

**OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT
ANALYSIS/MODEL COVER SHEET**

1. QA: QA

Page: 1 of 33

Complete Only Applicable Items

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| Describe use: Used to develop in-package chemistry abstraction for TSPA. | |

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| Describe use: Used to develop in-package chemistry abstraction for TSPA. | | |

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**OFFICE OF CIVILIAN RADIOACTIVE WASTE
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1. Page: 2 of 33

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Initial Issue

This document supercedes ANL-EBS-MD-000050 REV 01. A math error in Attachment II was corrected.

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ACRONYMS

| | |
|-------|--|
| AMR | analysis/model report |
| CD | compact disc |
| CPU | central processing unit |
| CRWMS | Civilian Radioactive Waste Management System |
| CSCI | Computer Software Configuration Item |
| CSNF | commercial spent nuclear fuel |
| DHLWG | defense high-level waste glass |
| DIRS | Document Input Reference System |
| DOE | U. S. Department of Energy |
| DSNF | DOE spent nuclear fuel |
| DST | drift-scale test |
| DTN | data tracking number |
| EBS | engineered barrier system |
| EDA | enhanced design alternatives |
| FEP | features, events, and processes |
| FFTF | fast flux test facility |
| IRSR | Issue Resolution Status Report |
| LLNL | Lawrence Livermore National Laboratory |
| M&O | Management and Operating Contractor |
| MOX | mixed oxide |
| NRC | U.S. Nuclear Regulatory Commission |
| PC | personal computer |
| PWR | pressurized-water reactor |
| QA | Quality Assurance |
| SCFT | solid-centered flow-through |
| SCM | Software Configuration Management |
| SCR | Software Change Request |
| SQR | Software Qualification Report |
| THC | thermal-hydrologic-chemical |
| TSPA | Total System Performance Assessment |
| UOX | uranium oxide |
| YMP | Yucca Mountain Site Characterization Project |

1. PURPOSE

As directed by the Technical Work Plan (CRWMS M&O 2000e), the purpose of this document is to examine the probable range of in-package fluid chemistries likely to result from the influx of ambient fluids into, and their reaction with, breached waste packages containing either commercial spent nuclear fuel (CSNF) or codisposed U.S. Department of Energy (DOE) spent nuclear fuel (DSNF) and defense high-level waste glass (DHLWG). The intended use of this analysis/model report (AMR) is to develop in-package chemistry for Total System Performance Assessment (TSPA). This model provides input to the solubility and colloid models, which are principle factors. The scope of this work is to examine the primary processes likely to control the major element chemistry of reacting in-package fluids, which include: equilibration with gas phase carbon dioxide and oxygen at near-atmospheric levels; dissolution of steel alloys used to construct the basket materials and the waste packages; dissolution of high-level waste glass and fuel elements; and the growth of secondary oxides, silicate, and carbonate minerals. Sorption by the latter phases is not considered here because sorption is not envisioned to control concentrations of major elements. Sorption may control dissolved phase concentrations of trace elements.

The objective of this document is to examine the likely variation in major-element composition of in-package fluids. Estimated fluid compositions feed directly to a number of other calculations critical to a performance assessment of the proposed repository, including estimation of radionuclide transport into the engineered backfill system and, ultimately, the biosphere. Important compositional data that must be estimated before radionuclide solubilities can be constrained include pH, Eh (the electrode potential with respect to the standard hydrogen electrode - volts), dissolved carbon levels, and ionic strength. Note that these all are likely to vary as a function of time. Time scales of interest begin with the first breach of the waste package and often extend for at least 50,000 years, which is often the amount of time required for a substantial portion of the waste package solids to react with incoming fluids. The document deals primarily with reactions that occur after the original thermal pulse has passed, and temperatures have returned to ambient levels. There is, therefore, no consideration of early-stage, high-temperature phenomena. In other words, initial failures are not included in the present analysis. Pervasive wet degradation of waste package components is not expected to prevail until sufficient quantities of liquid-phase water are able to enter breached waste packages, an event envisioned to occur only after passage of the thermal pulse.

To perform such a calculation, termed a reaction-path simulation, requires a number of specific inputs, some of which are known only semi-quantitatively. All of these are discussed in Section 4. For the latter (e.g., fluid flux rates, degree of clad failure), bounding ranges of inputs are used. The primary input parameters needed for the in-package geochemistry reaction-path simulation include:

1. Input fluid composition and flux
2. Degree of clad failure
3. Glass and fuel degradation rates
4. Steel alloy corrosion rates
5. Identities of secondary phases likely to form.

The input values will be tracked for ultimate use in the Process Model Reports and Total System Performance Assessment (Site Recommendation and License Application). The numerical code that simulates the reaction of fluids with the waste form is EQ3/6 (Wolery 1992). With a few exceptions (see Section 4.1.5), the alteration phase identities are calculated from the EQ3/6 database. The design information used for the calculation is largely EDA (enhanced design alternatives) II. A pre-EDA II CSNF waste package geometry is used, but subsequent changes in design are not expected to materially change the reaction trends discussed here. The results of the in-package chemistry AMR will not be affected by minor changes in the EDA design (see Section 5, Assumption 5.7 and 5.8).

2. QUALITY ASSURANCE

An activity evaluation (CRWMS M&O 2000e, Enclosure 1), which was prepared per AP-2.21Q, *Quality Determinations and Planning for Scientific, Engineering, and Regulatory Compliance Activities*, determined that the Quality Assurance (QA) program (DOE 2000) applies to the activity under which this analysis was developed. Control of the electronic management of data was accomplished in accordance with the controls specified by CRWMS M&O (2000e, Enclosure 4).

