water is based on a single calculation for a set of mineralogic, gas-phase, and temperature constraints. Each point calculation is assumed to represent the fluid reacted with the concrete for the duration that the abstracted gas composition and temperature regime is valid. The assumption of local equilibrium is imposed and the reaction path evaluates the relative capacity of the concrete/cement to fix $CO_2$ and potentially exceed the amount available for that period. While this approach does not account for the changing physical parameters of the concrete (porosity, density, etc.) driven by the potential changes in the mineral assemblage over the modeled time period, it is only meant to represent a first order estimate of the capacity of the concrete to compete with the $CO_2$ system for control of the water composition (specifically pH) in the NFGE.

In the absence of quantitative kinetic data for the cement and aggregate phases, relative reaction rates were used to do the analyses similar to the approach in Hardin et al. (1998, Section 6.3.3). These rates were chosen to represent the coarse-level behavior in the system, and then sensitivity analyses were performed to evaluate the significance of the relative rate values. The relative reaction rates (EQ6 input variable *rk1*) of the cement and aggregate phases were chosen with regard to (a) the observed rapid reaction of cement phases relative to aggregate phases (Berner 1990; Neall 1994, see discussion above) and (b) recreating the observed behavior of cement phase dissolution sequences (Table 4-24). To elucidate the effect of the relative rates on the chemistry of the reacted fluid a sensitivity study was performed. Two issues were investigated: first, the effect of the magnitude of the rate values on the reacted chemistry; and second, set all

rates to the same value to see if that could recreate the observed dissolution behavior of cement (Table 4-24).

To test how the magnitude of the relative reaction rates influenced the reacted fluid chemistry the baseline *rkl* values for all of the concrete components were multiplied and divided by five in two separate suites of simulations. An assumption of this approach is that the relative reaction rates for each phase were assumed to vary independently of each other, i.e., increasing the reactivity of one phase had no effect on the reactivity of any other phase. In this manner the relative rates were either increased or decreased for the whole set of reactant phases. It is possible that this was not a good assumption, for example it may well be possible that increasing the relative reaction rate for one could act to decrease the rate for another phase. However, in the absence of experimental data it was not possible to investigate this any further. The *rkl* values used in the simulations are listed in Table 4-25.

The second study, to test how well the chosen baseline rates recreated the dissolution behavior of cement as outlined by Berner (1990) was tested by setting the *rkl* values for all of the concrete components to constants. Two suites of simulations were performed where *rkl* was set to 1.0 and 0.1, respectively, for all of the reactants used in the EQ6 input files.

Changing the relative reaction rates required that the gas reservoirs be rescaled accordingly, the values of the EQ6 input variable *moffg* (moles of fixed fugacity gas) for oxygen and carbon dioxide used in the simulations are provided in Table 4-26.

**Effect of Suppressed Phases on Resultant Fluid Chemistry** - In the course of a reaction path calculation, some mineral phases are dissolved (reactants), others precipitate (products), and yet others precipitate and then redissolve later in the reaction path (meta-stable products). In the absence of kinetic data, a geochemical code such as EQ6 does not have the built-in logic to decide if a phase that saturates during a calculation may be kinetically inhibited from forming; it simply precipitates a phase based on equilibrium thermodynamic considerations. Therefore, phases may form in the modeled system that would never be observed in its analog natural system because of kinetic constraints impinging on the attainment of equilibrium. In such cases, it is the judgment and experience of the modeler to decide which phases should be prevented from forming during the reaction-path calculation. Some basic chemical guidelines are generally followed in deciding which phases should not be expected to form. These include the temperature/pressure regime of occurrence for particular minerals, and the relative kinetics of one phase compared to another.

As an exercise to determine how the choice of suppressed phases influenced the reacted fluid composition, two suites of simulations were performed and the results were compared to the baseline concrete-reacted fluid chemistry. In the first suite of simulations additional phases were suppressed compared to the baseline simulations. In the baseline simulation six phases were suppressed: talc, tridymite, wollastonite, antigorite, magnetite, and maximum microcline. An additional four phases were suppressed for the sensitivity study: epidote, epidote-ord, tremolite, and diopside. These phases were chosen because they were calculated to form during the baseline simulations and their likeliness of occurrence for the modeled system seemed improbable. For the second suite of simulations all phase suppression was turned off, i.e., the *nxmod* parameter in the EQ3 pickup files was set to zero. No additional EQ3 runs were

performed, the same pickup files were used and the EQ6 input deck edited (as discussed above) to either include additional phases or remove the baseline-suppressed phases.

#### 4.4.3.2.3 Spent Fuel

Because the spent fuel represents a large material mass, its capacity to affect the bulk fluid composition was evaluated for the NFGE. The tool used for these analyses is the general reactive-transport code AREST-CT, version 1.2 (Chen et al. 1995; 1996; 1997; 1998; Chen 1998). Using this program, this evaluation considers both equilibrium and kinetically controlled chemical reactions between solid phases, aqueous solutions, and gas under flowing conditions. These analyses were done to reflect conditions within either Period E or Period F (see Section 4.5.1.1) for both active alteration of spent-fuel to secondary phases, and subsequent dissolution and alteration of the secondary phases to a tertiary set of uranium minerals. The spent fuel is represented as a one-dimensional porous medium with various specific surface areas. These results for spent fuel effects on water composition are discussed in Section 4.6.2.2.2. The results of the waste form evolution, secondary uranium phases constraints, and the release/retention of neptunium by these phases, are discussed more fully in Chapter 6 on waste form degradation/mobilization.

As water seeps into a failed waste package (WP), it will react with CSNF. The reactions between water and CSNF will change the composition of water. This section addresses how water composition would change within waste packages using a model for reaction of water and spent fuel.

The model is a mechanistic one that utilizes the general reactive-transport simulator AREST-CT. The AREST-CT code was developed at Pacific Northwest National Laboratory (Chen et al. 1995, 1996, 1997, 1998) and modified within the Performance Assessment Operations group of the M&O (AREST-CT version 1.2—Chen 1998). The code includes chemical interactions among solid, gaseous, and aqueous phases under flow conditions. The mathematical basis of AREST-CT is a set of coupled, nonlinear, partial differential equations that describes the time change rate of the solute concentrations of pore water in a porous medium, and the alteration of solid phases. In AREST-CT, the following processes are accounted for:

- Kinetic dissolution of solid phases
- Kinetic precipitation and dissolution of secondary phases
- Aqueous equilibrium speciation
- Gas-aqueous equilibria
- Redox reactions
- Advection
- Diffusion
- Dispersion
- Nucleation thresholds for precipitation of new solids.

Other physical and chemical features in the code are:

- 1-D or 2-D simulation domains

- General interface to take user specified chemistry
- Nonisothermal or isothermal chemistry
- Ionic strength correction according to modified B-dot equation (Wolery 1992b)
- Spatially varying distribution of solid phases
- Effective reaction surface depending on texture of solids.

The primary output of AREST-CT consists of:

- Concentrations of aqueous species as a function of time and space
- Chemistry of aqueous solution exiting the simulation domains
- pH changes
- Radii, surface areas, and volume fractions of solids as a function of time and space
- Dissolution/precipitation rates of solids
- Porosity changes.

The computer code takes a number of input parameter types. One type of input is the set of system parameters relevant to the design and hydrological/geochemical conditions of the repository. The other input is the thermodynamic and kinetic parameters that quantify the chemical reactions.

To avoid confusion, the computer code AREST-CT version 1.2 that is used to implement the model is referred to as *the code*. The integrated product, including the conceptualization of the processes, the assumptions adopted, the input parameters, along with the code, is referred as *the model.*

Two stages of spent fuel-water reaction were evaluated with this coupled reactive-transport approach. The modeling of the first stage focussed on the primary alteration stage of spent fuel and its capacity to affect the bulk fluid composition (referred to as Stage-1 below). Two sets of analyses were done for the evaluation of Stage-1 using two data sets (DS-1 and DS-2). The differences in these two data sets encompass some of the physical parameters and some of the thermochemical and kinetic data utilized in the calculations. These two data sets are developed in the sections below with discussion of the derivation of the parameters and data sources used to produce these two data sets. The differences between the DS-1 and DS-2 data sets are also discussed below in this section.

The Stage-1 analyses provide bases for conceptual scenarios of the time frame for which spent fuel may have a substantial impact on bulk water composition. In addition, comparison of the Stage-1 analyses with experimental observations and natural analogues provides confidence in the model.

The second stage (Stage-2) modeling focussed on the reaction of water with secondary minerals formed during the first stage. Although its main purpose is to evaluate the concentration of neptunium in the solution for differing degrees of incorporation into secondary and tertiary uranium phases, the analyses and results regarding the major water-composition parameters will be presented in this chapter. These Stage-2 analyses use the DS-2 set of thermodynamic/kinetic

data, and the Stage-2 results have been abstracted into the TSPA-VA analyses as constraints on dissolved Np concentrations based on trace incorporation into secondary/tertiary uranium phases.

#### 4.4.3.2.3.1 Stage-1 Analyses

The model for Stage-1 starts from the time of WP failure. These analyses were done for a range of exposed spent fuel (1 percent and 100 percent) to assess the magnitude and duration of changes to the water composition. As stated above, two data sets were used (DS-1 and DS-2). These data sets represent (1) different water flux scenarios through the waste package: all seepage goes through packages (DS-1) versus reduction of seepage by open patch area of the waste package (DS-2) (see Chapter 6, covering EBS transport), and (2) different thermo-chemical/kinetic databases and constraints. The parameters that differ are (1) pore-water velocity; (2) equilibrium constants of uranophane, soddyite, and Na-boltwoodite; (3) rate constants of schoepite and soddyite dissolution; and (4) specific surface area of CSNF. As discussed below, the results show that the basic conclusions regarding the effects on water composition from primary alteration of spent fuel based on Stage-1 analyses using DS-1 do not change for the calculations done using DS-2.

**Input and Assumptions** - *Physical Configuration of the Simulation Domain*—The model represents a waste package of CSNF as a 1-D porous medium column (Figure 4-28). The length of the column is 1.56 m (CRWMS M&O 1995, p. 3-13, Table 3.5-1), the inner diameter of a 21-PWR waste package. Dripping water enters the column at the top and exits it at the bottom. The volume fraction of CSNF is 14 percent, equal to the waste form volume in a waste package divided by the void space of the waste package (Mattie 1998). Cladding and basket materials occupy 21 percent of the space, and they are assumed chemically inactive. Thus, the porosity inside a waste package is 65 percent.

*Pore-water velocity*—In all calculations, water saturation in the waste package is set to be a constant 70 percent, but the pore-water velocity was different for data set DS-1 versus data set DS-2. According to the seepage model results (see Chapter 2), at the average infiltration rate for the long-term average climate (5.544 cm/year-see Chapter 2), the mean seepage rate is 0.2318 $m^3$/year per waste package that sees dripping. Dividing this mean seepage rate by (a) the area of the projected horizontal cross-section of a waste package (6.5 $m^2$—see Chapter 5.1 for waste package dimensions), (b) the water saturation index (0.7), and (c) the average porosity inside the waste package (0.65—see above), gives an average pore-water velocity of 7.8 cm/year. This is the value used for the DS-1 data set. Within the DS-2 data set, an alternate conceptual model for water entering the package was included. The fraction of seepage water allowed to enter the package was set to the average fraction of patch-failure area according to the waste package model results (see Chapter 5). The average fraction of patch-failure area of a waste package is 0.442 (Chapter 5) and multiplying 7.8 cm/year by 0.422 yielded a pore-water velocity of 3.3 cm/year for data set DS-2.

*Incoming water composition, gas fugacity, and temperature*—As predicted by the WAPDEG model under dripping conditions for the TSPA-VA base case, WP failure starts at about 4,000 years after emplacement (Chapter 5). Based on the gas compositions and thermal history, six periods (A through F) were defined for the base case NFGE (Sections 4.4.2 and 4.5.1). Period E covers 4,000 years to 10,000 years and Period F covers 10,000 years to 100,000 years. After

100,000 years the system is back to ambient thermal conditions. Because the waste package failure time for Stage-1 is taken as 4,000 years, the conditions for Periods E and F (Sections 4.4.2, 4.5.1, and 4.5.2.2) were used in these analyses (see Table 4-42 in Section 4.5.2.2). These two periods reflect the cooling of the system, with Period E being at 70°C and Period F being at 30°C.

*Spent fuel available to react and cladding failure*—As predicted by the cladding corrosion model (Chapter 6), not all CSNF in waste packages would be exposed to seeping water because of the protection of zircaloy cladding. The available amount of CSNF is linearly proportional to the fraction of failed claddings. The rest of CSNF is assumed chemically inert, as it will not be exposed to the water. Simulations with different amounts of cladding failure are carried out, with a bounding value of 100 percent used for evaluation of the magnitude of changes to water composition. For the material exposed, the specific surface area of spent fuel was set to 9.5 $cm^2/g$ for DS-1 and 39.6 $cm^2/g$ for DS-2; the latter is the value used in the base case of TSPA-VA (Chapter 6).

*System components, species, and equilibrium reactions*—The chemical system evaluated consists of eight components. They are H, O, $CO_2$, $SiO_2$, Ca, Na, Cl, and U. For the pH conditions of interest, the major species of these components, consisting of 26 aqueous species and 2 gaseous species, were included in the model to represent these components. The pH value for species selection was taken as about 8, the pH value of the dripping water. As shown below, the pH within a waste package does not deviate drastically from 8; therefore, the selected species should be sufficient to represent the system. For the chosen species, 16 aqueous equilibrium reactions and 2 gaseous-aqueous equilibrium reactions were constructed. Reaction construction was done according to the EQ3/6 database (Wolery 1992a, b), with necessary reaction rearrangement to include only those species selected. The included equilibrium reactions are listed in Table 4-27. The equilibrium constants used in the simulation are taken from the EQ3/6 database data0.com.R22a (YMP Configuration Item Identifier: DATA0-V7-COM-R22a). They are fitted with a fourth-order polynomial function of temperature;

$$\log K^{eq} = a_0 + a_1 T + a_2 T^2 + a_3 T^3 + a_4 T^4 \qquad (4\text{-}2)$$

where T represents the temperature in °C. The coefficients of the polynomials used in the analyses are listed in Table 4-27.

*Spent fuel reaction*—Chemically, spent fuel is treated as pure $UO_2$. The reaction of spent fuel dissolution is given in Table 4-28. The equilibrium constant of uraninite ($UO_2$) (EQ3/6 database data0.com.R22a, YMP Configuration Item Identifier: DATA0-V7-COM-R22a) was used to represent spent fuel.

The dissolution of spent fuel is treated as a kinetically controlled process. As a mechanistic geochemical model, AREST-CT assumes kinetic reactions obey the general form of a Transition-State-Theory (TST) rate law (Fisher and Lasaga 1981, pp. 187-190). Therefore, a rate equation that is consistent with the TST rate law is required by the code.

Gray and coworkers studied the dissolution kinetics of CSNF under oxidizing conditions by flow-through experiments (Gray et al. 1992). Our current understanding about the repository is

that oxidizing conditions will prevail inside a WP once it is breached, with the oxygen content very similar to atmospheric (see Sections 4.4.2 and 4.5.1). Thus, Gray's experiment is relevant to the Yucca Mountain Repository. Several dissolution rate equations are given in that article. Furthermore, based on the same data set, another rate equation is derived to account for burn-up and other factors (Stout and Leider 1996; see also Chapter 6 of this document) and it is used for TSPA-VA base case analyses. However, among those rate equations of CSNF dissolution, only Equation (1) of Gray (Gray et al. 1992, pp. 50, Table 3) is consistent to the general form of TST rate law. Therefore, it was implemented in AREST-CT. Gray's Equation (1) is given as

$$\log R = 7.45 + 0.258\log[C] + 0.142\log[H] - 1550/T \tag{4-3}$$

where R represents the dissolution rate of U (mg/[$m^2$-day]), C (mol/kg) stands for the total dissolved carbonate concentration (that is, the sum of the $CO_3^{2-}$ and $HCO_3^-$ concentrations), [H] signifies the concentration of $H^+$ (mol/kg), and T symbolizes the temperature in Kelvin. In AREST-CT, this relation is implemented as the forward dissolution rate in the form of

$$R' = 0.00137 \times e^{\frac{29697}{RT}} a_{\sum CO_3^{2-}}^{0.258} a_{H^+}^{0.142} \tag{4-4}$$

where R' designates the dissolution rate of spent fuel in [mol/$m^2$-sec], R signifies the gas constant, and $a_{\sum CO_3^{2-}}$ and $a_{H^+}$ denote activities of [$HCO_3^-$ + $CO_3^{2-}$] and $H^+$, respectively.

*Secondary Uranyl Minerals*—Several secondary uranyl minerals are identified as the product of CSNF dissolution in ANL's drip-tests (Wronkiewicz et al. 1992, Finn et al. 1994, Finn et al. 1998). Similar uranyl mineral assemblages are observed at the natural analog site of Pena Blanca (Pearcy et al. 1994). The secondary uranyl minerals can be grouped into three categories: (a) uranyl-oxide hydrates, including schoepite, dehydrated schoepite, compreignacite, and becquerelite; (b) uranyl silicate hydrates: that is, soddyite; and (c) uranyl alkaline silicate hydrates, including uranophane, boltwoodite, Na-boltwoodite, and sklodowskite.

Within this set of modeling studies, four of those minerals, schoepite, soddyite, uranophane, and Na-boltwoodite, are included in the model. The first two represent the first two categories and the last two represent the third category. The choice of these minerals was based primarily on their abundance observed in laboratory experiments (Wronkiewicz et al. 1992) and natural analogs (Pearcy et al. 1994, p. 725, Figure 8). Another consideration for including these as secondary minerals is the availability of thermodynamic and kinetic data. The dissolution/precipitation reactions for those minerals are given in Table 4-28, written in the form consistent with those in the EQ3/6 database file (Wolery 1992a, b).

The equilibrium constants of those uranyl minerals ($K^{eq}$) used for DS-1 are from EQ3/6 database data0.com.R22a (YMP Configuration Item Identifier: DATA0-V7-COM-R22a). For the second data set (DS-2), the equilibrium constants for uranophane, soddyite, and Na-boltwoodite were from Nguyen's experimental study (Nguyen et al. 1992, pp. 374, Table 6).

The rate constants for these mineral reactions were derived from the experimental results reported by Casas (Casas et al. 1994, pp. 62-64, for uranophane), Bruno (Bruno et al. 1995, pp. 635, Table 1, for schoepite), and Perez (Perez et al. 1997, pp. 571, Eqn. 9, for soddyite). The rate constants were derived by assuming the forward dissolution rate equals to

$$R = k_0 e^{-\frac{E_a}{RT}} a_{H^+}^{\nu_{H+}} \tag{4-5}$$

where $\nu_{H^+}$ designates the stoichiometric coefficient of $H^+$ in the dissolution reaction for the mineral.

Using the pH conditions of the experiment, the value of $k_0 e^{-\frac{E_a}{RT}}$ can be derived. Because the experiments were carried out at one temperature, and no information was available to derive the activation energy $E_a$, it is assumed to be zero. Two sets of values were derived for schoepite and soddyite (DS-1 and DS-2), where DS-1 values underestimate the rate constants by orders of magnitude. As discussed below, the model results for NFGE are relatively insensitive to these differences for at least 5,000 years of modeled reaction time. The rate constants are listed in Table 4-29.

Two types of rate constants are given in the table. Values of $k_0$ are in unit of mol/m$^2$-sec, whereas $k_1$ values are in m/sec. Values of $k_1$ are derived from $k_0$ by assuming the minerals grains are spherical particles. The rate constant for Na-boltwoodite is estimated based on the uranophane data, since they are similar in crystal structures and chemical compositions. The estimation was done by assuming that the release rate of U from Na-boltwoodite dissolution is half that of uranophane dissolution, as one uranophane molecular contains two U atoms, whereas Na-boltwoodite contains only one U atom.

#### 4.4.3.2.3.2 Stage-2 Analyses

As discussed in Section 4.6.2.2.2 and in Chapter 6, both the laboratory observation and simulation results show that CSNF within a waste package will be totally consumed and converted to secondary uranyl minerals in about 100 to 1,000 years once the waste package fails and the spent fuel is exposed to water. For the time frame of performance assessment analyses, 100 to 1,000 years is a short period. In other words, CSNF will be quickly converted to secondary uranyl minerals once the WP is breached. Therefore, for the long-term performance of the repository, the period after CSNF is converted to secondary minerals is more important. The Stage-2 analyses were developed to evaluate the dissolution behavior of secondary minerals, the release of Np from them, and their effects on water composition. These process-level analyses were abstracted as constraints on the dissolved concentration of Np for use in TSPA-VA sensitivity analyses. The process-level results and the abstracted constraints focussing on Np are discussed in detail in Chapter 6, and the sensitivity analysis is given in Chapter 11. Only the water composition changes in terms of the bulk major-element chemistry are discussed below in Section 4.6.2.2.2.

**Input and Assumptions** - For Stage-2 analyses, only the DS-2 values were used. In the following discussion, only the differences between that data set and the DS-1 data set values are discussed. All other input parameters discussed above apply to the DS-2 data set, unless specifically indicated otherwise.