3. COMPUTER SOFTWARE AND MODEL USAGE

3.1 EQ3/6 SOFTWARE PACKAGE

The EQ3/6 software package originated in the mid-1970s at Northwestern University (Wolery 1992). Since 1978 Lawrence Livermore National Laboratory (LLNL) has been responsible for maintenance of EQ3/6. The software has most recently been maintained under the sponsorship of the Civilian Radioactive Waste Management System (CRWMS) of the DOE. The major components of the EQ3/6 package include: EQ3NR, a speciation-solubility code; EQ6, a reaction path code, which models water/rock interaction or fluid mixing in either a reaction progress mode or a time mode; EQPT, a data file preprocessor; EQLIB, a supporting software library; and several (> 5) supporting thermodynamic data files. The supporting data files contain both standard state and activity coefficient-related data. Most of the data files support the use of the Davies or B-dot equations for the activity coefficients; two others support the use of Pitzer's equations. The temperature range of the thermodynamic data on the data files varies from 25°C for some species to a full range of 0-300°C for others. Many of the thermodynamic data that are relied on in the present calculations were measured at 25°C (see Section 5 [#5.5] for further explanation). EQPT takes a formatted data file (data0) and writes an unformatted near equivalent called a data1 file, which is actually the form read by EQ3NR and EQ6. EQ3NR is useful for analyzing groundwater chemistry data and calculating solubility limits.

EQ6 models the consequences of reacting an aqueous solution with a set of solids, which dissolve according to kinetic rate laws. It can also model fluid mixing and the consequences of changes in temperature. This code operates both in a pure reaction progress frame and in a time frame. In a time frame calculation, the user specifies rate laws for the progress of the irreversible reactions. Otherwise, only relative rates are specified. EQ3NR and EQ6 use a hybrid Newton-Raphson technique to make thermodynamic calculations. This is supported by a set of algorithms, which create and optimize starting values. EQ6 uses an ordinary differential equation

integration algorithm to solve rate equations in time mode. The codes in the EQ3/6 package are written in FORTRAN 77 and have been developed to run under the DOS and Windows 95 operating environment.

EQ6 Version 7.2b, as originally distributed by LLNL, does not contain a solid-centered flow-through (SCFT) mode. An SCFT calculation much more closely mimics the likely path of waste package alteration, and is therefore critical. This mode was added to EQ6 per Software Change Request (SCR) LSCR198 (CRWMS M&O 1999c) and the Software Qualification Report (SQR) for Media Number 30084-M04-001 (CRWMS M&O 1998e).

3.2 SOFTWARE APPROVED FOR QA WORK

The software package, EQ3/6, Version 7.2b, was approved for QA work by LLNL and is identified as Computer Software Configuration Item (CSCI): UCRL-MA-110662 V 7.2b (CRWMS M&O 1998f; 1999e). An installation and test report was written and submitted to Software Configuration Management (SCM), and the proper installation was verified before the runs described in this calculation were made. The implementation of the SCFT mode is covered by SCR LSCR198 and the SQR for Media Number 30084-M04-001. The SCFT addendum was installed on three of the central processing units (CPUs) identified in block 16 of the SCR, and the installation and test reports were filed and returned to SCM before the calculations were run. All the EQ6 runs were performed on a Sandia National Laboratories system CPU (#S822733), a Dell 300 MHz Pentium II. In this study EQ3/6 was used to provide the following:

1. A general overview of the expected chemical reactions
2. Identification of degradation products from corrosion of the waste package components
3. An indication of resulting fluid compositions inside the waste form.

The programs have been used only within the range of validation in accordance with AP-SI.1Q, *Software Management*. The EQ3/6 calculations reported in this document used version 7.2b of the code, which is appropriate for the application, and were executed on Pentium series (including Pentium II) personal computers (PCs).

Its present custodian, LLNL, has verified the EQ3/6 package. The source codes were obtained from SCM in accordance with the Management & Operating Contractor (M&O) AP-SI.1Q procedure, *Software Management*. The code was installed on the Pentium PCs according to an M&O-approved installation and test procedure (CRWMS M&O 1998a). This involves decompressing code executables, compiling the EQ3NR database, running several test cases, and comparing these to published results to confirm satisfactory code execution. The input/output files of these test cases are located in Attachment III and on the Dell computer referred to above.

4. INPUTS

The EQ3/6 software package is used to predict the progress of reactions and to estimate the partitioning of waste package components between the solution and solid phase, concentrations remaining in solution, and the composition of the precipitated solids over time. To do this, several data inputs and a number of preliminary steps are required. To begin with, EQ3NR is used to determine a starting fluid composition. This requires identification of a likely influent

source and a thermodynamic database that can describe equilibrium chemical relations. The thermodynamic database is subsequently relied on in the reaction-path calculation, but the latter also requires dissolution rates and masses of waste package components.

4.1 DATA AND PARAMETERS

4.1.1 Waste Package Materials and Performance Parameters

The analysis begins with selection of data for compositions (moles), amounts (g), surface areas (cm^2), and reaction rates ($\text{mol}/\text{cm}^2 \cdot \text{s}$) of the various components of CSNF and codisposal waste packages. These quantities are then normalized to represent reaction of 1 liter of fluid. Given fluxes of influent water into a waste package, EQ3/6 estimates the compositions and amounts of solid products and of substances in solution as a function of time. Waste package characteristics that are used as input represent design assumptions that are general and describe the various types of wastes anticipated for disposal.