*Physical configuration of the simulation domain*—The basic configuration is the same as in Stage-1 analyses. However, the starting time reflects the point when spent fuel has been totally converted to secondary phases. Based on the results of the Stage-1 simulations (Section 4.6.2.2.2), schoepite is the major secondary uranyl mineral. It is taken as the surrogate of all secondary minerals and uniformly distributed throughout the WP. Furthermore, it was assumed that all the available CSNF has been converted to schoepite. That is, the amount of schoepite in the WP was set equal to the amount of initially available CSNF times the expansion factor of molar volumes from $UO_2$ to schoepite (2.684). Consequently, the porosity of the WP = $1-V_{schoepite} - V_{unavailable\ CSNF} - 0.21$, where 0.21 is the volume fraction of inert components, including cladding and basket materials. Two scenarios (referred to as Scenario-1 and Scenario-2 in the following), with 4.13 percent and 0.38 percent schoepite, are considered in these Stage-2 analyses. They correspond to 11 percent and 1 percent cladding failure cases (Cases E and F discussed in Section 4.4.3.2.3), respectively. The radius of a model schoepite grain was assumed to be 1 mm, with a specific surface area of 6.15 $cm^2/g$.

*System components, species, and equilibrium reactions*—In Stage-2 analyses, one more component, Np, was added. The Np component was represented with 12 aqueous species, including Np(IV), Np(V), and Np(VI) species. In the Stage-2 analyses, the total number of aqueous species is 38 plus 2 gaseous species. There are 25 complexation reactions, including 11 aqueous Np equilibrium reactions, 2 redox reactions, and 2 gaseous-aqueous equilibrium reactions (see Table 4-30).

*Np incorporation into uranyl minerals*—Based on an analyses of the crystal-chemical properties of U-O bond, Np-O bond, and Pu-O bond, Burns and his colleagues (Burns et al. 1997) predict that "the substitutions $Pu^{6+} \leftrightarrow U^{6+}$ and $(Np^{5+}, Pu^{5+}) \leftrightarrow U^{6+}$ are likely to occur in most $U^{6+}$ structures" (Burns, et al. 1997, pp.8, 5th Paragraph). Later, Buck and his colleagues at ANL (Buck et al. 1998) confirmed the prediction by TEM (transmission electron microscope) analyses of the corrosion product of spent fuel drip-tests. In their study, Np was found incorporated into dehydrated schoepite (Buck et al. 1998, pp.91). Therefore, it is reasonable to assume that Np will not be totally released into the aqueous phase during the period of CSNF corrosion, rather some of the Np will be segregated into the secondary schoepite[4]. The inventory of $^{237}Np$ was

[4] In the TSPA-VA base-case analyses, the Np source-term is based on the congruent release of Np given by the forward dissolution rate of the spent fuel combined with constraints on dissolved Np concentrations representing potential solubility limits of pure-Np phases (Chapter 6, Chapter 11). The incorporation of Np in trace quantities into secondary uranium phases, which form as the spent fuel alters, represents a different type of phase constraint on aqueous Np concentrations. Once the spent fuel is completely altered, the dissolution/alteration of the secondary uranium phases may control the concentration of Np in the solution. To provide abstracted values for the constraints on Np concentrations based on secondary uranium phase dissolution/alteration, process-level calculations of the reaction of water entering the package with the secondary phase schoepite were performed (the Stage 2 analyses). The abstracted constraints from these process-level model results were substituted into the TSPA-VA sensitivity analyses for the pure-Np-phase solubility constraints on dissolved Np concentrations. To assess the maximum possible aqueous Np concentrations set by these secondary uranium phases (i.e., conservative values), the entire inventory of Np was used to set the composition of Np in the schoepite used in the process-level calculations. This gives the maximum concentration of Np in the schoepite (assuming it is uniformly distributed throughout the secondary-phase mass) as a

adjusted to include both $^{241}Pu$ and $^{241}Am$, because they quickly decay to $^{237}Np$. ATM-103 fuel with a burn-up of 30 MWd/kg, and 10 years old was used as the reference fuel. The inventory for $^{237}Np$, $^{241}Pu$, $^{241}Am$ of this fuel is listed in Table 4-31. According to the inventory, the molar ratio of U:$^{237}Np$ is 1:0.0016. Therefore, for these analyses one mole of schoepite contains 0.0016 mole of Np. The dissolution reaction for schoepite is approximately written as

$$\text{Schoepite} + 2H^+ \Rightarrow UO_2^{2+} + 0.0016NpO_2^+ + 3H_2O. \quad (4\text{-}6)$$

*Combinations of conditions and scenarios*—Both Period E and Period F conditions were considered in Stage-2 analyses, and are referred to below as Condition-1 and Condition-2. There are four possible combinations for these conditions and the cladding failure scenarios described above. These four combinations, referred to as Case-1 through Case-4, are listed in Table 4-32 and represent the four simulations that were carried out. The results of these four simulations are presented and discussed in Section 4.6.2.2.2.

#### 4.4.3.2.4 Precipitates/Salts

This submodel was used to evaluate a set of bounding analyses of the mass and timing of precipitated minerals build up on the waste package surface and the capacity for generation of highly concentrated brines during the boiling period. These analyses were not used directly within the TSPA-VA calculations, but their results were used to assess the need for future work in this area (see Section 4.6.2.2.3).

##### 4.4.3.2.4.1 Modeling Approach

Predicting the geochemical evolution of refluxed water and its precipitates cannot be done with a high degree of certainty primarily because of a lack of thermodynamic data. Nevertheless, simulations are necessary because the evolution of water chemistry and mineral precipitates under the abstracted conditions has not been adequately studied in the laboratory. The first part of these analyses has been implemented using the EQ3/6 version 7.2b code package (Wolery 1992a, 1992b; Wolery and Daveler 1992). (The calculations also used the supporting data0.com.R2 thermochemical datafile generated by GEMBOCHS.V2-JEWEL.SRC.R3 02-aug-1995 16:45:06 thermochemical database.) This code package for geochemical calculations is one of the most advanced geochemical tools available. However, the complexity of the system extends beyond the capabilities of the thermodynamic data base for simulating the interactions of silica and carbonate at high pH (greater than 10), high ionic strength (greater than 1 m), and high temperature (greater than 25°C). The only alternative is to make simplifying assumptions based on mineral solubilities reported in the literature and proceed with semi-quantitative stoichiometric calculations. As a result, the effects on pH, the concentrations of chloride and other dissolved solids, and other potential precipitates has to be semi-quantitatively estimated.

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starting point for the process-level reactive-transport calculations. Further details of these analyses focusing on the Np aspects and the abstracted Np concentration constraints are given in Chapter 6. The abstracted results of these process-level analyses only replace the solubility-limited Np concentrations and do not change the forward-dissolution rate of the TSPA-VA analyses. As such, in the source-term of the TSPA-VA sensitivity study, Np is calculated to release continuously and there is no assumption of complete Np retention in the secondary phases, only a different potential concentration limit applied.

Another issue that is currently being addressed is whether certain minerals are allowed to precipitate if equilibrium calculations indicate that their formation is favorable. Some mineral phases may need to be suppressed (i.e., not allowed to precipitate despite calculated oversaturation) because of slow kinetics or other reasons. Which minerals to suppress is uncertain and difficult to answer. For these analyses, several minerals are suppressed based on available data, and solid solutions are not permitted to form. These constraints permit higher concentrations of dissolved solids in aqueous solutions and therefore are considered conservative assumptions.

#### 4.4.3.2.4.2 Early Evaporative Precipitation

In the current model, early evaporative precipitation refers to the precipitation that results as the reflux water becomes concentrated by evaporation to an ionic strength of 1 molal. This precipitation can be calculated using EQ6 using the com data base and the B dot equation for activity coefficients. The EQ6 input files contain the data and constraints developed in Section 4.5 and listed in Table 4-42.

The EQ6 calculations were set up such that solid solutions were ignored and supersaturation of several minerals was allowed. Ignoring solid solutions tends to decrease the amount of precipitation and increase the concentrations of ions in solution. Higher ion concentrations tend to increase the corrosivity of the fluid. In addition, potential precipitation of the following twelve minerals was suppressed: quartz, K-feldspar, stilbite, mesolite, pyearophyllite, scolecite, muscovite, dolomite, tridymite, clinoptilolite-Ca, albite, and maximum microcline. These same minerals have been suppressed in similar Yucca Mountain geochemical modeling studies (Delany 1985, pp. 23, 28; Murphy and Pabalan 1994, p. 4-38, Section 4.5.1.2). The primary reasons for these suppressions are slow precipitation kinetics and/or high uncertainty in thermodynamic data. Mineral suppressions will tend to allow the water to have higher concentrations of dissolved solids and therefore higher potential for corrosion of waste package materials. In the calculations, however, only five of these minerals became supersaturated: quartz, tridymite, K-feldspar, maximum microcline, and mesolite. While the latter three minerals became supersaturated in each of the boiling Periods A, B, and C, quartz supersaturation occurred only in Periods A and C and tridymite supersaturation occurred only in Period A.

#### 4.4.3.2.4.3 Late Evaporative Precipitation

As explained earlier, evaporation and boiling of reflux water beyond an ionic strength of 1 molal cannot be accurately modeled using the available geochemical codes and databases due to a lack of a usable Pitzer data base for Si and C at high temperature and high pH. Instead, the approach used for calculating the precipitation from these brines was to construct simple sets of normative binary salts to represent the precipitation of the remaining dissolved solids. The salts were primarily chosen based on mass balance and charge balance constraints; however, solubilities also played a role. Without a geochemical code to simulate interactions of all components in these high-temperature high-pH brines, it is difficult to determine relative solubilities in many cases. Sources of solubility data, such as the Handbook of Chemistry and Physics (Weast 1981), provide mineral solubilities in simple aqueous systems, but they do not provide mineral solubilities for the specific high-pH brines considered here. Nevertheless, this type of solubility

data was used in the selection of the salts that comprise the normative sets. The solubilities of various binary combinations of the Na and K salts at 100°C are presented in Table 4-33. Another simplification of this model is that the salts that precipitated in previous time periods were not allowed to be rereacted during the boiling period except in the case of $Na_2CO_3$ in period B to form $CaCO_3$. This analysis, although only semi-quantitative thermodynamically, provides a simple first look at the evolution and fate of salts on the waste package.

#### 4.4.3.2.4.4 Salt Dissolution and Brine Formation

The aqueous solutions will not boil and salts will not precipitate throughout the time that the temperature is above boiling for pure water. The reason is that the stability of a solid salt depends on the RH, and concentrated brines have water activities much below unity (Kinsman 1976). Because of this, salts will condense water out of the steam in the system at temperatures higher than the standard boiling temperature and at relative humidities below the standard RH for salt-free systems. These salts are hygroscopic, (i.e., they will absorb water vapor if the RH is high enough). RH effects on salt stability can be modeled using EQ6 only with the appropriate relations and datasets for concentrated brine systems. Even for these cases, the compositional space and thermal conditions that can be investigated are limited (Wolery 1992a, 1992b). Table 4-34 lists the maximum relative humidities at which many of the salts are stable and will not dissolve. Sustained relative humidities exceeding these maximum values will cause the salts to dissolve into a brine (Kinsman 1976).

Because the salt will eventually end up on the waste package, it is the waste package surface environment that will set the timing of condensation of water by these salts and subsequent brine formation. The RH and temperature at the average waste package over time has been predicted by the drift scale results of the multiscale thermal-hydrologic model. The RH values are plotted along with temperature in Figure 4-29.

### 4.4.3.3 In-Drift Colloids

The model implementation for in-drift colloids calculated colloid concentrations as a function of ionic strength based on a statistical fit of measured colloid concentrations. This statistical fit (see below) of measured colloid concentrations was calculated for particles greater than 100 nm in groundwaters of various ionic strengths from around the world (Degueldre et al. 1996a, 1996b; CRWMS M&O 1998a, Section 6.3.6). The data on colloid abundances covered groundwaters from the deep crystalline systems from the Central European Basement rocks in Germany, Northern Switzerland, and Alpine Switzerland; old granitic cratons such as in the Canadian and Scandanavian Shields; Yucca Mountain SZ tuffs; the laterized carbonatites of Morro De Ferro, Brazil; the marl formation of the Wellenberg system in Switzerland; the bedded sediments at Gorleben, Germany; glacial sands in the United Kingdom; the sandstone of the Athabasca Basin in northern Saskatchewan, Canada; and the metamorphosed sediments in Gabon, Africa (CRWMS M&O 1998a, Section 6.3.6.1). The water compositions from these areas are varied, ranging from oxic to anoxic; Ca-carbonate dominated to Na-sulfate-chloride or K-sulfate dominated; pH of 6 to 10 (CRWMS M&O 1998a, Section 6.3.6.1). The salt concentrations of the fluids cover 4 orders of magnitude, with total organic carbon contents covering the $10^{-5}$ to $10^{-2}$ range (CRWMS M&O 1998a, Section 6.3.6.1).

Although colloids smaller than 100 nm exist, the available data to constrain the colloid abundance relation are most accurate for the greater than 100 nm colloids because size distributions for colloids are more uncertain below sizes of 100 nm (Degueldre et al. 1996, Figure 7) and comparison of data from many different sites is most commonly possible for particle sizes greater that 100 nm (CRWMS M&O 1998a, Section 6.3.6.1). The colloid abundance relation and its associated uncertainty were implemented directly as part of the waste form/EBS source-term cells. In their paper on colloid stability and transport, Degueldre et al. (1996b) indicate that colloids of average particle size near 100 nm would probably be the most mobile candidates because they are more stable relative to larger colloids, which tend to settle out, and they are more mobile than smaller colloids, which tend to attach to rock surfaces faster.

Data from the Nevada Test Site provide some assessment on the relative abundance of colloids as a function of their sizes spanning the 100 nm diameter used here as an average. The data from well ER-20 of the Nevada Test Site was sampled and the water measured for Pu associated with colloids from the Benham nuclear event (Thompson 1998). The filtration experiments that were done indicate that some of the colloidal materials were smaller than 100 nm diameter (Thompson 1998, p. 15 and Appendix A part 4). The first series of filtration tests indicated that about 70 to 87 percent were larger than 500 nm and about 10-20 percent was larger than 6nm and smaller than 50 nm (Thompson 1998 p. 15). The second series of filtration tests indicated that about 20 percent were larger than 1000 nm, about 40 percent were between 1000 nm and 50 nm, and about 40 percent were between 50 nm and 6 nm (Thompson 1998, p. 15 and Appendix A part 4). Because the first filtration study showed very little colloidal material was between 50 nm and 500 nm in diameter, the fraction of colloids between 1000 nm and 50 nm found in the second series is probably mostly greater than 100 nm too. In addition, the data presented by Degueldre et al. (1996a, Figures 4 and 7) indicate that, although uncertain, the number of particles below 100 nm represents only a factor of 2 to 4 more than those greater than 100 nm. The relation developed here may therefore not include an amount of colloids that corresponds to at least about 10–40 percent of the total colloid loading in the water.

#### 4.4.3.3.1 Constraints on Colloid Stability

In order to constrain colloid stability relations as a function of fluid composition, data for colloid abundances in groundwaters from around the world (CRWMS M&O 1998a, Section 6.3.6.1) were used to derive the functional dependence of colloid concentration on the ionic strength of the fluid. The data are shown in Table 4-35 where the ionic strength was calculated as 4[Ca+Mg]+[Na+K]. This value provides a good approximation of the stoichiometric ionic strength of these fluid compositions. The resulting data were used to linearly regress the log colloid concentrations as a function of the ionic strength.

The uncertainty in the ionic strength was set at 10 percent based on the analytical uncertainties of the data (CRWMS M&O 1998a, Section 6.3.6.1) and the log[coll] values were also assigned an uncertainty of 10 percent. These values were used for the curve fitting that was done. Figure 4-30 a shows a linear fit of log[coll] as a function of the ionic strength, as given above, to all of the available data. This relation is given by

$$\log[coll] = 6.6 - 31I \tag{4-7}$$

where [*coll*] is the concentration of colloid particles > 100 nm in particles/ml and $I$ is the ionic strength of the solution. The standard deviation of the log colloid concentration assessed within this regression is given by

$$\sigma_{\log[coll]} = (0.04 + 144I^2 - 1.2I)^{1/2} \tag{4-8}$$

Because of the possibility that some amount of colloid particles smaller than 100 nm was being ignored, it was decided to repeat this same regression analysis without five of the lowest measured values from Table 4-35. This second fit will result in a more conservative (i.e., larger) estimate of colloid abundance for any given ionic strength. Figure 4-31 presents this second fit to the data without consideration of five of the values with low colloid concentrations. In this case, the regressed relation is given by

$$\log[coll] = 7.0 - 34I \tag{4-9}$$

and

$$\sigma_{\log[coll]} = (0.023 + 65.6I^2 - 0.57I)^{1/2} \tag{4-10}$$

where log[coll] represents the log of the colloid concentration in particles/ml, and I denotes the ionic strength.

For implementation into the TSPA-VA analysis code RIP (Golder 1998, Chapter 11), the relation shown in Equation (4-10) was transformed into a stochastic function for colloid mass concentration (kg/m$^3$). The conversion to this relation was accomplished by assuming spherical particles of radius 100 nm and a density of 2 gm/ml, resulting in the following relation:

$$\text{colloid concentration (kg/m}^3) = 8.4\text{x}10^{-12} * 10^{(S*\text{sigma}+7-34*I)} \tag{4-11}$$

where sigma = $(.023+65.5I^2-.057I)^{0.5}$ representing the uncertainty in the result, I stands for the ionic strength, and S signifies the sampling parameter used by RIP to produce a stochastic variation in the result. Within RIP, the parameter S is sampled from -3 to +3 uniformly in order to encompass 99 percent of the uncertainty in the relation. Using these same assumptions and the value of log [coll] for J-13 water in Table 4-35, the colloid mass concentration calculated for that measurement is about $3.3\times10^{-5}$ kg/m$^3$.

As was discussed above, 100 nm diameter particles are representative of the colloids of most concern, but because the colloids are distributed across a size range and larger particles are more massive than smaller particles, a 100 nm radius was chosen to coarsely capture some of the mass of larger particles and because the size distribution of Degueldre (1996, Figure 7) exhibits a peak at about 200 nm diameter. It is pointed out by Degueldre et al. (1996a) that because many colloids are actually plates, the spherical particle assumption probably overestimates the colloid mass. This again helps offset any mass of small particles that may exist and was not included explicitly in this assessment, and provides more slack for the larger particle sizes that may exist. The density of 2 gm/ml assumed for the mass conversion is based on the observations of colloids in Yucca Mountain groundwaters (Triay et al. 1996), those observed at the Nevada Test Site

(Thompson 1998), and in groundwaters from around the world (Degueldre 1996a, 1996b), all being dominated by either clay colloids, silica, or other silicates, with only minor amounts of iron oxide colloids occurring. Degueldre (1996a) indicates that a value of 2.0 gm/ml is a good approximation of the average density of colloids collected from many different environments.

For each of the abstracted time periods, the ionic strengths of fluids calculated from the model for the in-drift water-solids chemistry (Sections 4.5.2.2.1 and 4.6.2.2.1) were used with this relationship to assess the stability and concentration of the suspended colloids reacting with the waste form. Other than this connection, the in-drift colloid model is relatively independent of the other NFGE models (Figure 4-15). The amounts of iron-oxyhydroxide and clay colloids were assessed by this method directly within the system integration program RIP(see Chapter 11). A number of examples of colloid concentrations calculated using the relation above are given in Section 4.5.2.3. However, the colloid concentrations calculated internal to RIP (see Chapter 11) are used as input to the colloid sorption and transport model for plutonium, which is discussed within Chapter 6.

### 4.4.3.4 In-Drift Microbial Communities Growth

Armed with the need to address the concerns listed in Section 4.2. as they apply to total system performance, a conceptual model [Microbial Communities Model (MCM; CRWMS M&O 1997a)] and an associated computer code [Microbial Impacts to the Near-Field Geochemistry (MING; Ehrhorn and Jolley 1998; CSCI 30018 V1.0, DI 30018-2004)] were constructed to quantify bounding assessments of microbial growth to use as a basis for discussing their potential impacts on the near-field environment geochemistry. The initial plan for the both the MCM and the MING software was derived from the NFGE TSPA-VA abstraction-testing workshop (CRWMS M&O 1997a).

The model implementation for in-drift microbial communities was intended to be a bounding assessment on the masses of produced microbes and uses an idealized approach to assess the biomass production. At each time step, the MING analysis determines whether biomass production is limited based on either energy limitations in the system or nutrient supply limitations for microbes. The microbial production for that time step is taken to be the lower of the two values. The production rate and the cumulative biomass can then be tracked for the time of the analysis to determine the biomass yield and changing system limitations. These analyses were not used directly within the TSPA-VA calculations, but the results were used to assess the need for potential future work in this area (see Section 4.6.2.3).

#### 4.4.3.4.1 MING Code Development

MING (Ehrhorn and Jolley 1998; CSCI 30018 V1.0, DI 30018-2004) is used in this report to evaluate potential impacts that the committed repository would have on microbial populations and their associated impacts to radionuclide release and facilitated transport. The MING code takes into account the availability of nutrients in a given repository/drift environment, the energy necessary to convert those nutrients to microbes, the level of oxygen in the repository, as well as the temperature and moisture content of the repository atmosphere. Materials identified in the proposed repository design are decomposed into their basic elements over time and their contributions to the nutrient cycle of the microbes are included with the nutrients available in the

groundwater passing through the repository. This code and the associated conceptual model for microbial activity (see Section 4.2.5.2.4) does not attempt to quantify the effects of individual microbial colonies or biofilms that may be present on repository materials, but attempts to quantify the overall global bulk effect of microbes on the NFGE.

#### 4.4.3.4.1.1 Code Development Concepts

The purpose for developing MING is to provide a tool to implement the conceptual model (see Section 4.2.5.2.4) that can assess the microbial growth in a potential drift and the potential for microbial effects to bulk water compositions. MING can also provide a basis for discussing the other potential NFGE chemistry effects for the needs of performance assessment, given that microbial activity will occur in the proposed repository. The magnitude of such activity needs to be quantitatively analyzed. Three basic approaches are possible and have been previously documented in McKinley and Grogan (1991). They are as follows:

1. Mass balance approach—the biomass will inherently be limited by the inventory and/or supply rate of some essential element (e.g., C, N, P, and S) which may represent a very significant constraint. If the biomass is very low, it may be possible to justify neglecting microbial processes in comparison with competing purely inorganic reactions.

2. Thermodynamic approach—in addition to nutrients, constraints set by the available energy sources can be evaluated.

3. Kinetic approach—the evolution of a population of organisms in a particular evolving chemical system is explicitly modeled using either empirical or mechanistically derived kinetic data.

The kinetic approach is mathematically possible and in fact, other near field geochemical model computer codes (EQ3/6, AREST-CT), currently used in Performance Assessment analyses, could potentially be modified and used to simulate the kinetic approach. However, it is not possible to obtain the required information about all the relevant microbial processes at the resolution that is required to interface directly with these codes at this point in time. Thus, we chose to use the more simplistic approaches, similar to those used by the Canadian High-Level Waste Repository program (Stroes-Gascoyne 1989), and the Swiss Low/Intermediate-Level Waste Repository program (West et al. 1989; Capon and Grogan 1991; McKinely and Grogan 1991; and McKinley et al. 1997) which use both mass balance and thermodynamics to quantify the impacts of microbial populations. Subsequently, these two approaches are used as the basis for the development of MING. In the first aspect of this, abiotic processes are used to determine the rate at which nutrients become available to microorganisms, which is used as the rate that the microorganisms convert those nutrients to the products (i.e., instantaneously in this mass balance approach). The second uses limiting guidelines of energy availability and the availability of all the required nutrients in the proper ratio to get the rate at which this occurs (thermodynamics approach).

Scenarios (repository and waste package designs) can be examined by assessing various cases in which all of the available nutrients (derived from waste package materials, ground support

materials, gas flux, water flux, etc.) are converted into the appropriate products. All of the possible combinations of these parameter values will be used as input into MING in order to conduct a sensitivity analysis of the various repository designs, temperatures, relative humidities, gas fluxes, and water chemistries, etc. that are derived from other TSPA and process level modeling efforts. The objective is to be as transparent as possible considering the multiple time dependent inputs. However, obtaining degradation rates of all the introduced materials in the near field (concrete, steel, polymers, etc.) is not a realistic goal at this time.

#### 4.4.3.4.1.2 Software Development

The starting point for the MING software model development was taken from the software routine titled Estimation of Maximum Microbiological Activity also known as EMMA (Capon and Grogan 1991) and is based on the documented approach to modeling the Swiss Low/Intermediate Level Waste Repository found in Grogan and McKinley (1990) and McKinley and Grogan (1991). MING contains the same basic modeling approach and structure of calculating the nutrient and energy limitations described in Grogan and McKinley (1990) and McKinley and Grogan (1991).

Early on, it was determined that EMMA would not be able to serve as the vehicle to do the calculations without some major modifications. Many of the concepts to which modifications to EMMA were derived are documented in the NFGE Abstraction/testing workshop results (CRWMS M&O 1997a). However, as programming has developed, other requirements have been added and the original concept has been refined.

Essentially, there are two main components that were brought forward into MING from the Swiss modeling approach: (a) the numerical solution for solving the amount of energy available for microbial growth; and (b) the general method for calculating nutrient availability. However, smaller pieces of the approach were also maintained and used in MING including the average empirical microbial formula ($C_{160}(H_{280}O_{80})N_{30}P_2S$) with a dry weight 3994 g $mol^{-1}$ (McKinley et al. 1997). This formula represents the ratio of elements needed to form a microbe (e.g., 160 carbon atoms for every sulfur atom]. In addition, the implementation in MING also uses an average microbial water content of 99 percent and an average microbial volume of $1.5 \times 10^{-19}$ $m^3$ (McKinley et al. 1997). Multiplying this latter value by the density of water (1 $g/cm^3$-Weast 1981) produces an average microbe mass of $1.5\times10^{-13}$ g (Jolley 1998b).

Like the EMMA code, MING utilizes the same basic approach to thermodynamic modeling. Therefore, the evaluation of available energy for the chemolithotrophic organisms, which are the primary types of organisms that will inhabit the Yucca Mountain repository environment, is based on the assumption that all useable energy is derived from redox processes. Microbes use redox couples in order to supply the energy required to carry out their basic metabolic functions (i.e., aerobic respiration, nitrification and denitrification, methane oxidation, etc.). Because microbes tend to utilize specific, well-documented metabolic pathways (Amy and Haldeman 1997; Banfield and Nealson 1997; Pederson and Karlsson 1995), a list of appropriate redox half reactions was derived (see inputs below) based on the available nutrients in the system that will maximize energy production. The same assumptions were used by EMMA on the limits of usable energy available from a given full redox reaction such as where 15 kJ per mole of

electrons transferred is the lower limit of energy needed to create biomass and the need for 64 kJ to maintain 1 g of biomass (Grogan and McKinley 1991, Appendix 3, p. AIII-1).

The EMMA model is based on a simplified thermodynamic system where the pH is fixed at 12; the temperature in the repository is set to 25° C; and the Gibbs free energies ($\Delta G$) used to calculate the available energy for microbial production were fixed at STP values. For example, any redox reaction can be written in the general form

$$A + ae^- + bH^+ = B + cH_2O \tag{4-12}$$

for which a standard free energy of reaction ($\Delta G_r°$) can be specified. The $\Delta G_r°$ can be derived from standard free energies of formation ($\Delta G_f°$):

$$\Delta G_r^\circ = \sum \Delta G_f^\circ \text{(products)} - \sum \Delta G_f^\circ \text{(reactants)} \tag{4-13}$$

or from an equilibrium constant (K):

$$\Delta G_r^\circ = -RT \ln K \tag{4-14}$$

where R stands for the gas constant and T represents the absolute temperature. The calculations are made by combining independent half reactions and calculating the overall $\Delta G_r°$ for the reaction.

EMMA's simplified model is certainly not realistic in the sense that the repository environment will undergo temperature changes due to the hot waste packages. For MING, in order to account for a chemically variable system, the time dependent temperatures, gas fluxes, and water chemistries need to be accounted for over the time frame of the calculations. With the incorporation of these variables, the calculations should end up being as transparent as possible with other calculations currently being derived from other TSPA-VA abstractions

**Site-Specific Additions to the Software** - Some of the major enhancements to the original EMMA code are as follows:

- The addition of temperature dependencies on the $\Delta G$ calculations
- The stipulation that nutrient dependencies are calculated from the time dependent gas flux into the repository drift (to address autotropic and aerobic behavior) as well as the presence of other repository materials
- The addition of time dependent water chemistries entering the drift
- The addition of pH dependence on the governing redox equations (EMMA used a single fixed pH value of 12 for all calculations)

- The ability to degrade one repository material before another becomes available (such is the case with a layered waste package design where the CAM degrades well before the CRM)

- The addition of physical limitations to microbial growth as a result of temperature and RH.

*Corrections to $\Delta G_r^\circ$ for pH and Temperature*—It is important to note that within MING, only the standard-state free energies are used and these are not corrected for either Eh or the activity of dissolved species to derive the actual nonstandard-state free energies. By not calculating the nonstandard-state free energies, the calculation of available energy is not precise, but only represents a rough estimate of this value. Because the half-reactions are written as simple reduction reactions, the free energy of a full reaction constraint applies slightly more generally than purely standard-state conditions. It is actually constrained such that the ion activity ratios of the redox pairs are at isoactivities, which could be possible for ion activities different than unity (the standard-state conditions). For each full reaction, correcting for the actual pH brings the free energies of reaction further from the standard state values. However, using this simplified model should allow increased understanding of the complexity of the microbiological system and provide a mechanism to understand the bulk system at an approximate (order-of-magnitude) level.

In order to gain the detail needed to correct $\Delta G_r^\circ$ for the activity of dissolved species in the fluids, a much greater effort must be made than is possible at this time. Only the first step in this process has currently been completed, which is to correct for the actual pH of the system. To truly incorporate the system water chemistry effects, the effort would require iterative solution of changes to the activities of dissolved species for microbial processes.

Because the temperature of the repository will not be fixed over time, a method to incorporate temperature effect on reaction free energies was derived in order to build into the MING results the transparency required to incorporate the temperature histories provided from other TSPA-VA modeling efforts, which are documented in Chapter 3.

Regression analyses were performed on $\Delta G_r^\circ$ values at various temperatures (0°, 25°, 50°, 60°, 75°, 100°, 125°, and 150°) for a selected group of half reactions to define temperature dependent curves that could be incorporated into the energy calculations. The regression analyses are documented in Jolley (1998a) with the results shown on Table 4-36. The derived regression variables are used to calculate the temperature dependent $\Delta G_r^\circ$ that is used in the derivation of the available energy for a given reaction. The temperature dependent regression variables are used in MING in the following way:

$$\Delta G_{r\,(\mathrm{temp})}^\circ = B_0 + B_1 T + B_2 T^2 \qquad (4\text{-}15)$$

where $B_0$, $B_1$ and $B_2$ are the second order regression coefficients. Thus, both the effects of variable pH and temperature are accounted for in the calculations.

*Nutrient Supply*—As documented in the microbial modeling approach for the Swiss Low/Intermediate-Level Repository (Grogan and McKinley 1990), MING only considers the major elements essential for cell growth (C, N, S, and P). Other nutrients will be considered freely available (i.e., Na, K, Ca, and Cl) except for water.

The mass balance calculations conducted in MING consider three sources of nutrient supply: first, the time dependent flux of groundwater into the repository; second, the degradation of repository materials including the multilayered effects of waste packages (see Section 4.3 for a description of materials considered), and third, the time-dependent flux of gasses ($CO_2$, $N_2$, $O_2$, and perhaps $CH_4$) into the repository. The nutrient limits will be calculated by determining the appropriate ratio (relative molar concentration) of material (determined by available nutrient flux) needed to create the typical organism having a stoichiometry of $C_{160}(H_{280}O_{80})N_{30}P_2S$.

*Temperature and RH Effects on Microbial Growth*—The availability of water for microbial growth in the UZ at Yucca Mountain will be dependent on the thermohydrological conditions within the repository. In order to account for periods where there is not enough moisture to allow microbial growth ($a_w$ <0.95, see Section 4.2.1.3.3) the following relationship between RH and $a_w$, is assumed and used to allow for the unsaturated conditions in the repository.

$$a_w = \frac{RH}{100} \tag{4-16}$$

This approach assumes that the porous medium of the near field is in equilibrium with the atmosphere where the RH is measured.

Temperature will also affect the ability of a microbe to reproduce. The temperature dependency of microbial activity is set by the temperature within the repository environment where microbes are not allowed to reproduce and grow above temperatures of 120°C.

**Other Code Features** - MING is designed to consider all of the committed (not intended to be removed before permanent closure) materials that are included in the current repository and waste package designs, as well as the potential to evaluate any alternate design options that are relevant to microbial behavior. Section 4.3 above lists the various design materials, quantities, and compositions that are to be emplaced in the repository and are evaluated herein. For example, in MING, a committed material (e.g., steel sets, concrete liner, etc.) is broken down into its individual chemical composition and allowed to enter the nutrients available in a time step based on a fractional corrosion rate (1/estimated material lifetime) for that given material.

In calculating nutrient availability, MING also will allow a sequential introduction of committed materials. This means that a sequential layered model of the waste package can be defined, where the CRM and other internal waste package materials are not allowed to mutually degrade and be released into the nutrient stream until the CAM is completely used up.

Another tool that MING can utilize is a "special reactant" flag where the intermediate breakdown products (other than the basic chemical composition) can be identified. Potential items that fall into this area are substances such as organic admixtures, which are common components of cement mixtures and tend to be resistant to biodegradation. These items can then have their

releasable compositional quantities split among the several associated species that are included in the redox model.

MING is also designed to incorporate variable gas flux calculations and incoming water chemistries as documented in this chapter (see Section s 4.2.5.1.1 and 4.2.5.1.2) and provide these inputs to both the nutrient and energy calculations.

#### 4.4.3.4.2 MING Parameter Inputs

The use and format of the MING input needs are documented with in the MING code and associated users manual (Ehrhorn and Jolley 1998; CSCI 30018 V1.0, and DI 30018-2004) Any case specific inputs will be documented in Section 4.6.2.3 for each modeling case presented. However, four general types of inputs are needed for a MING model run. They are as follows:

**Environment inputs**—These include time-dependent temperature and RH values, time-dependent water chemistries (includes pH and infiltration rates) and time-dependent gas fluxes (includes $CO_2$, $O_2$, and $N_2$). These results are provided from other TSPA-VA modeling efforts (TH calculations, NFGE incoming water, NFGE incoming gas)

**Design materials**—These inputs include the proper formatting and documenting of quantities and elemental compositions of all the repository and waste package design materials that may be placed into the repository (discussed in Section 4.3). This also includes designation of expected material lifetimes and the designation of breakdown codes and specifying of material reactants necessary for utilization of the redox half reactions that are used to calculate the model energetics.

**Internal Inputs**—The most important of these is the redox reaction table and the associated temperature-dependent coefficients for each selected half reaction (see Table 4-36).

**User-elicited inputs**—These include the following single-value items that are required to implement the conceptual model: temperature cutoff, humidity cutoff, tunnel diameter, tunnel length, porosity, and the energy cutoff.

Inputs that are universal or nearly universal to most of the modeling reported in Section 4.6 and that are important for evaluating the modeled results are documented below.

Table 4-37 includes the user-elicited inputs that are required to make the modeling runs. Table 4-36 represents the redox half reactions and associated temperature dependant coefficients as described above that have been selected to represent generalized microbial catalysis reactions. They include selected half reactions that cover the following known microbial metabolic pathways: aerobic respiration, nitrification and denitrification, methane oxidation, manganese and iron oxidation, sulfur oxidation, manganese and iron reduction, sulfate reduction, and methanogenesis. The thermodynamic data used to derive this table are found in the GEMBOCHS thermodynamic database (DTN# MO98CST0980300.000) and are documented in Jolley 1998a (B00000000-01717-0200-00170).

Table 4-36 sets the constraints for how each material can be broken down into appropriate chemical species so that the energy calculations can be done. Each repository or waste package material modeled using MING has a given elemental composition, but that elemental composition has to be related to a given redox state and associated with the selected redox equations that represent the microbial metabolic pathways. Table 4-38 represents the associated species, termed reactant compositions, for all of the materials that are documented in Section 4.3 and are used in the calculations documented in Section 4.6.2.3.

#### 4.4.3.4.3 MING Outputs

Output from MING is designed to define only the bulk system redox chemistry of the near-field system given the variable temperature and pH of the system, it does not reflect the actual chemical speciation or reactions that might occur at a more localized scale. The chemical output is designed to capture molar quantities of the production of byproducts (such as $CO_2$, $H_2S$, and $H^+$ ions) over one linear meter of repository drift. Output is also designed to enable the evaluation of the quantities of microbes produced, the limits to microbial growth from both nutrients and energy, and the stipulation of which nutrient is limiting growth in the repository.

Note: MING 1.0 is currently undergoing a final qualification process. Although at this time, we do not feel that there are errors in the code (with the code having passed all its validation tests), all results are classified TBV until the finalization of the SQR (software qualification report, CSCI 30018 V1.0, DI 30018-2003).

### 4.4.4 Major Uncertainties in the NFGE Models

This section provides a general discussion of sources of uncertainties in the NFGE models that are described in specific detail in Sections 4.5.3. Much of the uncertainty for the NFGE stems from conceptual model uncertainties. This is particularly true for models of in-drift materials that use thermochemical data (equilibrium and kinetic parameters). The coupling among geochemical effects and physical processes in real systems cannot be incorporated comprehensively into the current NFGE models. The inability to represent this coupling is another large contributor to conceptual uncertainty in these models; this is particularly the case for the evolution of the gas composition in this system. Thermal-hydrologic processes interact strongly to drive gas flow and generation of certain gas constituents. However, reactions among the gas, water, and minerals occurring simultaneously in this flowing system are only coupled in a limited manner in the NFGE component. Limited representation of coupling is also true for the models of concrete effects that do not explicitly evaluate system flow or address permeability changes of the concrete caused by mechanical evolution or precipitation of alteration phases.

Further conceptual uncertainty is related to the inability to observe processes for geologic time spans, which introduces uncertainty about the appropriate time scale for applying those processes. Observations of analogs provide some insight, particularly into the state that a system has evolved to over geologic time. However, only portions of the system can be observed generally (usually only the solids), and chemical and flow conditions must be inferred to extract quantitative information from the analogs. Applying observations of analogs to another system that may not be governed by the same conditions is another source of conceptual uncertainty.

Part of the conceptual uncertainty for coupled processes stems from limitations of the modeling tools applied to these types of systems. In general, a tradeoff must be made between tools that allow evaluation of a more comprehensive chemical system and those that allow an idealized geochemistry to be coupled to the thermal-hydrology. Uncertainty in the mathematics of the model, or representational uncertainty, is generally relatively small for the geochemical aspects of the NFGE models in comparison to the conceptual uncertainties. However, computer codes that provide a representation more closely coupled to the hydrology of the system, tend to have larger mathematical or numerical uncertainties.

Parameter uncertainty may be large for models using thermochemical data if well constrained measurements are not available or are not available for the conditions needed (e.g., higher temperature). Lack of data for the appropriate species in a system is a type of conceptual uncertainty because the chemical processes involving those species cannot be included in the model.

The general approach to the large amount of conceptual uncertainty in the geochemical system is to separate the major potential contributors to water compositional changes into various subsystem models (e.g., gas phase, concrete, and microbes). These separate models can be used individually to assess the relative capacities of these processes to alter compositions of various chemical phases at various times. Such uncoupled models facilitate identification of the processes that may control the bulk chemistry for various time frames. Then, the dominant processes can be assigned to the appropriate time frames, or the models that need to be coupled can be identified.

A first level of coupling can be achieved by identifying conceptual scenarios that link the various processes along a pathway for water reaction. These pathways can be examined both with and without a particular subsystem model included as a means to bound the conceptual uncertainty in that subsystem model. For example, modeling scenarios for the in-drift water-solids chemistry with and without concrete capture the major portion of the conceptual uncertainty in the effects of concrete ground support. This approach does not encompass all sources of conceptual uncertainties because they also exist within each model, for example, the local equilibrium assumption in the water-solids submodels. These additional submodel conceptual uncertainties, together with parameter and representational uncertainties, are reflected in the parameter output distributions generated by the various subsystem models for each scenario analyzed in the TSPA-VA.

### 4.4.5 Tracking Parameter Inputs and Calculation Results

The entire set of performance assessment analyses are currently being brought under the control of the Quality Assurance (QA) program. This is being done to keep track of data sources, conceptual models, conditional assumptions for models, QA status of codes utilized for calculations, and the values used within the total system performance assessment calculations. As part of this effort two tables are included in this document for tracking (a) input values used in the NFGE component models (Table 4-39), the sources of those input parameters, and the QA status of those data; and (b) the output results of calculations (Table 4-40), their input/output files, the code and version used to generate them, and their location within the technical data

tracking system of the project. In all cases the input data or results are not qualified and will need to be verified (TBV) for use in quality affecting analyses in the future.

## 4.5 BASE CASE ANALYSES FOR NFGE

The results of the near-field geochemical model analyses are presented in sections that follow. The focus is on results that provide quantitative inputs either for other TSPA-VA component models or for the TSPA model, and are therefore incorporated into the system-level performance assessment results (e.g., see Sections 3.4 and 5.3). Other analyses conducted in this NFGE component of the TSPA-VA provide preliminary constraints on the potential magnitude of additional issues having large uncertainties. The results of those analyses are presented in Section 4.6 and used to evaluate the potential need for incorporation of those additional processes into system-level assessments. Such analyses also provide a basis for planning and directing process-level and performance-assessment-level investigations and model enhancements to be used in future analyses of performance.

### 4.5.1 Incoming Gas, Water, and Colloids

The results for the analyses conducted for the models of incoming gas and incoming water are presented in this section. As discussed in Section 4.4.2.3 for implementation of the incoming colloids model, all the results for colloid concentrations are discussed in Section 4.5.2.3 covering the in-drift colloids. The results of the incoming gas and incoming water models form the boundary conditions for the analyses of in-drift reaction discussed in Sections 4.5.2 and 4.6.2.

#### 4.5.1.1 Incoming Gas

Time variation in gas composition (carbon dioxide and oxygen) provided by incoming gas model of the NFGE component is shown in Figures 4-32 and 4-33. Figure 4-32 shows the gas fugacities to 10,000 years, whereas Figure 4-33 shows them to 100,000 years. The values are back to ambient by 4000 years, as stated in Section 4.4.2.1. These abstracted gas composition values are given in Table 4-41 with the abstracted time periods and the temperature conditions to which they correspond. Also in Table 4-41 are the cumulative gas fluxes for carbon dioxide and oxygen gas species moving into the drift. These values correspond to the cumulative flux per linear meter of tunnel up to the time at the end of that period. These are derived from the continuous cumulative fluxes of these components that are shown in Figure 4-34 (to 5,000 years) and Figure 4-35 (to 100,000 years). The gas fluxes shown in Figures 4-34 and 4-35 also include the nitrogen content. The fluxes shown in Figures 4-34 and 4-35 are given in units of $kg/m^2$ of tunnel surface area. To convert to the values shown in Table 4-41, take the cumulative flux value from Figure 4-34 and 4-35, multiply by the tunnel diameter corresponding to a 1-meter length of the drift (5.5 m tunnel diameter—see Chapter 1 and Section 4.3), and convert the kilograms of species considered to moles. The abstracted cumulative gas fluxes shown in Table 4-41 are used as a portion of the constraints on total fluxes of these constituents into the potential drifts for the mass balance calculations presented in Section 4.6.2.1.