Waste packages considered include CSNF and codisposal wastes. CSNF waste packages are made up of several reactive components: Al alloy, 304L low-carbon stainless steel, A516 carbon steel, borated and non-borated 316 stainless steel, 316 stainless steel containing GdPO_4 , and Zr-clad fuel rods. CSNF is primarily UO_2 . The spent fuel composition used in the EQ6 runs is for 10,000-year old, 4.9% ^{235}U -enriched, 34GWd/MTU pressurized water reactor assemblies minus noble gases and trace constituents (those making up less than 0.06% on a molar basis). This composition was modeled to represent nominal compositions. Note that output fluid chemistries are not strong functions of burnup or enrichment because degradation is non-isotope specific and trace amounts of fission products do not impact the resulting major element chemistries. Noble gases were deleted because they are volatile and will escape from breached packages. The trace elements were removed to make the EQ6 calculation more efficient. The oxygen content of the CSNF was recalculated assuming formula units of NpO_2 , PuO_2 , BaO , MoO_3 , Nd_2O_3 , ZrO_2 , Cs_2O , and CeO_2 . Solid compositions in mole fractions were calculated from weight percentage values by dividing the latter by the respective elemental molecular weight.

Codisposal wastes cover a broad range of compositions (CRWMS M&O 1998d) but have in common the fact that the waste packages will include a DSNF canister surrounded by five containers of DHLWG. Instead of modeling the large number of combinations to arrive at the broad limits of in-package geochemistry (there are over 250 types of DSNF alone [CRWMS M&O 1998d, Section 6.2.1.3]), the fast flux test facility (FFTF) and Fermi waste packages were used as the DSNF component.

Surface areas and moles of waste package components were calculated from the geometries of the waste form components and come from data tracking number (DTN): SN9911T0811199.003 and CRWMS M&O (1998b, Tables 5.2.2-3, 5.2.3-2, and 5.2.3-3) (CSNF) (see Section 5, Assumption 5.7). Each case assumed that the interior sleeve of the waste package would be made of 5-cm-thick 316 SS and that each end would be made of 10-cm-thick 316 SS. For a CSNF waste package with a void volume of 4511 liters, an inner diameter of 1.4234 m, and an inner length of 4.585 m, the surface area of 316 stainless steel sleeve exposed to a liter of fluid = $(1/4511) * 2\pi * 0.7117 * 4.585 + 2 * \pi * (0.7117)^2 = 0.00525 \text{ m}^2 = 52.5 \text{ cm}^2$. The total number of

moles involved then is equal to $[1/4511 \text{ l}][2\pi*0.7117 \text{ (m)}*4.585\text{(m)}*0.005\text{(m)} + 2*\pi*(0.7117)^2*0.01\text{(m)}]*7980000 \text{ g m}^{-3}/100 \text{ g mol}^{-1} = 23.75 \text{ mol/l}$.

For the codisposal FFTF waste package, the surface area = $(1/5807)*2\pi*0.94*4.617 + 2*\pi*(0.94)^2 = 0.00565 \text{ m}^2 = 56.5 \text{ cm}^2$. The total number of moles involved then is equal to $[1/5807 \text{ l}][2\pi*0.94 \text{ (m)}*4.617\text{(m)}*0.005\text{(m)} + 2*\pi*(0.94)^2*0.01\text{(m)}]*7980000 \text{ g m}^{-3}/100 \text{ g mol}^{-1} = 26.82 \text{ mol/l}$. Note lastly that the waste package characteristics used represent prevailing design assumptions that, although valid at the time of use, are subject to change (see Section 5).

4.1.2 Chemical Composition of Influent Water

The water composition likely to enter the waste package cannot be predicted accurately ahead of time, but is assumed to be similar to some combination of the water found in the unsaturated zone today and saturated zone J-13 well water (Table 1), subsequently modified by evaporation and/or condensation and fluid-rock interaction. Up to 80% of J-13 well water comes from the Topopah Spring member of the Paintbrush Tuff, which is the formation in which the repository is to be built. J-13 well-water composition is very similar to that of waters from other wells from the shallow, aerated zone in and near Yucca Mountain (Harrar et al. 1990). K and Mg levels differ significantly, but these are not expected to have any broad consequence in near-field reactions. The primary characteristics of the fluid that are expected to affect metal corrosion, waste-form leaching, and radionuclide migration—pH, bicarbonate levels, and redox state—are those characteristics of J-13 that are thought to be the most broadly representative of the unsaturated zone waters at Yucca Mountain (Harrar et al. 1990). In addition to J-13 composition water, two additional water compositions (see below) were also reacted with CSNF, Fermi, and FFTF waste forms/waste packages. The purpose of this exercise was to determine if the composition of the fluid exiting the waste package was sensitive to the composition of the fluid entering the waste package. The two additional water compositions used in the simulations were J-13 that had been evaporated to remove approximately fifty percent of the water, and a synthetic water composition from the thermal-hydrochemical modeling effort. The evaporated J-13 was chosen to reflect a more concentrated J-13 that could result from evaporative processes either in the drift or in a waste package, while the synthetic water composition was supposed to represent water entering the drift in the post-thermal period of the repository evolution. DST (drift-scale test) compositions represent an average of waters collected from Alcove 5 near the DST and were used as input compositions for modeling of thermal-hydrologic-chemical coupling in the near-field environment. DST water is thought to have moved appreciably through fractures and interacted with the rock matrix and, therefore, is assumed to have a composition predicted from thermal-hydrologic-chemical (THC) modeling over time as the thermal pulse from the waste passes through the repository horizon.

The results of these simulations were compared to results using J-13 well water where all of the inputs were the same with the exception of the water composition. The J-13 well water composition came from a prequalified version of DTN: MO0006J13WTRCM.000 to which were added low concentrations ($1.0\text{E}-16 \text{ mol}$) of trace elements present in waste package components. The parameter of primary interest is the effluent time-pH profile, the reason being that pH controls the chemical state of the system (at fixed gas pressures) and, thus, can be used to monitor the state of the system.