These results are for the center of the potential repository as discussed in Section 4.4.2.1, and the gas compositions apply to the entire region near the drift, within and outside the drift. During the boiling period (0–2,000 years for the center portion of the modeled repository), these gas

components are diluted by steam generation. A relatively large decrease in the levels of these gases can be seen from 200 to 1,000 years (Figure 4-32), which corresponds to the peak boiling conditions. It is also at these times when gas fluxes are changing most (Figure 4-34). Although there are several smaller changes after 1,000 years, the model values of carbon dioxide and oxygen fugacities return to ambient levels at around 4,000 years. The reduction in oxygen content may provide some benefit to any degradation processes dependent on oxidation (waste package, cladding, or waste form). However, because this reduction occurs primarily at conditions above boiling, no WP degradation would be expected (see Chapter 5).

For the corresponding edge areas, the return to ambient gas composition occurs around 1,000 years (Table 4-8). On the 100,000-year time scale shown in Figure 4-33, the effects of gas composition appear relatively short-lived even for this more strongly perturbed central portion.

#### 4.5.1.2 Incoming Water

The results for the model of incoming water compositions in terms of pH, the total dissolved carbonate concentration ($\Sigma CO_3^{2-}$), and ionic strength are shown in Figures 4-36 (10,000 years) and 4-37 (100,000 years). The major features of these results (Figure 4-36) are the increase in pH to values greater than or equal to 10 during the intense boiling period (200 to 2000 years). This reflects the low carbon dioxide content of these periods. This effect is subdued but still present out to 4,000 years, when the system reverts to the ambient gas values. The ionic strength also shows some variations during this period, notably increasing during the boiling period due to the 10-fold concentration caused by the evaporation. All of the concentrations of the fluid components are given in Table 4-42 and are used by the in-drift water-solids chemistry submodels as the starting fluid composition for reaction. On the scale of 100,000 years (Figure 4-37), these changes can be seen to be relatively restricted to a short time frame.

### 4.5.2 Evolution of In-drift Chemistry

The results for the analyses conducted for the in-drift models of the NFGE component are presented in this section and include assessments of the base-case in-drift gas and in-drift water-solids chemistry. This latter represents the reaction of the incoming water with the corrosion products of the waste package. As discussed in Section 4.4.3.3 for implementation of the in-drift colloids model, all the results for colloid concentrations are discussed in this section also. The results of the in-drift gas, water-corrosion products reactions, and in-drift colloids models form the base-case NFGE conditions. All other analyses performed for the TSPA-VA were done either for process-level sensitivity analyses or TSPA-VA sensitivity analyses and are discussed in Sections 4.5.2 and 4.6.2.

#### 4.5.2.1 In-Drift Gas

The major assumptions for this model are that the gas composition is set by the externally derived gas flux coming into the drift and that the composition of gas in the drift is homogeneous throughout, including any breached waste package. This means that the results for incoming gas compositions presented in Section 4.5.1.1 are directly applied to the in-drift system. This is shown in Figures 4-32 and 4-33 by the links from the carbon dioxide and oxygen results to all parts of the drift. A sensitivity analysis of the potential for changes to gas composition is

performed within Section 4.6.2.1 to evaluate the potential for changes to carbon dioxide or oxygen reaction with introduced materials.

### 4.5.2.2 In-Drift Water-Solids Chemistry

For the base-case results provided to the TSPA-VA analyses, the assumption is that the concrete liner has physically degraded in a relatively short time such that most direct water pathways to the waste package are free of concrete. Therefore the incoming water composition reacts directly with corrosion products on its pathway into the waste package. Because a corrosion pathway must be completed prior to water getting into a waste package, any water moving into a package will be reacting predominantly with such products, as opposed to fresh metal.

#### 4.5.2.2.1 Corrosion Products

The results for the in-drift model for reaction of incoming water compositions with the corrosion products are shown in Figure 4-38 (10,000 years) and Figure 4-39 (100,000 years) in terms of pH, the total dissolved carbonate concentration ($\Sigma CO_3^{2-}$), and ionic strength. Equilibration with Goethite did not strongly change the incoming fluid composition in terms of these parameters, although there is a slight shift in pH and ionic strength during the boiling periods. The major features of these results (Figure 4-38) are the increase in pH to values greater than or equal to 10 during the boiling regime periods (200 to 2000 years). This reflects the low carbon dioxide content of these periods. On the scale of 100,000 years (Figure 4-39), these changes can be seen to be relatively restricted to a short time frame. This is very similar to those for the incoming water model given above (Section 4.5.1.2).

These major effects are subdued but still present out to 4,000 years, when the system reverts to the ambient gas values. The ionic strength also shows some variations during this period, notably increasing during the boiling period due to the 10-fold concentration caused by the evaporation. These values represent the expected values for the base-case set of in-drift water compositions provided by the NFGE to the TSPA-VA analyses. All of the concentrations of the fluid components are given in Table 4-43 and are used by the other in-drift water-solids chemistry submodels (in particular the water-spent fuel model) as the starting fluid composition for reaction. In Table 4-43, the effect on the fluid composition in terms of dissolved iron can be seen by comparison to Table 4-42, but the concentration of this constituent is minor.

### 4.5.2.3 In-Drift Colloids

The relation derived for colloid abundance as a function of ionic strength (Equation 4-11) was used directly within the system integration program RIP (Section 4.4.3.3 and Chapter 11). External to the system code, the relation was used to generate colloid amounts for values of ionic strength to ensure that the fit coefficients reproduce the data used and produce reasonable values for the amounts of clay and iron-oxyhydroxy colloids in the drift. A couple of examples are provided here. The NFGE models for water compositions (e.g., incoming water, water reacted with corrosion products) provides stoichiometric ionic strengths to be used by the in-drift colloids relation. The stoichiometric ionic strength is calculated as one-half the sum of the products of the cation and anion molalaties and their charges squared (see Wolery 1992b for a discussion of solution ionic strength).

Using the relation given as Equation (4-11) indicates that an ionic strength of about $3 \times 10^{-2}$ molal (boiling regime) corresponds to a colloid concentration of about $8 \times 10^{-6}$ mg/mL, and ionic strength of $5 \times 10^{-3}$ molal (cooling regime and ambient) corresponds to about $6 \times 10^{-5}$ mg/mL. These values correspond to about $1 \times 10^{6}$ and $7 \times 10^{6}$ particles per milliliter, respectively, calculated using the relation in Section 4.4.3.3. As was stated in Section 4.4.3.3, the relation is incorporated directly into the TSPA-VA analyses and evaluated stochastically. There are no additional process-level sensitivity analyses on the concentration of these colloid types. All the base-case results and sensitivity analyses on colloids are covered in other chapters of this technical basis document. The sorption of radionuclides to these colloids, the additional colloids types included within TSPA-VA analyses (waste form) and their transport through the EBS are discussed in Chapter 6. Colloid transport of radionuclides through the geosphere is discussed in Chapters 7 and 8. The performance-assessment-level results of the colloid model for release at the edge of the engineered barrier system, at the water table, and at the accessible environment are discussed in Chapters 6, 7, and 8, respectively, with the total system performance results in Chapter 11.

### 4.5.3 Development of Parameter Distributions for TSPA-VA (RIP Inputs)

The general approach to the large amount of conceptual uncertainty in the geochemical system was to separate the major potential contributors to either gas or water compositional changes into various subsystem models (e.g., gas phase, concrete, and microbes). These decoupled models can then be coarsely recoupled by identifying conceptual scenarios (or pathways) that link the various processes sequentially along that pathway for water reaction. To assess the major conceptual uncertainty in the system resulting from one of the subsystem models, these pathways can be examined both with and without a particular subsystem model included. For example, modeling scenarios for the in-drift water-solids chemistry with and without concrete capture the major portion of the conceptual uncertainty in the effects of concrete ground support. This method has been referred to as "alternate conceptual scenarios" or "alternate conceptual models." However, this approach does not encompass all sources of conceptual uncertainties because these also exist within each subsystem model. For example, the local equilibrium assumption in the water-solids submodels may be only a poor approximation in reality. This would be particularly true if flow pathways were fast and water fluxes were high. These additional submodel conceptual uncertainties, together with parameter and representational uncertainties, are reflected in the parameter output distributions generated by the various submodels for each scenario analyzed in the TSPA-VA.

The model value shown for gas compositions in Figures 4-32 and 4-33, and for water compositions in Figures 4-36 and 4-39, were assumed to represent the expected values of those parameters. However, because processes in the NFGE have a large amount of associated uncertainty, these deterministic results were also used to generate probability distributions for the base case. Because of the complex nature of the geochemical calculations, explicit error propagation is not straightforward in order to assess uncertainties within the calculated values (Criscenti et al. 1996). Criscenti et al. (1996) showed through their analysis that the uncertainty in a calculated result can be due primarily to only a few, or even less, parameter values that control the results.

Because this is the first attempt to construct the NFGE component models for the TSPA analyses, the focus was on delineating the expected values and the assessment of uncertainty was performed in two stages: (a) the definition of alternate conceptual reaction pathways to address major conceptual uncertainty and (b) the assignment of standard deviations to the calculated expected values of those reaction pathways to address additional model uncertainties. These latter uncertainties were defined semi-quantitatively based on the experience of the performance assessment abstraction core-team members (CRWMS M&O 1997a). The uncertainty in the results that were used within the TSPA-VA analyses of the base-case was assessed by viewing these calculations as order-of-magnitude estimates. That is to say that they are expected to be accurate (at about the 99 percent level to plus or minus an order of magnitude). The standard deviation that corresponds to such an analysis is 0.3 log units and this was applied to all values incorporated into the TSPA-VA results. The uncertainties assessed for the model results were used to construct the distributions, which were defined as log normal for dissolved constituents (this corresponds to a normal pH distribution—see Sections 4.4.4 and 4.5.3).

Figure 4-40 shows an example of the inputs from the NFGE component showing the probability density functions for pH conditions within the drift at various times. These probability distributions are used to explicitly include some of the uncertainty in the modeled pH conditions within the analyses. The probability density functions are shown at the final time of their applicability to the system. For example, the probability density function shown at 100,000 years is applicable from 10,000 years to 100,000 years. The expected values for the TSPA-VA base-case distributions are shown by the peaks Figure 4-40 for water reacted with iron oxides, together with ambient site values applied after 100,000 years. The uncertainties reflect a standard deviation of 0.3 pH units (i.e., 1 order of magnitude on either side of the expected value should capture 99 percent of the uncertainty). The use of these data for waste package corrosion models, waste form dissolution models, and UZ transport models is detailed in Chapters 5, 6, and 7, respectively. All of the base-case parameter inputs to the TSPA-VA code RIP are shown in Table 4-44.

## 4.6 SENSITIVITY STUDIES FOR NFGE

In addition to the NFGE analyses for the TSPA-VA base-case parameter values presented within Section 4.5, a number of sensitivity studies were conducted. These included evaluation of (1) possible variations in gas due to different thermal-hydrologic conditions or from reaction with components in the drift, (2) additional materials reaction with water (concrete, spent fuel, precipitated salts), and (3) the potential for growth of microbes within the NFGE. Only the baseline sensitivity results to water composition from the concrete modified water were utilized directly within TSPA-VA level sensitivity analyses. The results of the spent fuel modifications to water chemistry were used for conceptual discussion of the magnitude and duration of water reacted with the spent fuel; however, the Np-concentration constraints developed in those same analyses for secondary phase alteration (see Chapter 6 for details) were used as waste-form inputs to TSPA-VA sensitivity studies. The sensitivity analyses on alternate gas conditions, precipitates/salt buildup, and microbial growth are all focused on assessing their significance from the process-level analyses and are used to discuss which areas may need to be incorporated into future analyses and how the PA may be affected. There are no additional process-level sensitivity analyses on the NFGE concentrations of the incoming or introduced colloid types.

All the sensitivity analyses on colloids are covered in Chapters 6, 7, and 8 of this technical basis document, with the TSPA-VA level results presented in Chapter 11.

### 4.6.1 Incoming Gas, Water, and Colloids

The sensitivity analyses for the submodels of the incoming gas, water, and colloid model focus on evaluation of the possible thermal perturbations to the incoming gas composition. Changes to the incoming gas constraints that deviate from the ambient system conditions have the potential to affect the incoming water chemistry and the reactions that occur from that point onward. Changes to the constraints on the gas that would be closer to the ambient case should be bounded by the ambient geochemistry and the calculation results presented in Section 4.5.1.1.

#### 4.6.1.1 Incoming Gas

All of the discussion here is based on evaluation of the 2-dimensional thermal-hydrologic analyses of a cross section (N233,400) through the middle of the potential repository (see Section 4.4.2.1; Chapter 3 for the other thermal-hydrologic results). The conclusions presented here are drawn from those results, which are based on the full water and gas flow that are represented in those models and have been applied for different climate/infiltration conditions. As such, any uncertainties within those thermal-hydrologic results are inherent also in this discussion. The perturbed gas conditions induced during the thermal perturbation are very different for the edge regions of the repository compared to the center portion. For the repository edge areas, the time in the boiling regime is much shorter than it is in the central portion of the repository, and the return to ambient conditions occurs more rapidly. In addition, changes to the gas composition during the boiling period are more subdued for the edge regions with the abstracted air mass fraction only dropping to about 0.01 (Table 4-8). Furthermore, the total cumulative air flux at the edge appears to be of the same order of magnitude as for the center, but is lower after 10,000 years (Figure 4-19) Because the thermally induced changes are shorter and less substantial in the edge and intermediate regions compared to the center region, the evolution of the NFGE in these additional regions is bounded by modeling only the central portion of the potential repository.

### 4.6.2 Evolution of In-drift Chemistry

The sensitivity analyses for the in-drift gas model focus on evaluation of the possible introduced materials perturbations to the in-drfit gas composition. Reactions of gas constituents with solids in the drift could deplete the system of some of those components. If this occurs, then the conditions under which the chemical interactions of water and materials (for example) have been assessed may not apply as has been assumed here. Such conditional changes to either the oxygen or carbon dioxide content of the gas phase have the potential to affect the in-drift water-solids chemistry and all the other reactions that occur from that point onward. If such changes appear to have a large potential to occur, then some representation of these should be included within the model analyses. Only the major sink terms for the oxygen and carbon dioxide gas constituents have been evaluated here by assessing the relative masses of sink terms and the rate of supply of the volatile species to the potential drift environment.

#### 4.6.2.1 In-Drift Gas

A simple bounding, mass-balance calculation was used to evaluate the likelihood of depletion of oxygen during package corrosion producing reducing conditions for waste form reactions. This section provides the mass comparison and the resulting assessment of whether effective oxygen depletion appears to be a likely condition. To decrease the oxygen fugacity to a reducing condition (reduced by at least 2 orders of magnitude), the waste packages must be able to use effectively all of the oxygen as it is supplied. Based on the waste package design data transmittals, the total mass of iron from waste packages and pedestals was estimated to be approximately $5 \times 10^4$ moles/meter of tunnel (see Section 4.3 for QAP-3-12 design data transmittal information). Given the stoichiometry of oxidizing Fe to $Fe_2O_3$, only 0.75 moles of oxygen are used to oxidize each mole of Fe.

The cumulative fluxes of oxygen into the drift via the gas-phase flow is given in Table 4-41 for each of the six abstracted time periods. These values, given in moles of $O_2$ per meter of tunnel, represent almost all of the oxygen fluxing into the drift that would be available for reaction with materials. The flux of oxygen into the drift via the water flux is calculated from the equilibrium concentration of oxygen dissolved in the water and the percolation flux for the climatic regime of that period (see Chapter 2). For the first 5,000 years the climate is the present day dry, then from 5,000 to 95,000 it is the longe-term average climate, and then the present-day dry climate again until 100,000 years (Chapter 2). The infiltration rates used are 7.96 and 45.3 mm/year, respectively (Chapter 2), multiplied by the following oxygen concentrations for the abstracted time periods: Period A, $1.6 \times 10^{-7}$ m; Period B, $1.6 \times 10^{-11}$ m; Period C, $1.6 \times 10^{-6}$ m; Period D, $1.6 \times 10^{-5}$ m; Period E, $1.6 \times 10^{-4}$ m; Period F, $1.6 \times 10^{-4}$ m. This leads to the following cumulative $O_2$ fluxes to the end of each period: Period A, 0.0 moles per meter; Period B, 0.0 moles per meter; Period C, 0.1 moles per meter; Period D, 1.5 moles per meter; Period E, 210. moles per meter; Period F, 5,200. moles per meter. These values are very small compared to those based on the gas flow given in Table 4-41.

The cumulative mass flux of oxygen from both the gas and water fluxes indicates that oxygen levels may be low during the peak boiling period (out to about 1,000 years). However, by 4,000 years the cumulative oxygen gas flux is up to about $1.7 \times 10^5$ moles of oxygen gas per meter of drift, or about 450 percent of the oxygen gas needed for full oxidation. At 100,000 years, about seven times that mass of oxygen has been fluxed through the drifts. Therefore, reducing conditions in the drift do not appear very likely as a result of this mechanism and a depletion of oxygen does not appear to need to be incorporated into modeling assessments based on these simplified mass balance calculations.

A second mass-balance analysis was also done to assess whether the amount of carbon dioxide entering the drifts was sufficient to completely carbonate the cement. This mass-balance analysis was based on the assumption that all the calcium in the cement must bond with carbonate to prevent an increase in alkalinity. The cumulative mass flux of carbon dioxide from both the gas and water flux provides about 51,300 moles of carbon dioxide per meter of tunnel fluxed through the drift over the first 100,000 years. Most of this carbon dioxide is supplied as dissolved materials in the groundwater, assessed as above for oxygen but using the dissolved carbonate values given in Table 4-43 for each abstracted time period. At 10,000 years, only

about 4,200 moles of carbon dioxide have passed through the drift, and the gas and water fluxes contribute about equally to this mass.

To form calcite, one mole of carbon dioxide is needed for every mole of calcium. Based on the mass of concrete in the tunnel (Section 4.3), there are about 20,000 total moles of calcium per meter of tunnel. Therefore, there is more than twice as much carbon dioxide than is necessary to carbonate all the cement in 100,000 years. However, only about 20 percent of the carbon dioxide needed to carbonate the cement will have been supplied to the drift in 10,000 years. Other reactions will need to play a major role in neutralizing the alkaline capacity of the large masses of concrete planned for ground support, or alkaline fluids will be likely over at least the first 10,000 years. Because this is the case, the analyses of concrete-water reaction were done in a manner to allow for a variable $CO_2$ fugacity (i.e., gas composition) if the reaction consumed the potentially available mass of $CO_2$ (discussed below in Section 4.6.2.2.1).

### 4.6.2.2 In-Drift Water-Solids Chemistry

Three aspects were investigated for this area. First, results of analyses of the reaction of concrete with water and gas are presented in Section 4.6.2.2.1. Because of the large mass of concrete planned to be used in the system (4.35 $m^3$ per meter of potential emplacement drift—see Section 4.3), this material represents one of the single largest components, in terms of mass, within the potential repository system. In addition, the unique chemistry of concrete, the cement in particular, is extremely different from the ambient system composition and provides a number of potential major reaction perturbations to this system. The baseline results of these analyses are used in a TSPA-VA sensitivity analysis. Second, the commercial spent nuclear fuel (CSNF) itself represents a relatively large mass of unstable (chemically) materials in this oxidizing environment and therefore has some potential to affect the bulk composition of the major elements in the water, not just supply radionuclides. These interactions to begin defining the potential magnitude and duration of such effects are done using a sophisticated coupled reactive-mass transport approach and a model that has been developed for the dual purpose of these analyses (presented in Section 4.6.2.2.2) and explicit evaluation of Np retention/release by secondary uranium phases (presented in Chapter 6). Third, an assessment of the possible magnitude and types of salt deposits that could potentially form on a waste package due to evaporation/boiling in this system has been completed. This analysis integrates the incoming water compositions with models of the seepage flux (Chapter 2) in order to estimate the masses of salts per waste package and the timing of brine formation from these salt constituents. The results of these analyses are presented in Section 4.6.2.2.3 and are utilized for assessing possible waste package sensitivity analyses and planning of further work in these areas.

#### 4.6.2.2.1 Concrete and Corrosion Products

Within these analyses, the steel fibers within the concrete (see Section 4.4.3.2.2.1) are altered to oxide phases. As such, these analyses already reflect saturation with respect to oxidized iron minerals that represent the waste package corrosion products, and thus no further reaction of the resultant fluids was conducted beyond these calculations.

#### 4.6.2.2.1.1 Results of Baseline Concrete Sensitivity Analyses

The baseline sensitivity results for the TSPA-VA calculations are presented in Table 4-45. Plots of pH, stoichiometric ionic strength, and total carbonate versus time are displayed in Figures 4-41 through 4-43. The chemical system controlling concrete reacted fluid chemistry for all of the periods is the $Ca(OH)_2 - CO_2 - H_2O$ system. The resulting fluid chemistry for each period is largely dependent on carbon dioxide availability - its fugacity and total reservoir size for a given period and the presence of portlandite in the mineral assemblage. The simulation results show that high pH conditions (pH>10) prevailed throughout the thermal pulse 0 – 2000 years (Periods A-C), and during the cooling down period 2000 – 4000 years (Periods D and E). During Period F (10,000 – 100,000 years) the pH returned to near "normal" levels.

An interesting aspect of the evolved fluid chemistry during the first 10,000 years (Periods A-E) is that the pH is less than the value of ~12.4 that would be expected for portlandite dissolution at 25°C. The reason for the lower than expected pH is due strictly to the effect of temperature on the hydrolysis of portlandite, where the equilibrium pH decreases at temperatures above 25°C. The temperatures of the abstracted Periods A through E are either 95°C or 70°C (Table 4-41).

The reason for the elevated pH during the thermal periods, with the exception of Period B, was the expenditure of the $CO_2$ budget via carbonation of cement phases (i.e., the formation of calcium carbonate), which exhausted the possible $CO_2$ supply and allowed the portlandite to set the pH. In other words, the total $CO_2$ budget was used up in the formation of calcium carbonate, leaving an insignificant amount to buffer the high-pH produced by the cement phases to more neutral conditions. During Period B, the $CO_2$ does not get expended on carbonation reactions, but rather the very low $CO_2$ fugacity carbonates a small percentage of the cement minerals and high-pH conditions prevail in the presence of excess $CO_2$ at very low fugacity.

During period F, the $CO_2$ budget is large enough to support carbonation and buffer the system pH. A reflection of the increased $CO_2$ availability during Period F is shown in Figure 4-43, where the total carbonate during Period F increases by approximately 2 orders of magnitude relative to Period E, where $CO_2$ and $O_2$ have the same fugacity as Period F. This is primarily due to the long time period represented by Period F and there may be some time beyond the end of Period E during which alkaline pH values would continue to be imposed.

Figures 4-53 and 4-54 summarize the resultant fluid compositions for 10,000 years and 100,000 years respectively. These results are the parameter inputs to the TSPA-VA baseline concrete fluid sensitivity study.

#### 4.6.2.2.1.2 Results of Reaction Rates Sensitivity Analyses

The results of varying the relative reaction rate by a factor of 5 are listed in Tables 4-46 and 4-47, and are graphically displayed in Figures 4-44 through 4-46 with a comparison to the baseline sensitivity values. The second set of results, where rk1 was set to a constant, are tabulated in Tables 4-48 and 4-49, and are displayed graphically in Figures 4-47 to 4-49.

Figures 4-44 through 4-46 show that by varying the relative reaction rates over an order of magnitude range has little effect on the chemistry of the concrete reacted fluid. The most

significant effect of changing the relative reaction rates is on the solution ionic strength. Increasing the reaction rates by a factor of 5 had a greater effect on the ionic strength during Periods A – E then it has on Period F. The cause of this nonuniform response is difficult to pinpoint and likely results from a combination of factors rather than a single cause. Overall, the changes in ionic strength relative to the baseline simulation reflect the changes in the reaction rates, with higher ionic strength for increased reaction rates, and lower ionic strength for decreased reaction rates.

Setting the reaction rates to constant values for all reactant phases (cement minerals, aggregate phases, and iron fiber) had a dramatic effect on the reacted fluid chemistry compared to the baseline simulation. Figures 4-47 through 4-49 display the pH, ionic strength, and total carbonate for these simulations. The pH remains low (~8.1) for the entire duration of the simulated period including the thermal and cool-down periods when the pH of the baseline simulation is in the range of pH = 11. Because the system is complex, it is difficult to determine the exact cause of the pH depression. However, it appears that the pH is being controlled by the carbonate system. Since the relative reaction rate for portlandite was decreased from the baseline value of 5.0 to the sensitivity values of 0.1 and 1.0, the "carbonation potential" was decreased, thereby freeing more $CO_2$ to act as a pH buffer. Figure 4-49 shows that for all periods, except Period B, the total solution carbonate was greater than the baseline values, suggesting that carbonate was responsible for buffering the pH.

An interesting effect of varying the relative reaction rates is the change in the chloride ion concentration – a conservative ion in terms of the mineralogic reactions occurring in the concrete system. Comparison of the chloride ion molal concentrations between Table 4-46 and Table 4-48 for Period A shows a decrease of about 65 percent from rk1 = 0.2 to rk1 = 1. This change is due to dilution of the chloride by the increased dissolution rates, in the case where rk1 =1, of hydrated cement phases. Increasing the relative reaction rate of ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}{:}26H_2O$) from 2.0E-02 (rk1 = 0.2) to rk1 =1 has the effect of adding 93 grams of water compared to 468 grams water when rk1 =1. Therefore, it only appears as if chloride is behaving in a nonconservative manner when actually water is being added

The results from this set of sensitivity analyses lend support to the baseline relative reaction rates chosen for the reactants in the TSPA-VA calculations. As was stated above, the baseline values of the relative reaction rates were chosen to recreate the expected dissolution behavior cement (Berner 1990). By using constant values of the relative reaction rates it was shown that none of the expected chemical signatures were observed in the model, thereby supporting the baseline values. Secondly, this sensitivity analysis showed that increasing or decreasing all of the relative reaction rates by a constant factor resulted in fluid chemistries that are very similar in character and magnitude to the baseline calculated fluid chemistries.

#### 4.6.2.2.1.3 Results of Suppressed Phases Sensitivity Analyses

The results of the sensitivity analyses are tabulated in Tables 4-50 through 4-53, and are graphically displayed along with the baseline values in Figures 4-50 through 4-52.

As the figures clearly display, phase suppression had no effect on the concrete reacted fluid chemistry. The probable reason for this is that if a suppressed phase becomes saturated another

available phase forms in its place with minimal change to the fluid chemistry. This could be an artifact of the thermochemical database having an abundant number of surrogate phases of similar composition to substitute for the suppressed phases. In all calculations of this type, the phases contained in the database for the specific chemical system being investigated play a large role in the possible outcome of the calculations. Based on these findings it may be concluded that the choice of mineral phases suppressed in the baseline simulations had little effect on the resultant fluid chemistry.

#### 4.6.2.2.2 Spent Fuel

The results presented below represent the bounding evaluation assessment of the magnitude and timing of changes to the in-drift water composition based on reaction with the spent fuel. This evaluation allows assessments of what periods of time the radionuclides may be responding to water chemistry altered from that entering the package, and what magnitude of change that may be.

##### 4.6.2.2.2.1 Results of Simulations for Stage-1 Analyses

The model for Stage-1 starts from the time of WP failure. These analyses were done for a range of exposed spent fuel (1 percent and 100 percent) to assess the magnitude and duration of changes to the water composition. As stated above, two data sets were used (DS-1 and DS-2). These data sets represent (1) different water flux scenarios through the waste package: all seepage goes through packages (DS-1) versus reduction of seepage by open patch area of the waste package (DS-2) (see Chapter 6, covering EBS transport), and (2) different thermo-chemical/kinetic databases and constraints. The parameters that differ are (1) pore-water velocity; (2) equilibrium constants of uranophane, soddyite, and Na-boltwoodite; (3) rate constants of schoepite and soddyite dissolution; and (4) specific surface area of CSNF. As discussed below, the results show the basic conclusions regarding Stage-1 using DS-1 do not change.

Using the DS-1 data set, four simulations were carried out to evaluate the effects of water composition during the active period of CSNF alteration. The four simulations were carried out at 70°C and 30°C with two different percentages of cladding failure (two different amounts of spent fuel available to react with water—1 percent and 100 percent). The bulk composition of the water at the end of the one-dimensional pathway was assumed to be the resulting water composition for consideration in the NFGE. These four cases are referred to as Case A: T = 70°C, 100 percent cladding failure; Case B: T = 30°C, 100 percent cladding failure; Case C: T = 70°C, 1 percent cladding failure; and Case D: T = 30°C, 1 percent cladding failure.

Figure 4-55 shows the calculated water composition as well as the volume fractions of major solids as functions of time for Case A. The calculations indicate that spent fuel should be totally consumed in about 2,000 years and that the major secondary phase would be schoepite. At times less than about 2,000 years, the pH value at the bottom of the column is lower than the pH values at the inlet, as can also be seen for the other components (Figure 4-55). However, once spent fuel has disappeared, the water composition tends to revert to the inlet composition.

The pH changes for all four cases are plotted in Figure 4-56. The pH effects are shown during the active primary alteration stage at early times in which $UO_2$ is converted to the first set of secondary phases. At both higher (70°C) and lower (30°C) temperatures, the water chemistry is affected to a larger extent if all of the fuel is exposed to reaction.[5] At 70°C, the ability of the spent fuel to alter the pH (and other characteristics of the water) begins to decrease almost immediately and is almost entirely dissipated after about 2,000 years. This reflects the conversion of spent fuel to the major secondary phase, schoepite. Once the exposed spent fuel is converted to schoepite, the water composition tends to revert to the incoming composition. This conversion takes longer at 30°C because the spent fuel dissolution reaction rates are lower than at 70°C.

Using the DS-2 data set, two additional simulations were carried out for the Stage-1 analyses. Both of these were done for 70°C, and cladding failure rate of 11 percent and 1 percent, referred to as Case-E and Case-F, respectively. Calculations using the DS-2 data set generally show faster reaction of spent fuel compared to those performed with DS-1 (discussed above). This results primarily from the larger specific surface area used for the spent fuel grains in DS-2 versus DS-1. In spite of the large differences in some values in the data sets, the results for 1 percent exposed fuel calculated using DS-2 appear consistent with those performed using DS-1 out to at least 5,000 years. Because the calculated dissolution of CSNF using DS-2 to be even more rapid, the conclusion that the spent fuel can substantially affect bulk water composition for only a short period of time—thousands of years at most—still appears valid. The results for Case-E are discussed in detail.

The calculated dissolution rate and volume changes of spent fuel for Case-E are presented in Figure 4-57. Figure 4-57a shows that the dissolution rate of CSNF is almost constant, both spatially and temporally. Figure 4-57b shows the available CSNF is totally consumed in less than 500 years for Case-E.

The development of secondary phases throughout the one-dimensional column of spent fuel is shown in Figures 4-58 and 4-59. Schoepite (Figure 4-58a) is the major secondary uranyl mineral and is distributed almost uniformly within the WP, except for the top portion (~0.2 m) of the WP. At 1,000 years about 4 percent schoepite (volume fraction of the WP) precipitates uniformly through the lower 1.3m of WP. The volume ratio of schoepite to the originally available spent fuel is about 4/1.54 = 2.597. That number is very close to the expansion factor of molar volumes from $UO_2$ to schoepite, which is (66.08 $cm^3$/mol / 24.618 $cm^3$/mol) = 2.684 (Wolery 1992, EQ3/6 database data0.com.R22a [YMP Configuration Item Identifier: DATA0-V7-COM-R22a]). That means more than 90 percent of the original $UO_2$ is converted to schoepite. The rest has either formed uranophane or soddyite, or it has been removed by transport. After 500 years, schoepite starts dissolving at the top of the column.

As shown in Figure 4-58b, uranophane precipitates mainly in the top portion of the waste package. That is because the precipitation reaction rapidly depletes Ca in the incoming water. For a similar reason, soddyite precipitates at the top of WP, due to the consumption of Si.

[5]The initial pH of water entering the waste package is about 8.2.

However, soddyite redissolves after spent fuel is consumed, because of the decreasing U concentration. In contrast to soddyite, uranophane keeps growing even after spent fuel disappears. This is driven at the top of the waste package column primarily by removal of dissolved uranium from the water that occurs between 500 and 1000 years. This reaction results from the continued influx of water carrying Ca and silica species that stabilize uranophane relative to soddyite. this latter phase is dissolving slightly downstream and is precipitating further downstream, however, the uranophane precipitation occurring near the inlet is being fed by the aqueous phase via chemically-driven diffusion of uranyl species. Na-boltwoodite is not observed in the simulation.

Scrutinizing the developing of the precipitation fronts of secondary minerals reveals that uranophane forms at the expense of schoepite and soddyite. The reactive-transport model is based on the average of many solid grains and does not provide meaningful results for individual grains. Therefore, the simulation results do not represent, in strict sense, the paragenetic sequence of secondary minerals. However, a general sequence of mineral formation can be derived from the movement of reaction fronts. Figure 4-60 is the derived formation sequence of secondary minerals based on the simulation results for Case-E. Stable phases are shown as solid lines and dashed lines represent meta-stable phases. Both schoepite and soddyite become meta-stable after spent fuel is consumed.

Figure 4-61 shows the pH and U(total) concentration at the bottom of the waste package (outlet) as functions of time. The pH drops initially and then reverses to its initial value, though the change is quite small ( only 0.25 pH unit). The concentration of U(total) increases first and then decreases, due to the precipitation of secondary minerals. The final U concentration is about $6 \times 10^{-5}$ mol/kg.

As one would expect, the impact of reactions between CSNF and water is larger than for Case-E than for Case-F, because there is more fuel being reacted (11 percent versus 1 percent). It is expected that this will also prove true for the 100 percent-exposed-fuel case when it is simulated using DS-2. Given the results evaluated so far, it is likely that those future calculations will result in comparably short time frame for primary dissolution of spent fuel.

A detailed comparison of the analyses using DS-2 with experimental observations and natural analogs is given in Chapter 6. The comparison demonstrated that the model reproduces experimental results and field observations in many aspects. More important is that no contradiction among them has been found yet. It strongly indicates that the model, consisting of the computer code, the conceptualization, and the data used in the simulation, is a reasonable representation of the real system and the model should be regarded as usable for its intended purpose. These confidence building activities, though still partial and preliminary, show the capabilities of the model for predicting the behavior of CSNF under the potential repository conditions. Such comparisons provide a level of confidence that establishes this as a working spent-fuel-dissolution model.

#### 4.6.2.2.2.2 Results of Simulations for Stage-2 Analyses

As discussed above and in Chapter 6, both the laboratory observation and simulation results show that once the CSNF becomes exposed to the water in the NFGE, the exposed spent fuel

will be totally consumed and converted to secondary uranyl minerals in $10^2 - 10^3$ years. For the time frame of performance assessment analyses, $10^2 - 10^3$ years is a short period. In other words, CSNF will be quickly converted to secondary uranyl minerals once the WP is breached. Therefore, for the long-term performance of the repository, the period after CSNF is converted to secondary minerals is more important. The Stage-2 analyses were developed to evaluate the dissolution behavior of secondary minerals, the release of Np from them, and their effects on water composition. The results of the Stage-2 analyses are discussed in detail in Chapter 6 in terms of Np concentration in the aqueous phase. The discussion here focuses on the bulk chemical effects on the water composition.

Because the results of the four simulations are quite similar, only Case-1 will be discussed in detail. Figure 4-62 and Figure 4-63 are the profiles for schoepite and uranophane. They show that schoepite is dissolved with time and replaced by uranophane. Schoepite dissolution and uranophane precipitation take place across the whole WP before 10,000 years. After 10,000 years, the replacement is localized to the dissolution/precipitation front, which advances from upstream to downstream. At about 50,000 years, schoepite is totally replaced by uranophane. Neither soddyite nor Na-boltwoodite is observed.

Figure 4-64 shows the calculated concentration of U for Case-1 increases with depth into the WP and reaches its maximum (~ $2 \times 10^{-5}$ mol/kg) at the bottom. The U concentration at the bottom does not change much until about 50,000 years, when schoepite is totally replaced by uranophane. It appears that before 50,000 years, the controlling mineral for U concentration is schoepite. After that, the controlling mineral is uranophane.

Figures 4-65 through 4-67 are the calculated pH profiles (Figure 4-65), $\sum CO_3^{-2}$ concentration (Figure 4-66), and ionic strength (Figure 4-67) for Case-1. For dissolution and alteration of schoepite, the pH change is less than 0.2 unit. The changes in $\sum CO_3^{-2}$ and ionic strength are about 10 percent. These results reveal that the modification of water composition due to secondary mineral dissolution/alteration appears to be minor for the primary parameters of interest for TSPA-VA (see Sections 4.4 and 4.5). It should be noted that the Ca content of the fluid was decreased substantially while alteration was occurring.

#### 4.6.2.2.2.3 Uncertainties

As noted in the beginning of this discussion, this study is our first attempt to apply a new approach to evaluate CSNF dissolution and radionuclide mobilizations. The available data are sparse and the quality of existing data is yet to be fully evaluated. Therefore, the results should be regarded as preliminary. The following caveats are advised.

A. The thermo-chemical and kinetic properties of uranyl minerals have not been well measured. The effects of inaccuracy in those parameters on water composition have to be evaluated.

B. The effects of basket material corrosion on the water chemistry are not considered in the model. These effects should be investigated in the next round of analyses.

C. Radiolysis effects are not included in the model and its effects should be analyzed.

D. The effects of differences in the incoming water composition, its velocity, and other factors have not been analyzed. A number of analyses for various environmental boundary conditions should be done in the future.

E. The hydraulic assumptions of porous-medium behavior have not been evaluated.

#### 4.6.2.2.2.4 Summary and Recommendations

A model has been constructed for spent fuel dissolution and secondary phase precipitation. Confidence in the applicability of this model has been assessed by comparing modeling predictions against laboratory experiments and natural analogs. The simulation results show that the modification on water chemistry due to the reactions between CSNF and water is short-lived or relatively minor, whereas the modification due to the reactions between secondary uranium minerals and water is minor. That conclusion provides a basis to narrow down the uncertainty associated with radionuclide solubility distributions.

We recommend in the next iteration of TSPA, the following issues be addressed.

A. Numerical model: it is the first time the new reactive-transport model was applied to this type of analysis. As the theory and algorithms of reactive-transport modeling are not matured yet, the uncertainty associated with the numerical model needs to be evaluated.

B. Kinetic data: the kinetic data for the dissolution of uranyl minerals used in this analysis are the only available data to us. Although the data appear to be high quality, they need to be fully evaluated. Project experiments to obtain higher quality data and to fully quantify the kinetic behavior of these uranyl minerals would be very useful. Moreover, as far as could be determined, the kinetics of Na-boltwoodite have not been studied. Since it is the major secondary mineral in ANL's high-drip tests (Finn et al. 1998), a kinetic experimental study on Na-boltwoodite is highly recommended.

C. Thermodynamic data: the quality of the thermodynamic data of some uranyl minerals needs to be improved. Their temperature dependency is unknown. Such data can certainly affect the accuracy of these analyses and more fully constrained values would decrease the uncertainty with these analyses.

#### 4.6.2.2.3 Precipitates/Salts

As discussed in Section 4.4.3.2.4, the thermal perturbation will drive boiling and evaporation processes that can lead to precipitation of dissolved solids within the rock, and potentially on the waste-package surface. The results below are a set of bounding analyses for the timing, accumulation, and total amount of those phases that may end up on the surface of a waste package.

#### 4.6.2.2.3.1 Early Evaporative Precipitation Results

Execution of the early evaporative precipitation model developed in Section 4.4.3.2.4 results in the calculated evolution of reflux water composition in periods A, B, and C is plotted in Figures 4-68, 4-69, and 4-70. The evolution of mineral precipitates is shown in Figures 4-71, 4-72, and 4-73. The pH and the logarithms of the concentrations of dissolved elements and inventories of precipitated minerals are shown in these figures as functions of the percentage of reflux water that has not been vaporized. Note that 100 percent reflux water is equivalent to 90 percent vaporized, or 10 times concentrated, seepage (J-13) water during these boiling periods; thus, the percentages in the figures are in addition to the original 90 percent vaporization. The water compositions calculated at an ionic strength of 1 molal are also presented in Table 4-54.

The results show that the most soluble components, Na, Si, S, Cl, K, and F, increase in concentration in proportion to the amount of vaporization. This is indicated by the constant and equal slopes of these components in the figures. Highly soluble nitrate would behave similarly and would plot just below Cl if it were included in the abstracted reflux water chemistry. Though Na, Si, and K precipitate in small quantities to produce the precipitated minerals, changes to their total dissolved concentrations as they appear in the figures are negligible. Changes in carbonate concentrations are similar to these soluble components; however, because carbonate concentration is a function of pH and the partial pressure of carbon dioxide, deviations from direct proportionality occur. In each period as the water becomes more saline and approaches an ionic strength of 1 molal, the pH increases to values between 10.3 and 11.7. High pH is common in evaporite waters (Eugster and Hardie 1978).

Precipitation reactions cause concentrations of Ca, Al, Mg, and Fe to decrease or remain essentially unchanged as water vaporizes. As a result, approximately 98 percent or more of these dissolved solids are precipitated as the reflux water becomes 98 percent vaporized. Such low concentrations are negligible in terms of overall salt precipitation calculations. Ca concentrations are controlled primarily by calcite ($CaCO_3$) or wollastonite ($CaSiO_3$), depending on the pH and the partial pressure of carbon dioxide. The Al concentrations are controlled in the calculations by celadonite ($KMgAlSi_4O_{10}(OH)_2$), sanidine high ($KAlSi_3O_8$), analcime ($Na_{0.96}Al_{0.96}Si_{2.04}O_6{:}H_2O$), and natrolite ($Na_2Al_2Si_3O_{10}(OH)_2$). For Mg, celadonite and diopside ($CaMgSi_2O_6$) are the controlling minerals. Fe concentrations are controlled by the precipitation of andradite, $Ca_3Fe_2(SiO_4)_3$. Both Fe and andradite are not shown in the figures because of their extremely low concentrations resulting from the low concentrations of iron in reflux water (less than $10^{-23}$ m).