Table 1. Major Element Chemistry for J-13 Well Water

| Constituent | Concentration ^a |
|-------------|----------------------------|
| pH | 7.00 |
| Eh | 0.793 |
| Ca | 3.25E-04 (mol/kg) |
| Mg | 8.31E-05 |
| Na | 2.00E-03 |
| K | 1.29E-04 |
| Cl | 2.02E-04 |
| S | 1.92E-04 |
| F | 1.15E-04 |
| C | 2.50E-03 |
| Si | 1.12E-03 |

NOTE: ^aAll concentrations expressed as mg/L. Eh is in volts.
 Source: MO0006J13WTRCM.000 (see preceding text)

The evaporated J-13 well water composition was simulated in EQ6 by removing 26 moles of water such that 29.6 moles of water remained. This simulation was performed assuming a temperature of 25°C, oxygen fugacity of 10^{-0.7} atm, and carbon dioxide fugacity of 10^{-3.0} atm.

Note that relative to J-13 well water some of the elemental concentrations in the evaporated J-13 are greater while others are less than J-13. The reason for this is that during evaporation less soluble phases tend to precipitate, thus depleting the solution of their constituent ions, while ions of more soluble phases become concentrated in the residual solution. The ions forming less soluble phases include calcium and magnesium, which precipitate as carbonates, and silica, which forms chalcedony. Therefore, Ca, Mg, and Si are all depleted relative to J-13, and Na, K, Cl, S, F, and N are concentrated relative to J-13.

4.1.3 Simulated Fluid Entering the Drift

The results of the thermal-hydrochemical modeling provided fluid compositions entering the drift during the repository lifetime. The MDST2 composition was taken from Section 3.2.3.0 of the *Near Field Environment Process Model Report* and was chosen to react with the different waste form/waste package combinations as it represents a simulated fluid composition that would enter the drift environment after the thermal pulse subsides (CRWMS M&O 2000d, Section 3.2.3.0) and when waste package breach is likely to occur.

Preparation of the MDST2 fluid composition for use in EQ6 reaction path simulations required pre-processing using EQ3NR. The results of the EQ3NR simulation provided solution properties such as mineral saturation states, speciation information, ionic strength, and solution electrical balance among other solution properties. In the case of the MDST2 composition, EQ3NR output revealed that the solution was electrically out of balance where the total equivalents of the anions exceeded that of the cations. However, it is not possible to ascertain which ion(s) are responsible for the imbalance. Therefore, prior to using the MDST2 composition in EQ6 runs an additional EQ3NR run was performed to correct the electrical imbalance and adjust the solution chemistry to reflect the gas boundary conditions used in the EQ6 runs. The electrical imbalance was corrected by adjusting the solution pH to accommodate the imbalance. In addition to adjusting

the pH, the bicarbonate concentration was set to be in equilibrium with carbon dioxide at a fugacity of $10^{-3.0}$ atm, and the redox state of the solution was set by the oxygen fugacity of $10^{-0.7}$ atm. These two additional measures were taken because they represent the conditions assumed for the EQ6 simulations.

To best assess the impact of alternate input fluid compositions on the in-package chemistry, the highest water flux scenario (15 l/yr) was used as boundary condition for the simulations. This is the most conservative case because the kinetic laws for the reactants are independent of the water flux, and, thus, the ratio of reactants (solutes) to water (solvent) is the least. Additionally, for the CSNF runs, the fuel was assumed to be 90 percent exposed, i.e., 10 percent cladding coverage.

A series of six EQ6 runs was performed covering the two water types and the three waste forms. The output from each run was compared to its equivalent run that used J-13 well water as the infilling solution.

4.1.4 Drip Rate of Influent Water into a Waste Package

Fluid influxes from 0.15 to 15 l/yr were used to assess reaction paths. The latter value corresponds to a percolation velocity of 8 mm/year (CRWMS M&O 1998c—even though this reference has been revised, the information used from the cited version has not changed and was valid at the time it was referenced).

4.1.5 Secondary Phases

In the EQ6 runs, the growth of a number of alteration phases was suppressed. The suppressed phases include high-temperature minerals that, although thermodynamically favored to form at 25°C, rarely do. Celadonite, annite, Ni_2SiO_4 , phlogopite, zircon, and muscovite fall into this category. Dolomite growth was suppressed because it is rarely seen to grow at 25°C. The growth of BaZrO_3 was prevented because of suspicions about data quality. Quartz growth was suppressed because repository waters are often supersaturated with respect to quartz, suggesting that if it is growing near the repository horizon, it is doing so slowly. CaZrO_3 was suppressed because it is not known to form at low temperature. Hematite, goethite, and andradite garnet were likewise suppressed; the net effect of this being that the end product of steel degradation is predicted to be $\text{Fe}(\text{OH})_3$.

4.2 CRITERIA

Programmatic requirements for this document are listed in the Technical Work Plan (CRWMS M&O 2000e). That Technical Work Plan specifies that this document and all analyses described herein must adhere to the requirements of AP-3.10Q, *Analyses and Models*, and must address applicable U.S. Nuclear Regulatory Commission (NRC) issue resolution status report (IRSR) criteria (NRC 1999). Although the ultimate goal is to meet all acceptance criteria, they are not expected to be fully satisfied in this first round of analysis.

Below is a summary of the applicable NRC review methods and acceptance criteria outlined in the IRSR that applies to model development for the following near-field environment key technical issue sub-issue effects: (1) coupled thermal-hydrologic-chemical processes on the waste package chemical environment, (2) coupled THC processes on the chemical environment

for radionuclide release, and (3) coupled THC processes on radionuclide transport through engineered and natural barriers (NRC 1999).

4.2.1 NRC IRSR Criteria

4.2.1.1 Data and Model Justification Acceptance Criteria

1. Consider both temporal and spatial variations in conditions affecting coupled THC effects on the chemical environment for radionuclide release (NRC 1999, Sections 4.1.1, 4.2.1, 4.3.1, 4.4.1, and 4.5.1).
2. Evaluation of coupled THC processes shall consider site characteristics in establishing initial and boundary conditions for conceptual models and simulations of coupled processes that may affect the chemical environment for radionuclide release (NRC 1999, Sections 4.1.1, 4.2.1, 4.3.1, 4.4.1, and 4.5.1).
3. Sufficient data shall be collected on the characteristics of the natural system and engineered materials, such as the type, quantity, and reactivity of materials, in establishing initial and boundary conditions for conceptual models and simulations of THC coupled processes that may affect the chemical environment for radionuclide release (NRC 1999, Sections 4.1.1, 4.2.1, 4.3.1, 4.4.1, and 4.5.1).
4. Sensitivity and uncertainty analyses (including consideration of alternative conceptual models) shall be used to determine whether additional new data are needed to better define ranges of input parameters (NRC 1999, Sections 4.1.1, 4.2.1, 4.3.1, 4.4.1, and 4.5.1).
5. If the testing program for coupled THC processes on the chemical environment for radionuclide release from the engineered barrier system is not complete at the time of license application, or if sensitivity and uncertainty analyses indicate that additional data are needed, specific plans to acquire the necessary information as part of the performance confirmation program shall be identified (NRC 1999, Sections 4.1.1, 4.2.1, 4.3.1, 4.4.1, and 4.5.1).

4.2.1.2 Data Uncertainty and Verification Acceptance Criteria

1. Reasonable or conservative ranges of parameters or functional relations were used to determine effects of coupled THC processes on the chemical environment for radionuclide release. Parameter values, assumed ranges, probability distributions, and bounding assumptions shall be technically defensible and reasonably account for uncertainties (NRC 1999, Sections 4.1.1, 4.2.1, 4.3.1, 4.4.1, and 4.5.1).
2. Uncertainty in data due to both temporal and spatial variations in conditions affecting coupled THC effects on the chemical environment for radionuclide release shall be considered (NRC 1999, Sections 4.1.1, 4.2.1, 4.3.1, 4.4.1, and 4.5.1).
3. Evaluation of coupled THC processes shall consider the uncertainties in the characteristics of the natural system and engineered materials, such as the type, quantity,

and reactivity of materials, in establishing initial and boundary conditions for conceptual models and simulations of THC coupled processes that may affect the chemical environment for radionuclide release (NRC 1999, Sections 4.1.1, 4.2.1, 4.3.1, 4.4.1, and 4.5.1).

4. The initial conditions, boundary conditions, and computational domain used in sensitivity analysis involving coupled THC effects on the chemical environment for radionuclide release shall be consistent with available data (NRC 1999, Sections 4.1.1, 4.2.1, 4.3.1, 4.4.1, and 4.5.1).
5. A performance confirmation program shall be developed to assess whether the natural system and engineered materials are functioning as intended and anticipated with regard to coupled THC effects on the chemical environment for radionuclide release from the engineered barrier system (EBS) (NRC 1999, Sections 4.1.1, 4.2.1, 4.3.1, 4.4.1, and 4.5.1).

4.2.1.3 Model Uncertainty Acceptance Criteria

1. Appropriate models, tests, and analyses shall be used that are sensitive to the THC couplings under consideration for both natural and engineered systems as described in the following examples. The effects of THC coupled processes that may occur in the natural setting or due to interactions with engineered materials or their alteration products include: (1) Thermohydrologic effects on gas and water chemistry; (2) hydrothermally driven geochemical reactions, such as zeolitization of volcanic glass; (3) dehydration of hydrous phases liberating moisture; (4) effects of microbial processes; and (5) changes in water chemistry that may result from interactions between cementitious or waste package materials and groundwater, which, in turn, may affect the chemical environment for radionuclide release (NRC 1999, Sections 4.1.1, 4.2.1, 4.3.1, 4.4.1, and 4.5.1).
2. Alternative modeling approaches consistent with available data and current scientific understanding shall be investigated, and their results and limitations shall be appropriately considered (NRC 1999, Sections 4.1.1, 4.2.1, 4.3.1, 4.4.1, and 4.5.1).
3. A reasonable description of the mathematical models included in analyses of coupled THC effects on the chemical environment for radionuclide release shall be provided. The description should include a discussion of alternative modeling approaches not considered in its final analysis and the limitations and uncertainties of the chosen model (NRC 1999, Sections 4.1.1, 4.2.1, 4.3.1, 4.4.1, and 4.5.1).

4.2.1.4 Model Verification Acceptance Criteria

1. The mathematical models for coupled THC effects on the chemical environment for radionuclide release shall be consistent with conceptual models based on inferences about the near-field environment, field data and natural alteration observed at the site, and expected engineered materials (NRC 1999, Sections 4.1.1, 4.2.1, 4.3.1, 4.4.1, and 4.5.1).

2. Accepted and well-documented procedures shall be adopted to construct and test the numerical models used to simulate coupled THC effects on the chemical environment for radionuclide release (NRC 1999, Sections 4.1.1, 4.2.1, 4.3.1, 4.4.1, and 4.5.1).
3. Abstracted models for coupled THC effects on the chemical environment for radionuclide release shall be based on the same assumptions and approximations shown to be appropriate for closely analogous natural or experimental systems. Abstracted model results shall be verified through comparison to outputs of detailed process models and empirical observations. Abstracted model results shall be compared with different mathematical models to judge robustness of results (NRC 1999, Sections 4.1.1, 4.2.1, 4.3.1, 4.4.1, and 4.5.1).

4.3 CODES AND STANDARDS

No specific codes and standards have been identified as applying to this work activity.

5. ASSUMPTIONS

Process models are developed from a framework of underlying physical principles and assumed system behavior that simulates the behavior of the natural system. The in-package chemistry model basis entails the following assumptions:

- 5.1 Aqueous solutions fill all voids within waste packages, and water circulates sufficiently so that all degraded solid products are able to react with each other through the fluid. The basis for this assumption is that this provides one bound for the extent of chemical interactions within the waste package. This assumption is used in Section 6.
- 5.2 It is assumed that the thermodynamic database effectively predicts the local equilibrium state of the system during the reaction-path calculation and minor adjustments made to the database before qualification do not negatively impact the calculations below. These include the following.