#### 4.6.2.2.3.2 Late Evaporative Precipitation Results

Based on the concentrations of cations in the reflux water in boiling periods A, B, and C as presented in Table 4-42, $Na^+$ and $K^+$ account for more than 99.9 percent of the positive charge. As a result, Na and K salts are responsible for the overwhelming majority of all salt precipitation in these calculations. The other cations are Ca, Mg, and Fe, which are much less soluble than Na and K, as shown in EQ6 calculations in the previous section. In the EQ6 calculations, Ca either precipitates as calcite or wollastonite; however, for the late precipitation analysis it is assumed that all calcium precipitates as calcite. Either way, the low concentrations of Ca allow only a small amount of precipitation compared to Na and K salts. Mg and Fe concentrations in the

reflux water are many orders of magnitude lower than Ca and therefore would result in proportionately lower salt buildup. These small quantities would contribute negligibly to the total salt accumulation and are therefore not considered further in the late precipitation analysis. In alkaline waters, Al hydrolyzes and becomes anionic. Its concentration in the reflux water is below Ca in boiling periods A and C, but it is approximately equal to the Ca concentration in period B when the pH of the reflux water is higher. Because its concentration is low in the reflux water and would contribute less than Ca to the buildup of salts on the waste package, Al is also not included in the late precipitation analysis.

For the aqueous solution composition, Si, Cl, S, C, F, and N account for the major anions in the reflux water. For Si, the predominant anions in dilute waters are $H_3SiO_4^-$ between pH values of about 10 and 11.7 and $H_2SiO_4^{2-}$ for pH values above 11.7 (Drever 1988, p. 100). For C, the predominant species in dilute waters are $HCO_3^-$ in the pH range of 6.4 to 10.3 and $CO_3^{2-}$ above pH 10.3 (Drever 1988, p. 51). In brines, these pH ranges may shift slightly due to ion interactions. Cl, S, F, and N predominantly occur as $Cl^-$, $SO_4^{2-}$, $F^-$, and $NO_3^-$ in these waters.

Though nitrate ($NO_3^-$) was not included in the abstracted reflux water, its high solubility and relatively high concentration in ambient groundwater indicate that it is important in these vaporization calculations. Nitrate occurs in J-13 groundwater at a concentration of 8.78 mg/L (0.000142 m) (Harrar et al. 1990). Like the other soluble components, it will concentrate without precipitating as water is removed by vaporization. Because the abstracted reflux water during the boiling period is 90 percent evaporated J-13 groundwater, the nitrate concentration in the reflux water is set at ten times the J-13 nitrate concentration, 87.8 mg/L (0.00142 m).

The normative binary salts for each boiling period, chosen based on their solubilities as explained in Section 4.4.3.2.4.3, relative ion activity products, and conservation of mass and charge, are listed in Table 4-54. The normative salts for boiling period A were chosen as follows. All Ca is assumed to precipitate as calcite ($CaCO_3$) due to its low solubility and an excess of carbonate. After Ca precipitates, the only cations remaining are Na and K. According to the solubility data in Table 4-33, the sulfates are the least soluble. While potassium sulfate is slightly less soluble than sodium sulfate, the ion activity product of sodium sulfate in the reflux water is approximately 2 orders of magnitude higher than for potassium sulfate due to an approximate ten-fold higher sodium concentration. As a result, the sodium sulfate solubility limit is reached first and will force precipitation of sodium sulfate. The high concentration of sodium relative to sulfate will tend to cause the complete depletion of sulfate while depleting the sodium concentration by approximately 20 percent.

The next solubility limit reached after sodium sulfate precipitates is less certain. The solubility data in Table 4-33 indicate that KCl, $K_2CO_3$, KF, and $KNO_3$ are more soluble than the corresponding sodium salts. A complete set of solubility data for the silica salts is not available. However, if the trend holds that the potassium silica salts are more soluble than the sodium salts, then it is safe to assume for these calculations that the sodium salts will precipitate before the potassium salts. As long as the sodium concentration continues to be much higher than the potassium concentration and the solubilities of the sodium salts are approximately equal to or lower than the potassium salts, saturation and precipitation of the sodium salts will occur, allowing continued enrichment of dissolved potassium.

In the absence of silica salt solubility data at high pH and predicted values for pH in these concentrated brines, it is assumed that nitrate will precipitate last along with potassium. Either way, both types of salt will precipitate when water is completely boiled away. Because there is slightly more nitrate than potassium in the reflux water, the excess nitrate is precipitated as sodium nitrate. Consistent with mass balance and charge balance constraints, the remaining components, Na, Cl, C, F, and Si, are precipitated as the Na-salts: NaCl, $Na_2CO_3$, $NaHCO_3$, NaF, $Na_2Si_2O_5$, and $Na_2SiO_3$.

Because of the high pH, the hydroxyl ion ($OH^-$) contributes largely to the total negative charge in the alkaline reflux water. However, instead of treating $OH^-$ as an anion that must be paired with a cation to form a normative salt, it was incorporated into the carbonate and silica components by hydrolysis, as would occur at high pH. For example, solid NaOH would not co-precipitate with $NaHCO_3$, $SiO_2$ or $Na_2Si_2O_5$ because these salts would dissolve when contacted by a concentrated solution of NaOH. Instead, as vaporization occurs, the hydroxyl ion in solution would react with $HCO_3^-$, $H_4SiO_4^0$ (aq), or $H_3SiO_4^-$ to form $CO_3^{2-}$, $H_3SiO_4^-$ or $H_2SiO_4^{2-}$, respectively (as was computed by EQ6 in the early precipitation analysis). This is illustrated well by the observations that $HCO_3^-$ predominantly converts to $CO_3^{2-}$ above pH 10.3 and $H_3SiO_4^-$ predominantly converts to $H_2SiO_4^{2-}$ above about pH 11.7 (Drever 1988, pp. 51, 100). Accordingly, C and Si contributions to the total negative charge were increased by first increasing the $CO_3^{2-}$ / $HCO_3^-$ ratio and then by increasing the $H_2SiO_4^{2-}$ / $H_3SiO_4^-$ ratio until the total negative charge of the hydroxyl ion was completely transferred to these species. This transfer of charge resulted in a shift to the more alkaline normative salt, that is from $NaHCO_3$ to $Na_2CO_3$ and from $Na_2Si_2O_5$ to $Na_2SiO_3$.

A similar approach was taken for each of the three boiling periods. As a result, the salts that are not pH-dependent or dependent on carbon dioxide fugacity ($Na_2SO_4$, NaCl, NaF, $KNO_3$, and $NaNO_3$) had essentially the same normative values in each period (see Table 4-55). The carbonate and silica salts, whose precipitation depends on the pH of the reflux water or on the carbon dioxide fugacity, had different normative values in each period. In the first boiling period, due to the moderately high pH of the reflux water and the relatively high partial pressure of carbon dioxide, the normative carbonate salt concentrations (particularly $NaHCO_3$ and $Na_2CO_3$) are large. In period B, the carbon dioxide fugacity drops four orders of magnitude, leaving no normative carbonate salts except for $CaCO_3$.

Based on the low solubility of calcite at high pH, it was decided that for period B all Ca would precipitate as $CaCO_3$ despite the lower concentration of dissolved carbonate relative to Ca. Extra carbonate was taken from rereacting previously precipitated $NaHCO_3$ and $Na_2CO_3$ on the waste package. This small amount of carbonate dissolution negligibly affects the inventories Na, C, $NaHCO_3$ and $Na_2CO_3$ on the waste package. The alternative would have been to have Ca precipitate as wollastonite ($CaSiO_3$), as occurred in the EQ6 results of the early precipitation analysis, or to partition some into fluorite ($CaF_2$) as was seen in boiling calculations in Hardin et al. (1998, Section 6.2.2). However, the total amount of wollastonite precipitation is limited by the low concentration of Ca. As a result, wollastonite precipitation would negligibly affect the precipitation of the chosen normative silica salts, though it would affect the accumulation of calcite and wollastonite on the waste package. Regardless of which mineral is more likely to occur, the more important point is that neither of these calcium minerals, due to the low amount that could precipitate, will markedly affect the brine that develops during the boiling period.

Precipitation of fluorite is also expected to be minor, however, this phase is in general less soluble than NaF and would perhaps result in lower dissolved fluoride concentrations as the salt phases redissolve. Because fluoride is a key ion for cladding performance, this is one area that could be evaluated further in the future.

To maintain electrical neutrality for period B solutions, dissolved silica was calculated to hydrolyze in the alkaline brine to $H_2SiO_4^{2-}$ and was effectively substituted for the lost carbonate. Thus, the normative silica salt switches from $Na_2Si_2O_5$ to $Na_2SiO_3$. In period C, the abstracted carbon dioxide fugacity rebounds five orders of magnitude and results in large quantities of $Na_2CO_3$ in the normative salt distribution. The pH remains fairly high, however, resulting in major contributions of both $Na_2Si_2O_5$ and $Na_2SiO_3$.

The total accumulation of these normative salts on the waste package is directly proportional to the seepage rate, which is much lower than the ambient percolation flux (see Chapter 2). According to the results of the UZ flow model (presented in Chapter 2), the average seepage per waste package is 23.2 kg/year for the first 5,000 years. The potential rate of accumulation of normative salts on the average waste package during the boiling period is determined by multiplying this rate by the normative salt concentrations in the reflux water listed in Table 4-55. The accumulation and inventory of salts and their components are plotted in Figures 4-74, 4-75, 4-76, and 4-77.

#### 4.6.2.2.3.3 Salt Dissolution Results

At early times, the temperature is high and the RH is low, allowing all normative salts to precipitate, and all reflux water that drips onto the waste package surface vaporizes. The projected evolution of RH at the waste package surface in a potential drift is shown in Figure 4-29 based on the thermal-hydrologic model results (see Chapter 3). Figures 4-74 through 4-77 show that dissolution of salt phases is essentially instantaneous once the RH exceeds the maximum allowed for a stable solid phase. This is consistent with the observation that puddles of dissolved salt (primarily NaCl) occur overnight on salt flats when the RH rises above the maximum equilibrium RH for solid NaCl (76 percent), but remains far below the dew point (Kinsman 1976). These same puddles then evaporate during the day as soon as the RH falls below 77 percent.

The first critical RH encountered as the potential drift cools corresponds to the nitrate phases, which have the highest solubilities (see Table 4-33). At about 160 years, the RH rises above 50 percent and the temperature falls to about 117 °C. Based on the maximum RH data in Table 4-34 and the solubility data in Table 4-33, this is taken as the approximate RH value that would cause $NaNO_3$ to dissolve. Also, the temperature is below the boiling point of a concentrated solution of $NaNO_3$, which is around 120 °C (National Research Council 1928, V. 3, p. 326). Thus, precipitated $NaNO_3$ is assumed to condense water from the in-drift gas phase and dissolve to a saturated solution at this point in time. Although maximum RH data are not available for $KNO_3$, it is more soluble than $NaNO_3$ and therefore it was also allowed to dissolve at this RH value.

A brine composed of several salts can have a lower vapor pressure, or equilibrium RH, than the brines composed of any of the salts alone. A brine in equilibrium with excess NaCl, $KNO_3$, and

$NaNO_3$ has a measured equilibrium RH of 30.49 percent at 16.39 °C (Weast et al. 1981, p. E-44). This RH is more than 30 percent lower than a concentrated brine of any of these salts individually at the same temperature (Dean 1992, p. 11.6). Thus, in the current salt dissolution model, the assumption that persistent brines do not form until the RH reaches 50 percent may not be conservative. For example, if 30 percent RH is the threshold for the brine, then according to Figure 4.4-28, brines will not boil to dryness during the first 15 years or after about 60 years from the time of waste emplacement.

One possible feedback in this process is the potential for changing the RH in the potential emplacement drifts by the condensation of the water from the gas phase. In addition, this question was addressed to check that the needed mass of $H_2O$ was available in the gas phase to create such self-condensed brines. Because the gas phase in the drift is nearly all water vapor (i.e., the air mass-fraction is 0.01 or lower for periods A, B, and C as shown in Figure 4.4-5), the drift will contain over 100 kg of water vapor per waste package at an average temperature above the boiling temperature. This value is for an in-drift volume corresponding to that for a single waste package (see Chapter 3 for layout dimensions) corresponding to approximately 13 meters of drift length and a drift diameter of 5.5 meters. Subtracted from this total volume were the volume of the waste package (about 15 cubic meters, see Chapter 5 for dimensions) and the volume of ground support materials (4.35 cubic meters of concrete per meter of tunnel, see Section 4.3). Some of these materials are porous and the final gas-filled volume corresponds to approximately 75 percent of the total volume of the 13 m drift length. Compared to the amounts of $NaNO_3$ and $KNO_3$ on the waste package (ca. 0.5 and 0.04 kg, respectively) and the high solubilities of these salts, this would provide ample water vapor available to condense and dissolve $NaNO_3$ and $KNO_3$ completely while affecting the RH less than 1 percent. In addition, the flux of water vapor through the drift will moderate any effects to RH that might occur due to salt absorption of water vapor and brine formation.

The next RH threshold that is encountered occurs at approximately 80 percent RH, which corresponds to approximately 800 years (Figure 4-29). This value is based on the data for the Na and K chlorides and carbonates in Table 4-34, and NaCl, NaF, $Na_2CO_3$, $NaHCO_3$, $Na_2Si_2O_5$, and $Na_2SiO_3$ are expected to dissolve at this RH (see solubility discussion in Section 4.6.2.2.3.2). Except for NaCl, there are little data available on the maximum relative humidities for these solid phases. Like NaCl and NaF, the carbonate and silica salts are highly soluble, especially in high pH environments. Consequently, these salts may actually begin to dissolve at lower RH and earlier times. In addition, the actual RH thresholds for a given system depend on the relative concentrations of the various salts (Kinsman 1976). A more accurate representation of such salt dissolution processes could be made with experimental data to determine where these specific RH thresholds are for a particular salt assemblage

The final RH threshold is crossed at 1,250 years when the RH exceeds approximately 90 percent. This corresponds to the value for $Na_2SO_4$ given in Table 4-34. $Na_2SO_4$ is no longer stable at this approximate RH and will completely dissolve, representing the last of the highly soluble salts precipitated throughout the boiling period. This leaves $CaCO_3$ as the only normative salt remaining and accumulating on a potential waste package beyond 1250 years. Beyond this time, there will still be temperature and RH differences between the waste package surface and the drift wall (see Chapter 3 results). Because of these differences, any water getting on the waste package could possibly continually evaporate until it achieves the equilibrium brine composition

for the RH-temperature condition on the surface of the waste package. Evaluation of this effect is beyond the scope of this analysis and could entail the specific water flux onto the package surface, the evaporation rate, and the flow rate of water off of the package surface. The last aspect of this could be very dependent on the state of the package surface in terms of pitting and mineral crusts.

#### 4.6.2.2.3.4 Discussion of Potential Effects on Waste Package Corrosion

The results in this analysis of salts forming on a potential waste package should be viewed as bounding assumptions with a number of conservative assumptions included. These analyses use the thermal-hydrologic results for the center of the repository, which provides the longest period of boiling and thermally perturbed conditions possible. Shorter thermal perturbations will have less time, and hence less capacity, for salt deposition. Another conservative of these is that all of the salt that could be formed from the seepage flux is assumed to end up on the waste package. Although this represents a smaller mass than if the percolation flux were used, this value is still conservative because much of the soluble salts may in fact be precipitated within the rock matrix, and would not be able to move into the drift as salts deposited in fractures would. On the other hand, the seepage model (Chapter 2) is for ambient conditions and open drifts, but it is possible that the flux onto a potential package looks more like the percolation flux through the porous rock media once the potential drifts collapse onto the package. Therefore, these initial estimates of salt buildup provide a reasonable assessment of the magnitude of this process, but the details if needed could be more directly recovered from a coupled reactive-transport model that contains at least one of these simple salts, NaCl for instance. The distribution through time of that salt could be tracked and used to define the water salt composition at points outside the drift and on the waste package. The abundance of that salt could be used as a proxy for others and other salt abundances could be estimated using the relations inherent in the normative mineral calculations.

According to the results of this initial investigation of salt precipitation and dissolution on a potential waste package, approximately 5.7 kg of salt will accumulate on its surface from reflux water that drips onto it and boils away during the first 160 years after emplacement. During this time, brief episodes of corrosion could take place as reflux water wets the surface and boils away. Initially, the water drop in contact with the surface would be relatively dilute, but as boiling occurs, its pH will increase above 10 and corrosive ions such as $Cl^-$ will become concentrated. As the water drop completely boils away, all remaining salts precipitate. Though complete vaporization of the water that drips on the surface may be rapid, the high Cl concentrations and high pH generated during the boiling process may be important to corrosion rate calculations.

The bounding analysis above further indicates that after about 160 years, small parts of the surface of the waste package could be continuously wet. Most of the moisture will initially come from the absorption of water vapor by sodium and potassium nitrate. Thus, the liquid on the surface will be a highly concentrated brine. Although relatively dilute reflux water could mix with and dilute such a brine, the rate at which reflux water enters the drift would be small compared to the rate of vapor absorption by the nitrate salts. The rapid absorption of water vapor by salts at conditions above their maximum RH is well documented by Kinsman (1976). Furthermore, any dilution will be countered by boiling or evaporation while the potential waste package surface is still hotter and at lower RH than the drift wall.

The brine produced after 160 years will be alkaline and contain high concentrations of each of the soluble components. Solid salts containing chloride, carbonate, fluoride, and silica will persist for several hundreds of years, but fractions will dissolve into the newly generated brine as the salt assemblage equilibrates with it. Such brines are highly corrosive for particular alloys (see Chapter 5). Predictions of the potential corrosion that may be caused by this brine would depend on several factors, including the actual brine composition as a function of time and the degree to which this brine remains on the waste package surface.

As the RH increases, the remaining solid salts dissolve until there are no normative salts remaining on the waste package except for the highly insoluble phases, such as calcite. During this process, the equilibrated brine becomes more dilute but still contains relatively high concentrations of dissolved salts. The simple model used in this analysis indicates that all but calcite will dissolve within approximately 1,250 years from waste package emplacement. However, until the boiling period ends at approximately 2,000 years, reflux water will continue to boil and concentrate at least to the point at which it becomes saturated with respect to sodium sulfate.

Although these bounding analyses indicate that only about 10 to 20 kilograms of salt per waste package may form during the boiling regime, there are some conceptual aspects of this analysis that may provide alternate conceptual models for waste package corrosion scenarios. The results of this simple sensitivity analysis indicate that water could wet the average waste package on a continuous basis more than 10 times earlier than previously expected for the center of the potential repository. Such water will be in the form of an alkaline brine containing high concentrations of corrosive dissolved salts. In addition, because salts are hygroscopic, deposition of salts in fractures can lead to more common dripping that assessed currently in the seepage models. Because corrosion rates are important to the assessment of total system performance, the analysis of the evolution of salts and brine on the waste package is an area that could be analyzed in further detail in future analyses.

#### 4.6.2.3 In-Drift Microbial Communities Growth

The analyses presented below represent an initial bounding assessment of the microbial growth that may occur within a potential repository at Yucca Mountain. This allows evaluation of whether or not microbes should be an issue within the overall bulk geochemistry affecting the water composition within the drift, or if the microbial aspects of the system should be treated further only as they affect localized chemical conditions. Because MING is a new code and our overall model for microbial activity in the near field is relatively untested, we derived a simple plan to build confidence in our model. Presented below are three different case sets. The first two case sets build confidence in our model. The third set presents results that are repository specific.

Our presentation of the Swiss case demonstrates that our computer code functions adequately when compared to previous modeling activities using the same type of conceptual model and software code. The ambient cases (Cases 1-4 below) demonstrate that our selection of redox equations (Table 4-36) and how we handle the elemental breakdown of materials (Table 4-38) are adequate to produce results that are reasonable when compared to the actual measured system at Yucca Mountain. The 21PWR reference case (Case 5 below) is presented to evaluate the bulk

of the materials that are meant to be emplaced in the repository and is used to assess their potential to affect the natural system and the bulk geochemistry of the near-field environment. Sensitivities are also run for the 21PWR reference case (Cases 7-10 below) to test impacts to the system when material lifetimes (which are hard to estimate and are relatively unknown) are varied and when the groundwater composition returns to ambient conditions after the thermal perturbation of the repository (Case 6 below)

#### 4.6.2.3.1 Swiss Low-Level Case

To build confidence that MING was incorporating the portions of the Swiss LLW/ILW model correctly (Grogan and McKinley 1990, Grogan and Capon 1991), we decided to use the Swiss model input parameters and run MING. Both Grogan and McKinley (1990), and Grogan and Capon (1991) can be used as the source of parameter inputs. For detailed information on how the Swiss model parameter inputs were incorporated into a MING calculation, refer to Ehrhorn and Jolley (1998)

Before results of the benchmark calculation are presented below, two model differences should be spelled out that cause our results to differ very slightly from those reported in Grogan and McKinley (1990) and Grogan and Capon (1991). First, MING does not divide the Swiss calculation into an oxic and an anoxic phase. Therefore, the initial oxygen conditions are not reported in our results. The Swiss model limited this period to the time required to consume the oxygen, which was introduced into a normally anoxic environment due to construction. If we were to incorporate the early oxic phase, the results would be limited to the first year of the calculations, and would not show up in a significant way on our results plots. Second, MING does not incorporate radiolytic products that are generated within the waste package. Early on during MING model development, a decision was made not to incorporate this type of effect as there is little evidence that it would be of concern in a Yucca Mountain repository. This was based on the assessment that radiolysis outside waste package should be negligible for the given design thickness (Van Konynenberg 1996; see Section 4.2.1.3.3 above).

The results indicate that the portions of the nutrient and energy models used in the Swiss model and which are used in MING are operating correctly. Figure 4-78 shows a results comparison for both the energy and nutrient calculations reported by Grogan and Capon (1991) with those calculated with MING. From Figure 4-78, it can be seen that the results are virtually identical. However, examination of a table of results (Table 4-56) indicates that there is a slight difference in the energy calculations during the 271- to 3,030-year period. The difference is attributed to the nonincorporation into MING of the radiolitic products produced in the Swiss repository. This indicates that not incorporating those radiolytic effects for the Swiss case resulted in only very minor changes to the results.