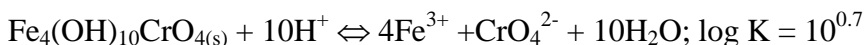
The solubility of Cr-Ettringite and the stability constant for $\text{CaCrO}_4^{\text{aq}}$ were taken from Perkins and Palmer (2000, pp. 1203-1218). $\text{Fe}_2(\text{MoO}_4)_3$ solubility was calculated by summing the following two reactions:

1. $\text{Fe}_2(\text{MoO}_4)_3 + 3\text{H}^+ \Leftrightarrow 2\text{Fe}^{3+} + 3\text{HMoO}_4^-$; $\log K = 10^{-26.1}$ (Titley 1963, pp. 196-204)
2. $\text{HMoO}_4^- \Leftrightarrow \text{MoO}_4^{2-} + \text{H}^+$; $\log K = 10^{-4.24}$ (Lindsey 1979)

to produce:

3. $\text{Fe}_2(\text{MoO}_4)_3 \Leftrightarrow 2\text{Fe}^{3+} + 3\text{MoO}_4^{2-}$; $\log K = 10^{-38.82}$

$\text{Fe}_4(\text{CrO}_4)(\text{OH})_{10}$ solubility was added (Anthony et al. 2000). This mineral is labeled “Cr-ferrihydrite” in the database and the relevant reaction is:



In order to take advantage of EQ3/6's ability to use complex kinetic rate laws to describe degradation of waste package components, it was necessary to add degradation reactions of a number of waste package components, namely mixed oxide (MOX), uranium oxide (UOX), commercial and spent nuclear fuel and DHLWG. Note that the MOX composition was slightly modified to compensate for round off errors in the EQPT program. Although unqualified, the data that were added to the database come from the peer-reviewed literature and consequently the impact of any errors likely to be produced is believed to be small. Moreover, this assumption is justified as experts have carefully scrutinized the majority of the data over the course of decades. This assumption is used in Section 6.

- 5.3 Waste form degradation may occur at temperatures up to 100°C but can be modeled adequately with the 25°C thermodynamic database. The calculations represent what occurs at times > 10,000 years, after the thermal pulse has passed and package temperatures are at, or below, 100°C. The basis for using 25°C thermodynamic data to model processes that might occur at somewhat higher temperatures is that many of the input thermodynamic parameters are not strongly sensitive to temperature over the range of 25 to 100°C (see the temperature-dependent equilibrium constants in data0.pvb), hence the broad scale features of the output fluid compositions are deemed independent of temperature. This assumption is used in Section 6.
- 5.4 Gases in the solution in the waste package remain in equilibrium with the ambient atmosphere outside the waste package, and the latter will be characterized by specific partial pressures (fugacities) of CO₂ and O₂ of, respectively, 10^{-3.0} and 10^{-0.7} atm (DOE 1998, pp. 3-67, and 3-69 to 3-72). The oxygen partial pressure is equivalent to that in the atmosphere. The basis for setting the carbon dioxide pressure to be somewhat higher than atmospheric is that ambient fluids drawn from near the repository horizon appear to be in equilibrium with above-atmospheric carbon dioxide levels. The basis for setting the oxygen partial pressure to atmospheric is that this is a conservative, maximum bound. This assumption is used in Section 6 but is considered specifically in Section 6.3.4.
- 5.5 The rate of entry of water into, as well as the rate of egress from, a waste package is equal to the rate at which water drips onto the package. The basis for this assumption is that for most of the time frame of interest (i.e., long after the corrosion barriers become largely degraded) it is more reasonable to expect that all or most of the drip will enter the degraded package than to expect that a significant portion will instead be diverted around the remains. Diversion of the water with a consequent lower entry rate has not been modeled by the lower drip rates incorporated into the present calculations. This assumption is relied on throughout Section 6 but is discussed further in Section 6.3.3.
- 5.6 Freshly precipitated minerals dissolve and grow instantaneously to maintain equilibrium with adjacent fluids. Instantaneously in the context of the calculations means over time scales shorter than those over which water is to react with waste package components—in other words, hundreds of years or less. The basis for the choice of minerals assumed to

- grow and dissolve in the calculation is that this is consistent with scientific fact. This assumption is used in Section 6.
- 5.7 The waste package materials properties roughly approximate the broad features of the waste package environment. The basis for this assumption is that it provides a starting bound for estimating the nature and extent of chemical interactions within the waste package. Large-scale changes in the design may alter this and may require subsequent reexamination of in-package chemistry. This assumption is used in Section 6.
- 5.8 Use of the pre-EDA II CSNF waste package geometry will not result in materially different predicted reaction paths. The basis for this assumption is that the primary output of this document, the range of in-package pHs, is insensitive to small (10-20%) changes in waste package component masses and surface areas such as are entailed in design changes. The insensitivity of output pHs to such small shifts in waste package parameters is documented in Section 6.2. This assumption is used in Section 6.
- 5.9 Addition of small amounts ($1.0\text{E}-16$ mol) of trace elements present in the waste package to the EQ3NR input file used to calculate J-13 fluid speciation does not affect the nature or extent of the waste package degradation pathway that is subsequently calculated using EQ6. The basis for this is that EQ6 requires that a tangible amount of each component in a reaction path calculation be present in the aqueous phase at the start of a calculation. $1.0\text{E}-16$ mol is an appropriately low default input as it is sufficiently far from saturation as to prevent any solid-phase accumulation of the respective component on its own. This assumption is used in Section 6.
- 5.10 It is assumed that a thermodynamic database that corresponds to the content of data0.pvb (DTN: SN0009T0811199.009) is adequate for the purposes of this analysis in EQ3/6 calculations. data0.pvb was derived from a preliminary version (data0.ymp.R0A.SRLCII: GEMBOCHS.V2-EQ8-data0.ymp.R0A, generated by GEMBOCHS.V2-Jewel.src.R9 24-mar-2000 16:56:16) of the Yucca Mountain Site Characterization Project (YMP) qualified data0 (data0.ymp.R0, DTN: MO0009THRMODYN.001) and differed only with the addition of a number of solids and the deletion of the H_2O_2 species (the latter had been erroneously calculated) (Attachment III). The major changes made to data0.ymp.R0A to create the qualified data set data0.ymp.R0 were the addition of thermodynamic data for a number of actinide species and removal of some high temperature extrapolated data that were considered to not meet qualification standards. In addition a number of numerical editorial errors were discovered and corrected. The basis for this assumption is that the work reported in this AMR does not involve actinide species, nor is it concerned with temperatures in excess of $100\text{ }^\circ\text{C}$, so further justification or verification of this assumption is considered unnecessary. Note that further changes to data0.pvb have been made subsequent to the calculations described here (DTN: SN0011T0811199.010). This assumption is used in Section 6.
- 5.11 It is assumed that the amounts and compositions of engineered materials that make up the waste packages will have the characteristics listed in Table 2. These waste package

characteristics represent design assumptions that are general and that describe the various types of wastes anticipated for disposal. The basis for this assumption is that it provides a reasonable starting point for calculations. This assumption is subject to change as plans for the waste packages chosen for disposal may change, but no further justification or confirmation is necessary. This assumption is used in Section 6.

Table 2. Chemical Characteristics of CSNF and Codisposal Waste Package Components

| Material | Formula | Amount (mol/l) | Degradation Rate (mol/cm ² •s); 25°C | Surface Area (cm ²) |
|---|---|---|--|---|
| CSNF Waste Package Parameters | | | | |
| Al alloy | ^a Al _{3.5831} Mg _{0.041143} Si _{0.0021353} Fe _{0.012534} Cu _{0.0043276} Ti _{0.00031238} Zn _{0.0038232} Mn _{0.0027303} | ^b 0.6423 | ^a 2.535E-13 | ^b 96.42 |
| A516 | ^a Fe _{1.7604348} Mn _{0.00190214} S _{0.0010915} P _{0.00113} Si _{0.01032} 56C _{0.023312} | ^b 11.948 | ^a 1.7976E-11 | ^b 504.160 |
| 316 SS | ^a Fe _{1.169177} Cr _{0.3269746} Ni _{0.20446461} Mn _{0.03640464} Si _{0.03560556} Mo _{0.02605795} C _{0.00249771} N _{0.00713942} P _{0.001452843} S _{0.0009355704} | ^c 23.75 | ^a 5.05468E-13 | ^c 52.500 |
| 316 SS/B | ^b Fe _{0.5699404} B _{0.0623405} Cr _{0.1924212} Ni _{0.1210848} Mn _{0.0191} Mo _{0.0137216} N _{0.0037597} S _{0.0004942} Si _{0.0140616} P _{0.0016906} C _{0.013154} | ^b 7.86 | ^b 1.169E-13 | ^b 156.010 |
| CSNF | ^{b,e} U _{0.3158} O _{0.6605} Zr _{0.0036} Pu _{0.0021} Mo _{0.0028} Nd _{0.0023} Cs _{0.0012} Ba _{0.0016} Ce _{0.0014} Np _{0.0006} | ^b 27.21 | ^d 2.33E-11(H ⁺) ^{0.41} + 8.71E-14 (HCO ₃ ⁻) ^{0.12} | ^b 96200 |
| Codisposal Waste Package Parameters - FFTF | | | | |
| 304L | ^f Fe _{1.218418} Cr _{0.365412} Ni _{0.1703868} Mn _{0.03640464} Si _{0.02670417} N _{0.00713942} C _{0.00249771} | ^f 6.384 (gpc) ^f 0.065 (ident) | ^a 8.65654E-12 | ^f 150.804 (gpc) 6.661 ^f (ident) |
| A516 | ^a Fe _{1.7604348} Mn _{0.00190214} S _{0.0010915} P _{0.00113} Si _{0.0103256} C _{0.023312} | ^f 18.375 | | ^f 129.615 |
| DHLWG | ^f Si _{0.7765} Na _{0.5767} B _{0.2912} Fe _{0.1722} Al _{0.0863} K _{0.0751} Mg _{0.0333} U _{0.0078} S _{0.0040} F _{0.0017} Ba _{0.0011} P _{0.0005} O _{2.7039} | ^f 24.821 | ^g 7.88 x 10 ⁻¹³ (H ⁺) ^{0.6} + 8.71 x 10 ⁻¹⁹ (H ⁺) ^{-0.4} | ^f 1915.142 |
| 316 SS | ^a Fe _{1.169177} Cr _{0.3269746} Ni _{0.20446461} Mn _{0.03640464} Si _{0.03560556} Mo _{0.02605795} C _{0.00249771} N _{0.00713942} P _{0.001452843} S _{0.0009355704} | ^f 0.946 (can) ^f 0.573 (assembly) ^f 0.423 (pins) ^f 26.82 (sleeve) | | ^f 24.134 ^f 27.267 ^f 257.913 ^f 56.5 |
| 316 SS/ GdPO ₄ | ^f Fe _{1.13167} Cr _{0.3164594} Ni _{0.1979051} Mn _{0.03523682} Si _{0.03446337} Mo _{0.02522204} N _{0.006910394} P _{0.01412484} S _{0.0009055582} Gd _{0.0127186} O _{0.0508744} | ^f 0.653 | ^a 5.05468E-13 | ^f 16.732 |
| UOX | ^f U _{0.370332} O _{0.7406648} | ^f 0.018 | ^d 2.33E-11(H ⁺) ^{0.41} + 8.71E-14 (HCO ₃ ⁻) ^{0.12} | ^f 72.072 |
| MOX | ^f U _{0.2746725} Pu _{0.09407909} Np _{0.001101603} O _{0.7397063} | ^f 0.393 | ^d 2.33E-11(H ⁺) ^{0.41} + 8.71E-14 (HCO ₃ ⁻) ^{0.12} | ^f 1559.382 |