#### 4.6.2.3.2 Ambient Case

To set up the proper framework for this case, we defined the input parameters for the natural system at Yucca Mountain . The section below describes the ambient microbial population.

#### 4.6.2.3.2.1 Ambient Microbial Populations

Microbial analyses conducted in the ESF have determined the existence of aerobic heterotrophs and autotrophs (Ringelberg et al. 1997). The organisms present include the following types: iron-oxidizing, sulfur oxidizing and nitrifying organisms. Cell counts for autotrophs range between 10 and 500 cells/g dry wt. and for the heterotrophs between $3.2 \times 10^4$ to $2 \times 10^5$ cells per gram. The samples were taken within a month of TBM excavation and sampling precautions were taken to ensure that there were no contamination problems from introduced microbes due to construction activities. Similar investigations were conducted on tuff samples taken from nearby Rainier Mesa and resulted in viable cell counts of about $10^4$ per g of crushed tuff (Keift et al. 1993).

Experiments were conducted on microbes cultured from tuff collected from the ESF to determine whhich, if any nutrients were the limiting factors in microbial growth (Kieft et al. 1997). The collected samples were thought to represent an uncontaminated ambient microbial population. The addition of both water and organic carbon to the cultured microbes caused substantial colony growth. From these experiments, the conclusion was that the potential for microbial growth is large, if nutrients and water are introduced into the environment.

Work done in several vadose zones in arid and semiarid sites indicate that the total numbers of microbes that are considered ambient populations range from $10^4$ to $10^7$ cells/g dry wt. (Kieft et al. 1993). Kieft et al. (1993) also stated that in the various vadose systems, there are many populations that are growth limited, most by water or organic carbon, but some systems were growth limited by nitrogen or phosphorous.

To compare the modeled results of the ambient system in MING with the above measured results, the ambient populations have to be converted to the equivalent unit of measurement that is reported by MING. Table 4-57 reports the grams (dry wt) of microbes in a one-meter length segment of TSw2 tuff having a repository drift radius of 2.55m. Documentation of this calculation is found in Jolley (1998b). Therefore, based on the ESF measurements, the mass of microbes in one lineal meter of repository drift ranges between 0.225 to 2.25 grams. If we were to do an equivalent calculation using a low $1 \times 10^4$ cells per gram (dry weight) value for Rainier Mesa, the value would be as low as 0.07 grams per lineal meter of repository drift.

#### 4.6.2.3.2.2 Ambient Case Inputs

Four ambient calculations (Cases 1-4) were done using MING to build confidence in the model and to bound the overall way that MING handles nutrient and energy calculations. The general intent of these calculations is that MING gives a reasonable answer, then we can assume that it would provide estimates that are at least in the order-of-magnitude range for the potential microbial abundance in the near field. These sorts of estimates form the starting point for evaluating which pieces of the system microbially-driven chemistry could have some capacity to influence.

In all four ambient cases the following input parameters were utilized: the average composition of J-13 water; an average cumulative influx of $O_2$, $N_2$ and $CO_2$; a repository temperature of 25°C; a RH of 0.99; and an Fe source within the TSw2 from biotite. The average J-13 water

chemistry values were taken from Harrar et al. (1990). These values are found on Table 4-58. Also included with the J-13 water composition was the addition of 1 ppm dissolved organic carbon ([DOC]; converted to the appropriate units and represented as $CH_2O$ in our simplified redox model; see Table 4-36) which seems to be the approximate value for DOC in the groundwater at Yucca Mountain (Jolley 1997). The cumulative gas influx values were determined using the late time values for instantaneous gas fluxes reported in Section 4.2.5.1.1 and are found on Table 4-59. The determination of the maximum mass of biotite that could be potentially found within a 1-meter repository drift volume (467 kg/m) and the available quantity (Wt. percent) of Fe that could be released from that amount of biotite (35 percent) are documented in Jolley (1998b) and are used in these calculations.

In addition to the universal inputs listed above, and those discussed in Section 4.2.5.2.4, each of the four cases differed by altering two inputs that were thought to be the biggest factors to natural microbial variability. They are the infiltration rate and the long-term release rate of $Fe^{2+}$ from biotite dissolution.

Due to cyclic climatic change, the infiltration rate at the surface of Yucca Mountain is thought to fluctuate (see Chapter 2). Therefore, two cases were used to look at the variability that infiltration has on the ambient system. First we used the long term average infiltration rate (I-LTA) as one of the variables and the present day dry infiltration rate (I-dry) as the second variable (see Chapter 2 for discussion on the climate and infiltration rates).

Release rates of $Fe^{2+}$ from biotite were determined using two simple hypotheses. The first is that biotite is thought to have altered into hematite and hematite is assumed not to be a syngenetic mineral. This provides a conservative bound on the rate of oxidation of the iron minerals in the rock because some, or all of the hematite in the rock could be syngenetic (CRWMS M&O 1998a, Section 3.5; Lipman et al. 1966). These rates should provide the largest amount of redox energy available for microbes to grow in the natural system. Since the volcanic eruptions that emplaced the tuff at Yucca Mountain occurred at least 10 million years ago and there is approximately 1 percent of each mineral in the current system, a material lifetime of 10 million years for remaining biotite dissolution was thought to represent a reasonable, but conservative, estimate for this value. Second, the Wt. percent of Fe in hematite is much larger than that of biotite and the Fe in hematite represents a much larger initial mass of biotite. Therefore, a lifetime of 1 million years was utilized as a largely conservative bounding approximation.

#### 4.6.2.3.2.3 Ambient Case Calculations

These analyses are presented in terms of the resultant growth of microbial mass. The mass of microbes that could be produced based on the limiting nutrient or the energy limitations of the system are both given in the figures. The lower of these two limitations provides the ultimate limit on the microbe mass. In addition, the amount of pH-corrected, standard-state redox couple energy available for microbes to use is presented.

**Case 1 (LTA biotite @ 1 million)** - The case-specific inputs into this calculation were the material lifetime of biotite set to 1 million years and the LTA infiltration rate to 42.06 mm/year. A plot of the results (Figure 4-79) shows that the modeled system would provide 0.137 g/year of

biomass. Additionally, the calculation shows that the system is energy-limited as the calculated available nutrients would yield a biomass of 1.627 g/year.

**Case 2 (LTA biotite @ 10 million)** - The case-specific inputs into this calculation were the material lifetime of biotite set to 10 million years and the LTA infiltration rate to 42.06 mm/year. A plot of the results (Figure 4-80) shows that the modeled system would provide 0.126 g/year of biomass. Additionally, the calculation shows that the system is energy-limited as the calculated available nutrients would yield a biomass of 1.627 g/year.

**Case 3 (PDD biotite @ 1 million)** - The case-specific inputs into this calculation were the material lifetime of biotite set to 1 million years and the PDD infiltration rate to 7.8 mm/year. A plot of the results (Figure 4-81) shows that the modeled system would provide 0.036 g/year of biomass. Additionally, the calculation shows that the system is energy-limited as the calculated available nutrients would yield a biomass of 0.302 g/year.

**Case 4 (PDD biotite @ 10 million)** - The case-specific inputs into this calculation were the material lifetime of biotite set to 10 million years and the PDD infiltration rate to 7.8 mm/year. A plot of the results (Figure 4-82) shows that the modeled system would provide 0.024 g/year of biomass. Additionally, the calculation shows that the system is energy-limited as the calculated available nutrients would yield a biomass of 0.302 g/year.

#### 4.6.2.3.2.4 Comparison of Ambient Case Results

Figure 4-83 compares the results provided in the four cases above with the actual measurements taken at Rainer Mesa and in the ESF. They show that all of the measurements are within an order of magnitude and seem reasonable in comparison to the inputs. Two factors may affect the variability of the results. First there could be some sort of nutrient contamination (not accounted for before sampling) or enhanced growth that allowed the measured ESF values to be elevated because the sampling took place at least a month after the ESF tunnel was constructed (Keift et al. 1993). Second, our model is somewhat simplistic, and therefore, we may not have included a measurable quantity of an energy-providing nutrient. Even with these two factors in mind, the ambient case results seem to indicate that we are modeling the bulk system adequately. Therefore, the ambient case allowing us to have some level of confidence that MING can produce reasonable modeling results for the more complex repository system.

#### 4.6.2.3.3 21 PWR Cases

To illustrate potential impacts that may occur as ambient rock conditions are disturbed because of construction activities and the introduction of repository design materials, 9 months after ESF excavation, microbial populations were resampled, resulting in a 5-fold increase in culturable populations. These increases were attributed to construction water use, diesel exhaust and other introduced materials (steel sets, concrete inverts, and conveyor belt residue; [Kieft et al. 1997])

The introduced materials (concrete, steel, waste packages, waste form, etc.) planned to be used in the current repository design most certainly will increase the numbers of microbes in and around the repository after construction is complete and operation of the repository begins. Therefore,

impacts on microbial growth and resulting populations from introduction of introduced materials are certain. The extent of those impacts is the focus of the MING calculations presented below.

#### 4.6.2.3.3.1 21PWR Case Parameter Inputs

Six separate calculations (Cases 5-10) were run using MING that modeled the effects of microbial growth from the construction of a repository drift with a precast concrete liner and the emplacement of a 21PWR waste package within the precast concrete liner repository drift. The following are universal inputs for all six of the runs presented below. Input values for the repository and waste package materials are discussed in Section 4.3, are shown on Tables 4-60 through 4-79, and are documented in Jolley (1998c and 1998d). The input for combined temperature, infiltration rate, and RH values for the waste package surface represent Section CC of the repository (see Chapter 3) where the first 5,000-year history represents the thermo-hydrological calculations for the PDD climate and infiltration rate (7.8 mm/year), and the remainder of the temperature history represents the LTA climate and infiltration rate (42.06 mm/year). This input is shown on Table 4-80. The input for the cumulative influx of $O_2$, $N_2$ and $CO_2$ is based on and corresponds with the repository temperature history derived from the thermohydrological calculations presented in Chapter 3. This input is found on Figures 4-34 and 4-35 and is discussed in Section 4.1.1.1 Other universal inputs needed for these calculations are discussed in Section 4.2.5.1.1.

Variable groundwater compositions are utilized in the six calculations below. These are based on the values calculated and presented in Section 4.2.5.1.2 (Table 4-23). These time dependent compositions are used in all six of the cases below with one exception. J-13 water (Table 4-58) replaces the compositional values from 100,000 years on in the Case 6 calculation.

Some materials used in the design evaluated below contain complex organic compounds that are known to be resistant to biodegradation (i.e., water reducer, and superplasticizer admixtures to the concrete design) as well as composite materials which contain organics, that are made up of more than one substance (i.e., electrical cable). These materials cannot be directly broken down into their basic elemental compositions and fed into the nutrient and energy stream. MING allows for a special reactant flag that allows for partial breakdown and/or multiple reactant compositions. The inputs used in the six cases below are found in Table 4-81 and have been documented in Jolley (1998e).

Another input that is varied in the calculations below is the material lifetimes used to calculate the availability of materials in both the nutrient and energy calculations. Material lifetime inputs for the six calculations below are given in Table 4-82. The reference case values are thought to be a reasonable lifetime of the given material based on general corrosion of like materials. In the case of the C-22 alloy and the cement, the selected values are subjective, thus the decision to include the four sensitivity calculations to attempt to bound the uncertainties. With this sort of uncertainty in input parameters, bounding the lifetime of the materials was attempted. Another objective behind altering these values in the calculations presented below is to determine how much impact the duration of a given material has on the amount of biomass produced.

Because the C-22 alloy and other internal waste package materials are not expected to be affected by microbial activity until the CRM material is penetrated, values for the layer flag in

MING need to be entered to allow the sequential degradation of the materials in question. Table 4-83 provides these input values for the 21 PWR cases.

#### 4.6.2.3.3.2 21PWR Case Calculations

**Case 5 (Reference Case)** - The reference case is defined by the inputs described above and those described in Section 4.4.3.4.

A plot of the results (Figure 4-84) shows that the modeled system would provide ~10 g/year of biomass during the lifetime of the mild steel components, ~1g/year over the lifetime of the C-22 alloy and the cement liner, and $1 \times 10^{-11}$ g/year after the materials are totally depleted when the nutrients are only provided by the incoming gas and water. Additionally, the calculation shows that the system is nutrient limited during the first 8,000 years after repository closure and energy limited for the remainder of the simulation. The results also indicate that either carbon or phosphorous are the limiting nutrients over the lifetime of the repository (Table 4-84).

**Case 6 (Reference Case with J-13 water added at 100k year)** - Case 6 is the same as Case 5 with the exception that at 100,000 years, J-13 water compositions (Table 4-58) were substituted for the incoming water used in Case 5. A plot of the results (Figure 4-85) shows that the modeled system would provide ~10 g/year of biomass during the lifetime of the mild steel components, ~1g/year over the lifetime of the C-22 alloy and the cement liner, and 0.1 g/year after the materials are totally depleted when the nutrients are only provided by the incoming gas and water. Additionally, the calculation shows that the system is nutrient limited during the first 8,000 years after repository closure and energy limited for the remainder of the simulation. The results also indicate that either carbon or phosphorous is the limiting nutrient over the lifetime of the repository (Table 4-84).

**Case 7 (21PWR CAM 5k CRM 50k Concrete 10k)** - Case 7 inputs are the same as those in Case 5 with the exception of the material lifetimes shown in Table 4-82. A plot of the results (Figure 4-86) shows that the modeled system would provide ~10 g/year of biomass during the lifetime of the mild steel components (5,000 year) and ~0.1g/year over the lifetime of the C-22 alloy (50,000 year). Impacts from the concrete liner (material lifetime of 10,000 year) are not distinguishable from the C-22 alloy values. Again, after the materials are depleted (at 50,000 years) $\sim 1\times10^{-11}$ g/year is calculated and is attributed to the incoming gas and water compositions. Additionally, the calculation shows that the system is nutrient limited during the first 5,000 years after repository closure and energy limited for the remainder of the simulation. The results also indicate that either carbon or phosphorous is the limiting nutrient over the lifetime of the repository (Table 4-84).

**Case 8 (21PWR CAM 5k CRM 50k Concrete 100k)** - Case 8 inputs are the same as those in Case 5 with the exception of the material lifetimes shown in Table 4-82. A plot of the results (Figure 4-87) shows that the modeled system would provide ~10 g/year of biomass during the lifetime of the mild steel components (5,000 year) and ~1 g/year over the lifetime of the concrete liner (100,000 year). Impacts from the C-22 alloy (material lifetime of 50,000 year) are seen as providing ~ 0.1g/year. Again, after the materials are depleted (at 100,000 years) $\sim 1 \times 10^{-11}$ g/year is calculated and is attributed to the incoming gas and water compositions. Additionally, the calculation shows that the system is nutrient limited during the first 5000 years after

repository closure and energy limited for the remainder of the simulation. The results also indicate that either carbon or phosphorous is the limiting nutrient over the lifetime of the repository (Table 4-84).

**Case 9 (21PWR CAM 10k CRM 250k Concrete 10k)** - Case 9 inputs are the same as those in Case 5 with the exception of the material lifetimes shown in Table 4-82. A plot of the results (Figure 4-88) shows that the modeled system would provide ~10 g/year. of biomass during the lifetime of the mild steel components (10,000 year) and between 0.1g/year and 0.01 g/year over the lifetime of the C-22 alloy (250,000 year). Impacts from the concrete liner (material lifetime of 10,000 year) are not distinguishable from the C-22 alloy values. Again, after the materials are depleted (at 250,000 years) ~$1\times10^{-11}$ g/year is calculated and is attributed to the incoming gas and water compositions. Additionally, the calculation shows that the system is nutrient limited during the first 10,000 years after repository closure and energy limited for the remainder of the simulation. The results also indicate that either carbon or phosphorous is the limiting nutrient over the lifetime of the repository (Table 4-84).

**Case 10 (21PWR CAM 10k CRM 250k Concrete 100k)** - Case 10 inputs are the same as those in Case 5 with the exception of the material lifetimes shown in Table 4-82. A plot of the results (Figure 4-89) shows that the modeled system would provide ~10 g/year of biomass during the lifetime of the mild steel components (10,000 year) and ~1 g/year over the lifetime of the concrete liner (100,000 year). Impacts from the C-22 alloy (material lifetime of 250,000 year) are seen as providing ~ 0.1g/year. Again, after the materials are depleted (at 100,000 years) ~$1\times10^{-11}$ g/year is calculated and is attributed to the incoming gas and water compositions. Additionally, the calculation shows that the system is nutrient limited during the first 10,000 years after repository closure and energy limited for the remainder of the simulation. The results also indicate that either carbon or phosphorous is the limiting nutrient over the lifetime of the repository (Table 4-84).

#### 4.6.2.3.3.3 Discussion of 21PWR Results

A few obvious results can be presented here from the calculations discussed above. First, it appears that a conclusion can be drawn about the order of magnitude of biomass produced, even when material lifetimes are not well known. Figure 4-90 plots the biomass produced from each of the 21-PWR cases. We see that regardless of the material lifetime, the peak and duration of biomass produced remain relatively constant. Table 4-85 shows the expected level of produced biomass for each major type of material that is emplaced in the repository. We can define the magnitude of any potential impact based on the materials that have been selected for use in the current repository design.

Second, with the differences that are shown between Case 5 and 6, the incorporation of colloidal iron (being the difference between the aqueous iron input in the incoming water calculated in Section 4.2.5.1.2 and that of J-13 water) and the addition of DOC into the system make a remarkable difference in the modeled results. Certainly, these two additions to the nutrient and energy calculations generate a certain level of biomass that seems to fit the ambient measurements of microbial populations. This level of activity seems to represent the system better than the extremely low values of biomass and energy that are produced without the return to ambient conditions (the use of J-13 water). Therefore, Case 6 is more representative of the

system than the other 21PWR cases based solely on the fact that the nutrients and energy values are so low.

Third, recognizable trends in the results can be attributed to the geochemical model that was built into MING. For example, in Cases 9 and 10 during the time that the only materials present are the C-22, the gas and the incoming water, we see that there is a slight increase of both energy and biomass produced over time. This could only be attributed to the long-term temperature decrease in the repository that results in an increase in energy available for MING. Other fluctuations that are not attributable to material depletion may also be the result of changes in pH of the water coming into the drift.

Note that the reason for the sloped dropoff between 200,000 and 260,000 years in Cases 9 and 10 is due to the way that MING calculates the results. MING calculates results for a given year based on when any of the inputs are expected to change or be depleted. Since there is no change to system inputs between 200,000 year and 260,000 year, there were no calculations done. Generally, the dropoff should be vertical and, therefore, it is concluded that the results in these two cases should actually reflect a vertical drop at 260,000 years.

#### 4.6.2.3.3.4 Conclusions and Recommendations

Ten grams of microbes produced from the materials in a 20.4 $m^3$ volume (one lineal meter of repository) does not seem to be significant, especially when compared to the masses of materials that are to be used in ground support and waste packages. In order to put the bulk impact into perspective, during the first 10,000 years for any given year, 10-12 grams of microbial mass would be generated from 17,750 kg (calculated from Jolley 1998c and 1998d) of material. This is equivalent to approximately 0.6 parts per million. Based on this small mass of microbes being generated, effects to the bulk chemistry in the drift are expected to be negligible. Although the bulk chemistry may not be affected by this level of microbial activity, there exists the potential to induce localized impacts to the near-field geochemistry. Microbes are known to produce inorganic acids, methane, organic byproducts, carbon dioxide, and other chemical species that could change the longevity of materials and the transport of radionuclides from the near field.

Certainly, 10-12 grams of microbes would have an impact on corrosion if they were located on a 1-meter segment of waste package as multiple biofilms, which could then greatly enhance the pitting corrosion of a waste package. Ten to 12 grams of microbes do represent a rather large number of potential organic colloids. The equivalent number of microbes this equates to is on the order of $8 \times 10^{13}$ microbes. To simplify and use a value of $10^{14}$ microbes/year/meter and convert this value to a flux, first multiply a 5.5 $m^2$ of drift cross section by the LTA flux of 42 mm/year. That would calculate a value on the order of $2.31 \times 10^5$ ml year. Dividing the $10^{14}$ microbes/year/meter by $2.31 \times 10^5$ ml/year gives an approximate particle flux of $4.3 \times 10^8$ microbes/ml, which could then be released from the repository each year.

Not only is the potential number of colloids a significant concern, but microbes tend to stabilize natural colloids by facilitating colloidal agglomeration (Hersman 1995) and act as chelating agents via production of siderophores (Hersman et al. 1993). Microbes can also act as surface reactants for dissolved metals (Fein et al. 1997). These three qualities can be significant in determining microbial impacts on the transport of radionuclides.

In light of the above findings, the focus of future work could be directed towards quantifying the ability of microbes to affect, and measuring the impact of microbes on, radionuclide transport, both as colloids, and to a lesser degree as producers of strong complexing agents of multivalent metal ions. The analyses above indicate that

A. The estimates of microbe masses growing in the potential repository system suggest that effects to the NFGE would be negligible

B. Microbial influence corrosion (MIC) and other localized microbial attack of materials cannot be precluded

C. Consideration of microbes as colloids could be pursued in future work

D. There is some potential for additional legands generated locally; however, the radionuclides would have to directly compete with many other available multivalent metals, and so this is a lower priority area for future work.

### 4.6.3 Interpretations, Uncertainties, and Development of Parameter Inputs for RIP

In the sections above, sensitivity studies are provided regarding the possible changes to the system gas and water compositions due to possible interactions with concrete, spent fuel, salt deposits, and microbial communities. Each of these modeling areas is in a different level of development and each section above (or the corresponding section in Section 4.4) covers part of the uncertainties involved with the model results. Because of the large mass of concrete included in the reference design of the potential repository (Section 4.3) and the ability of concrete/cement to affect the water composition for long time frames, this aspect of the system was abstracted into a sensitivity study for use by the total system performance assessment model. This was done for only the expected-value case, which is given directly by the results of the analyses. The values of pH, total dissolved carbonate, ionic strength, and oxygen fugacity are shown in Table 4-86 with the abstracted time periods to which they apply. These values for the NFGE were supplied to the TSPA model for use throughout the EBS (Chapter 11), as well as to the waste package degradation models for development of a specific waste package failure history for these conditions (Chapter 5).

## 4.7 SUMMARY AND RECOMMENDATIONS

Analyses for the TSPA-VA base case used a water composition that represents the incoming, thermally perturbed fluid that reacted with corrosion products (iron oxides). Because concrete is a major component of the repository design, near-field geochemical analyses were also performed to simulate the reaction of concrete and water. These analyses and results, although not part of the base case, are used for some of the TSPA-VA sensitivity studies. Those sensitivity studies evaluate the effect of concrete on both the total system performance and the EBS performance. Changes to the composition of water as it reacts with freshly exposed spent fuel and subsequent alteration products were also evaluated and those analyses were used as part of the conceptual representation of secondary-phase evolution for the waste form (see Chapter 6). Near-field geochemical analyses were also used to develop the conceptual scenarios for sensitivity studies of other component models.

### 4.7.1 Summary of Analyses Results

Within the TSPA-VA analyses, the representation of the NFGE has been vastly improved beyond that of the ambient geochemistry being imposed within the potential drifts for all of time. The models presented above and their results allow incorporation of thermal perturbations to the gas phase and water compositions that enter the drift and react with materials. The new incoming gas phase evolution is tied directly to the current thermohydrologic models results. In addition, these new analyses incorporate materials effects on the geochemistry within potential drifts, as corrosion products for the base-case analyses and concrete, and spent fuel in sensitivity cases. Included within the base-case analyses of the NFGE component is a model for the concentrations of natural and introduced colloids that could sorb radionuclides and transport them out of the system more efficiently than dissolved species. Process-level sensitivity analyses were conducted to provide initial estimates of salt deposition. In addition, sensitivity analyses were done to provide initial assessments of the potential for microbial growth within the drifts. The focus was to evaluate if microbes should be considered as potentially large contributors to the bulk geochemistry of the system, or viewed primarily as a process of potential local control on the waste package surface.

Incoming water and water reacted with goethite as a proxy for corrosion products have about the same composition. The pH is perturbed to high values during the boiling period because of decreased amounts of carbon dioxide in the gas phase. The ionic strength is also higher at this time because of the assumed 90 percent boiling of the fluids that may enter the drift during the boiling regime periods. The values of pH, total dissolved carbonate, and ionic strength are passed to both the waste package models and waste-form/EBS transport models for use in the base-case analyses for the TSPA-VA. These values are given in Table 4-44 for both the expected values and the uncertainties on these values. In addition, the model for concentration of colloids was developed as a function of ionic strength and implemented directly within the total system performance assessment code.

For implementation into the TSPA-VA analysis code RIP (Golder 1998, see Chapter 11), the relation shown in Equation 4-10 was transformed into a stochastic function for colloid mass concentration (kg/m$^3$). The conversion to this relation was accomplished by assuming spherical particles of radius 100 nm and a density of 2 gm/ml, resulting in the following relation:

$$\text{colloid concentration (kg/m}^3) = 8.4 \times 10^{-12} * 10^{(S*\text{sigma}+7-34*I)} \qquad (4\text{-}17)$$

where sigma = $(.023+65.5I^2-.057I)^{0.5}$ representing the uncertainty in the result, I stands for the ionic strength, and S signifies the sampling parameter used by RIP to produce a stochastic variation in the result. Within RIP, the parameter S is sampled from -3 to +3 uniformly in order to encompass 99 percent of the uncertainty in the relation.

The process-level sensitivity analyses for concrete-modified water were used to constrain a TSPA-VA sensitivity study of alkaline effects in the potential drifts. These represented a larger departure from the incoming water composition compared to reaction with corrosion products only. The water composition results are summarized in Figures 4-91, 4-92, and 4-93 for the NFGE through the first 100,000 years for pH, total dissolved carbonate, ($\Sigma CO_3^{2-}$), and ionic strength (I), respectively. In the figures, different modeled results apply to the different regions,

both within and outside the drift. During the boiling period (0–2,000 years for the center portion of the modeled repository), pH values are near 10 for both incoming water and water that has reacted with iron oxides. Later, the pH values drop. The total dissolved carbonate ($\Sigma CO_3^{2-}$) values show a large decrease until about 1,000 years. This decrease is caused mainly by changes to gas compositions as shown in Figures 4-32 and 4-33. The ionic strength of these fluids is about 10 times higher until about 2,000 years, primarily because of concentration by boiling.

By 10,000 years, the calculated pH values are near 8 for both incoming water and water reacted with iron oxides, which is in the range of measured ambient pH at the site. However, for the water that reacted with concrete and iron oxides, the pH values remain close to 11 for the entire 10,000-year period, and the total dissolved carbonate ($\Sigma CO_3^{2-}$) and ionic strength values are lower than for the incoming fluid. These lower values are caused primarily from interaction of water with the alkaline and sulfate components of cement in the concrete; even with additional reactions that bind calcium included, such as silicate-mineral formation, the alkaline components of the concrete still influence water pH.

For the period from 10,000 to 100,000 years, pH values are projected to be about midway between 7 and 8 for water that reacted with concrete and iron oxides. This range is slightly lower than for the cases without concrete. The total dissolved carbonate ($\Sigma CO_3^{2-}$) and ionic strength values are also slightly lower. These differences also result from the different bulk chemistry in the system with concrete, with the calcium content of the solids and fluid playing a primary role.

The model values shown for gas compositions in Figures 4-32 and 4-33, and for water compositions in Figures 4-91 through 4-93, were assumed to represent the expected values of those parameters. However, because processes in the NFGE have a large amount of associated uncertainty, these deterministic results were also used to generate probability distributions for the TSPA-VA base case analyses. The uncertainties assessed for the model were used to construct the distributions, which were defined as log normal for dissolved constituents (this corresponds to a normal pH distribution, see Sections 4.4.4 and 4.5.3).

The near-field geochemical analyses showing the effects of spent-fuel reaction on water composition were presented in Section 4.6.2.2.2. Those results indicate that the water composition will change the most where most of the fuel is available for reaction, with lesser effects if only a portion of the fuel is exposed to the water. In addition, maintaining such water composition changes depends on active alteration of primary spent fuel to secondary uranium phases. Once the fuel is completely altered, the secondary-phase evolution causes only minor changes to water composition. The modeled period for completely altering the spent fuel once it is exposed is about 2,000 years, but the calculated evolution of secondary phases continues over hundreds of thousands of years. These time differences indicate that reaction of spent fuel with water will produce either major changes to the fluid composition for relatively short times or minor effects over longer times.

At both higher (70°C) and lower (30°C) temperatures, the water chemistry is affected to a larger extent if all of the fuel is exposed to reaction. At 70°C the ability of the spent fuel to alter the pH (and other characteristics of the water) begins to decrease almost immediately and is almost entirely dissipated after about 2,000 years. The calculation predicts that exposed spent fuel will

be consumed in about 2,000 years, converted to the major secondary phase, schoepite. Once the exposed spent fuel is converted to schoepite, the water composition tends to revert to the incoming composition. This conversion takes longer at 30°C because the reaction rates are lower than at 70°C.

Additional analyses presented above (Section 4.6) for the reaction of spent fuel with water specifically included neptunium in the secondary phases. The results of these indicate that the pH of incoming water is changed by less than about two tenths of a unit during secondary phase dissolution. Although the dissolved calcium content decreases greatly, only small (about 10 percent) changes occur for dissolved carbonate and silica, and for ionic strength. These small effects indicate that the behavior of the secondary phases may be primarily controlled by the composition of the fluid entering the waste package. Because the major effects on fluid composition from spent fuel reaction appear either large but relatively short lived or minor for many constituents (depending on temperature and percentage of exposed fuel), the only aspect of the performance assessment that was modified to address these effects was the waste form component itself. This modification was accomplished in a sensitivity analysis by using the alteration rate of secondary uranium phases to assess the concentration of neptunium in the resulting fluids. These analyses are discussed in detail in Chapter 6.

Process-level sensitivity analyses were also performed in the areas of precipitates/salt build-up and microbial growth (Section 4.6). The models for salt buildup assess a normative salt assemblage based on the incoming water composition boiling to dryness. Based on the current seepage rates, these normative salts could potentially build up to tens of kilograms per waste package in the center of the repository. Because the salts will condense water and dissolve at relative humidities less than 100 percent, small amounts of brine will form even during the boiling period, but the built-up salts would be completely redissolved within about 1,300 years. Although there is not a large mass of salt per waste package, the presence of these salts substantially shorten the period during which the waste package would be dry.

An assessment of the potential limits to microbial growth due to both nutrient limitations and energy availability from oxidation/reduction reactions was completed using the newly developed MING code for this model that incorporates Yucca Mountain site-specific enhancements to a previously developed model (Section 4.6). The results for a 21 PWR waste package within the drift indicate that microbial growth appears to be limited to about a few tens of grams of microbes per meter of the waste package. This amount does not seem likely to be large enough for microbes to play a controlling role in the geochemical evolution of the system, but they may still be important from a localized corrosion standpoint, or as a source of organic colloids in the NFGE.

### 4.7.2 Implications for Performance Assessment Analyses

Some of the results have been used directly within TSPA-VA analyses, whereas others have only provided an initial assessment of the magnitude of particular aspects of the geochemical system. The NFGE component does not directly change a performance parameter such as release rate from the EBS. Rather the mechanism for the NFGE results to affect the system consequences is through the other TSPA-VA component models. These other components such as the waste package evolution and the waste form evolution can affect changes to the performance more

directly and the NFGE contributes to that only by how those models respond to the changes in environment parameters.

The near-field geochemical analyses for the composition of water reacting with concrete support components in the emplacement drifts indicate that water will have a pH near 11 for at least 10,000 years but for much less than 100,000 years. This pH change represents a substantial change to ambient water composition and may affect the ability of the EBS to contain radionuclides within the drift. This would in turn change the source term for total system performance analyses. In addition, higher pH fluids migrating into the geosphere can react with the host rock, potentially altering minerals along flow paths and providing an aqueous medium that enhances actinide transport in the UZ. Both of these aspects of the analysis were assessed with TSPA-level sensitivity studies (Chapter 11). As described in the following paragraphs, impacts on the source term and the EBS were explicitly addressed based on the changed fluid composition. The impacts on transport through the geosphere were evaluated through simulations using conservative assumptions.

The effects of concrete-modified water on a number of the components related to the source term have been explicitly evaluated. The waste-package corrosion models include a submodel for aqueous corrosion of the outer barrier, specifically designed to address pH conditions above 10 (Chapter 5). This submodel was used to generate a set of waste-package degradation histories for concrete-modified water. These waste-package models and results are presented in Chapter 5. The waste form dissolution models directly incorporate rates that depend on pH and total dissolved carbonate Chapter 6. Changes to the ionic strength for concrete-modified water were reflected in changes to colloid amounts (as discussed above in Section 4.5.2.3 and 4.4.3.3). These results were provided directly to the TSPA integration model, and impacts on performance were analyzed in a sensitivity analysis based on the expected value compositions for concrete-modified water (Chapter 11).

The migration of alkaline fluids into the UZ may have a number of effects, depending on the flow pathway and diffusion rates. Such fluids can alter the siliceous host rock, both along fracture pathways and in the matrix. The mineralogical changes, the distance over which they may occur, and the distribution of such alterations are still very uncertain but could produce changes in the amount of fracture-matrix interaction and the sorption of radionuclides within the UZ host rock. Because of the complex and uncertain nature of this alteration, current process models do not include any explicit representation of these potential changes to minerals along radionuclide migration pathways. In addition, the migration of a high-pH (alkaline) plume through the UZ would create aqueous pathways with little or no actinide sorption capability. Also, this potential effect has not been incorporated explicitly into process models. Because of the likelihood that alkaline fluids will be generated by water in contact with concrete in the repository (Section 4.6.2.2.1), this effect was included in sensitivity analyses of UZ transport. To bound the consequences of this effect, the UZ sorption coefficients for actinides (uranium, neptunium, plutonium, and protactinium) were set to zero (Chapter 7).

The potential impacts from concrete-modified water compositions assessed in the sensitivity results discussed above appear to be greatest for the 10,000-year period (see discussion in Chapters 5, 6, 7 and 11). The greater effects during the first 10,000 years are mainly caused by impacts to waste-package performance because earlier and more frequent failures allow greater

exposure of the waste form inventories at earlier times. These impacts cause the peak value of the expected dose rate for the first 100,000 years to occur at about 6,100 years (Chapter 11). This expected dose rate is qualitatively very different from the base case results and reflects the differences in source term behavior in the first 10,000 years.

For periods in which water composition is dominated by spent fuel reactions, different source-term constraints may be necessary than for periods of unaltered water composition. Spent fuel dissolution rates, radionuclide solubility limits, and radionuclide transport (colloidal and aqueous) should particularly reflect the altered solution composition. The impacts on performance from reaction with spent fuel depend on the magnitude of the water composition changes and the period over which the changes exist.

For the latter case, the current representations should be sufficient to bound the behavior of radionuclide release from the waste form. For the former case, the analyses could be improved by considering a short time period when water composition is dominated by releases from spent fuel followed by evolution of secondary uranium phases over geologic time.

Although changes to both solubility limits and colloid stabilities/abundances have not yet been evaluated for the geochemical conditions during the period of active spent fuel alteration, changing spent fuel dissolution rates are explicitly coupled to changing water chemistry in the completed near-field geochemical analyses. Because of the potential for incorporating other actinides (e.g., neptunium) into the secondary uranium phases, the primary focus of these sensitivity studies was the long period of secondary-phase evolution. Also, these secondary phases dissolve or alter at a much lower rate than the primary spent fuel (Chapter 6). The model incorporating neptunium into secondary uranium minerals and the resulting rates of release of uranium and neptunium is presented in Chapter 6 and the results of sensitivity studies using secondary-phase constraints on releases of neptunium over long time frames are discussed in Chapter 11.

There is a large potential for the NFGE model of precipitates/salts to affect the conceptual model of water on the waste package, although there does not appear to be a large mass of salt or any long time period that it would remain on the package. Such conceptual alternative models still need to be developed and will be facilitated by process-level evaluations of the salt buildup and dissolution with more coupled models. Colloids can enhance the transport of some radionuclides, but given the colloid abundances as constrained by their stabilities in systems from around the world, these effects do not appear large. The sensitivity analyses and results of colloid transport are covered in other chapters of this technical basis document (Chapters 6, 7, 8 and 11). Similarly, the microbial communities model indicates that there may not be a large mass of microbes growing within the drift and that bounding the specific effects of localized microbial pitting may be the major portion of assessing their chemical effects. However, another possibility is that microbes would represent another colloid source that could be as large as the others included. Such colloids may affect radionuclide transport if radionuclide attachment is stronger or less reversible than for colloids already considered. These could be of comparable abundance to those of the natural system or those generated as equilibrium concentrations from the introduced materials, but may have substantially different capacity for sorbing radionuclides.

### 4.7.3 Guidance for Future Project Activities

These results suggest that further consideration be given to substituting other ground support materials for the concrete in the current design. However, there are uncertainties within the models currently employed to evaluate the NFGE. To better constrain changes from materials evolution in the drift, further improvements could be made in the following areas:

- NFGE models to evaluate the interaction of water and concrete
- The waste-package degradation model for the outer package in alkaline (Chapter 5)
- Transport models for the waste form and the EBS (Chapter 6).

Specifically, the confidence in the near-field geochemical model for concrete could be improved with more comprehensive thermochemical data (both equilibrium and kinetic) for phases in the cement system, in particular at the higher temperatures expected for this system. The possible neutralization of the concrete alkalinity depends on the change in gas composition during carbonation of the cement phases. Therefore, a better understanding of gas composition changes in the unsaturated, thermally perturbed system would also improve confidence in the analysis. Such improvements could be based, in part, on measurements from the drift scale heater test. This further understanding, coupled with a two-phase, reactive transport model, would provide more confidence in the assessment of the constraints on concrete carbonation processes.

In addition, an evaluation of the chemical and mineralogical changes in the concrete mass during the preclosure period would allow assessment of the potential for concrete carbonation from the relatively large fluxes of carbon dioxide through the system over that period. A model for concrete based more on the mechanical changes would facilitate conceptualization of flow pathways through the degraded concrete materials. All of these developments would allow a coupled, reactive transport representation of concrete alteration that would provide more confidence in the assessment of the system.

Additional modifications to the waste form model to improve confidence in the model include solubility-limited radionuclide distributions that are explicitly dependent on the pH (actually, dependent on the total water composition as indicated by changing phase relations in the chemical system). Identifying sorption mechanisms and evaluating the dependence of sorption on the composition and mineralogy of the specific material would help to better incorporate sorption processes into the model. Incorporating both of these features into the model could enhance the understanding of radionuclide retention in the engineered barrier system.

Several concrete-related processes that are still relatively unconstrained are the coupling between concrete alteration, changes in concrete permeability, and flow through concrete. The model should include mechanical changes in porosity and permeability of the concrete. Additional concrete characteristics such as the mass of its organic constituents, as well as additional components of the waste-package materials such as nickel and chromium, should be included in evaluations of the NFGE. Finally, the migration of alkaline plumes from the concrete masses into the geosphere, with associated alteration of the host rock and radionuclide transport pathways, is not well constrained. The development of a coupled, reactive transport representation would aid the assessment of these potential effects.

In addition to the recommendations based on the results of performance assessment sensitivity analyses discussed in Chapter 11, a number of general conclusions can be drawn from the NFGE process-level analyses presented in Sections 4.4, 4.5, and 4.6. Given the gas flux through the mountain, local reducing conditions do not appear likely after the intense boiling period. Furthermore, the mass of concrete in the current design appears to have the capacity to be a major chemical perturbation for approximately 10,000 years.

Preliminary bounding assessments on precipitate/salt buildup during boiling indicate that masses may not be large. However, some alternate conceptual models for water in the drifts and on the waste package may need to be considered. Similarly, preliminary bounds on biomass production suggest that microbial growth may be nutrient limited within the potential drifts for long periods.

Based on these conclusions and the discussions regarding uncertainties in NFGE component models, a number of areas for future improvements to this work could be pursued. One possible area would be to use both theoretical techniques for estimating thermochemical data and experimental studies to better constrain the thermochemical (equilibrium and kinetic) data for phases in the cement system for a variety of conditions. This is also true for studies of secondary uranium phase stabilities and kinetic rate laws (in particular, for trace actinide incorporation, see Chapter 6). However, an alternate method for reducing uncertainty in this system would be to utilize experimental methods for evaluating the relative importance of the chemical reaction rate versus the fluid flow rate in a system. Such work can provide constraints on what conditions are well represented by simple models using equilibrium approximations, and provide criteria to evaluate the need for explicitly coupling processes together. Each of these types of effort benefits from being pursued in conjunction with an active process-level modeling effort that allows consistent interpretation of experimental measurements.

There are a number of areas to improve the confidence in the NFGE component, as well as the components that connect to it. One primary area is including a higher degree of coupling between thermomechanical-hydrochemical processes. This is particularly true for the thermal-hydrologic and UZ flow components. These areas would benefit from incorporation of more details of drift materials, both their physical-mechanical evolution and chemically induced changes to the permeability of the concrete. These aspects would improve the description of water flow pathways and allow for development of more specific NFGE scenarios tied to more realistic system evolution.

Areas in which confidence could be improved based on either field testing or laboratory experiments include the models of gas compositions, which could be tested against observed gas compositions in the rock and in the drift measured during the drift scale thermal testing. The concrete evolution model is another potential area for additional testing in terms of the response of the concrete pore waters to the different system gas and thermal conditions. This could include evaluating thermochemical data for specific phases, in particular kinetic data, so that coupled reactive transport models could be applied to clarify rock and water evolution along the concrete flow pathways, or pursuing experimental assessment of where the reaction rates are fast relative to the flow system such that equilibrium assumptions can be confidently applied. In addition, colloid transport could be assessed using well-constrained field data and colloid concentrations evaluated using more site-specific measurements.

Additional development within the conceptual framework of the NFGE component is needed to improve confidence in the analyses. Many of these enhancements would follow from the additional investigations presented in this section. For the region outside the drift these would include:

- A more comprehensive evaluation of the potential heterogeneity of water composition flowing through the fracture system and interacting with the drift environment
- Explicit $CO_2$ evolution from water and minerals coupled to the gas flow in the thermohydrologic system.

Similarly for the system inside the drift, these would include:

- Explicit coupling of flow and reaction tied to a model of mechanical evolution of the material in terms of fracture pathways and distribution throughout the drift
- Consideration of thermally aged concrete mineralogy and how that aging affects the alkalinity of concrete
- Coupled chemical alteration and changes to physical properties of the concrete to evaluate the changes in flow pathways as reaction proceeds
- Continued efforts to link biomass production with development of a more sophisticated approach to include specific microbial activity for local waste-package corrosion effects
- Consideration of a more comprehensive chemical system including organic materials (other than as nutrients for microbes).

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