Table 2. Chemical Characteristics of CSNF and Codisposal Waste Package Components (Continued)

| Material | Formula | Amount (mol/l) | Degradation Rate (mol/cm ² ·s); 25°C | Surface Area (cm ²) |
|--|--|---------------------|---|---------------------------------|
| Codisposal Waste Package Parameters - Fermi | | | | |
| DHLWG | ^f Si _{0.7765} Na _{0.5767} B _{0.2912} Fe _{0.1722} Al _{0.0863} K _{0.0751} Mg _{0.0333} U _{0.0078} S _{0.0040} F _{0.0017} Ba _{0.0011} P _{0.0005} O _{2.7039} | ^h 22.528 | ^g 7.88 x 10 ⁻¹³ (H ⁺) ^{0.6} + 8.71 x 10 ⁻¹⁹ (H ⁺) ^{-0.4} | ^h 1268.16 |
| 304L | ^f Fe _{1.218418} Cr _{0.365412} Ni _{0.1703868} Mn _{0.03640464} Si _{0.02670417} N _{0.00713942} C _{0.00249771} | ^h 6.16 | | ^h 143.94 |
| U-Mo fuel | ^a U _{0.377} Mo _{0.107} | ^h 1.259 | ^a 3.4601E-17 | ^h 77.092 |
| 316 SS | ^a Fe _{1.169177} Cr _{0.3269746} Ni _{0.20446461} Mn _{0.03640464} Si _{0.03560556} Mo _{0.02605795} C _{0.00249771} N _{0.00713942} P _{0.001452843} S _{0.0009355704} | ^h 1.7488 | | ^h 67.702 |
| A516 | ^a Fe _{1.7604348} Mn _{0.00190214} S _{0.0010915} P _{0.00113} Si _{0.01032} 56C _{0.023312} | ^h 9.715 | | ^h 103.925 |
| A516+Gd (shot) | ^a Fe _{1.7604} Mn _{0.0190} C _{0.0233} Si _{0.103} P _{0.0011} S _{0.001} | ^h 1.887 | ^a 1.7976E-11 | ^h 2882.28 |
| Al Alloy | ^a Al _{3.5831} Mg _{0.041143} Si _{0.0021353} Fe _{0.012534} Cu _{0.0043276} Ti _{0.00031238} Zn _{0.0038232} Mn _{0.0027303} | ^h 0.2154 | | ^h 56.951 |

NOTES: ^cSee preceding paragraph
^eMost abundant 11 elements

Sources: ^aCRWMS M&O (2000f, Section 5)

^bCRWMS M&O (1998b, Tables 5.2.2-3, 5.2.3-2, and 5.2.3-3)

^dCRWMS M&O (2000a, Section 6.2) multiplied by 3 to normalize stoichiometry

^fDTN: SN9911T0811199.003

^gCalculated from CRWMS M&O (2001, Section 6). gpc = glass pour canisters. All mols and surface area values truncated three digits right of the decimal point for clarity. Masses are normalized to a liter of solution. The molecular weights of all components are 100 g/mol, except for borated 316 SS: MW = 52.49 g/mol.

^hCRWMS M&O (1999d, Section 5) converted to EDA II waste package volume.

6. ANALYSIS/MODEL

The intended use of this model is to provide estimates of principal factors and, therefore, it is ascribed primary importance (Level 1).

Conceptual Model—The conceptual model explored here envisions dilute solutions entering and exiting a breached waste package at constant and equal rates. Waste package component steels and fuels are envisioned to react with these solutions according to kinetic rate expressions, forming a variety of secondary oxide and clay phases in the process. Formation of secondary phases and speciation of the aqueous phase is assumed to be instantaneous (Assumption 5.6), as is equilibration with atmospheric carbon dioxide and oxygen (Assumption 5.4).

Validation—General confidence in the model proceeds in part from the successful utilization of EQ3/6 to describe natural fluid-rock reaction paths such as hydrothermal ore formation, alteration of mid-ocean ridge basalts, mineral dissolution in laboratory reactors and natural systems, and speciation and evaporation of seawaters (Wolery and Daveler 1992). Nevertheless,

validation of the in-package chemistry model is as yet incomplete. Planned validation exercises will involve using EQ3/6 to model some combination of the processes listed below.

1. Alteration observed during drip-tests performed at Argonne National Lab
2. Formation of ore deposits that might constitute natural analogues
3. Glass, mineral, and steel corrosion measurements done in the laboratory.

6.1 EQ3/6 CALCULATIONS AND SCENARIOS MODELED

The primary uncertainties involved in the waste package degradation calculation are the drip rate and the degree of clad coverage (for commercial spent nuclear fuel). These parameters were varied widely to examine wide-range variations in major-element chemistry. Most of the runs were named A_XZ.6i:

A = csnf (CSNF runs); fftf (fast flux test facility); and fermi (fermi)

X = 0 (0% clad coverage); 1 (90% clad coverage); 2 (99% clad coverage) - for CSNF runs only (X = 0 for all fftf1 and fermi runs)

Z = 0 (0.00015 m³/yr H₂O flux into the waste package); 1 (0.0015); or 2 (0.015)

For example, the file csnf_00.6i represents input for the CSNF waste package fluid flux of 0.00015 m³/yr, and no credit is taken for cladding. The file fftf_02.6i is the fast flux test facility run done assuming a fluid flux of 0.015 m³/yr. Input files for runs that stalled and had to be restarted were named, for example, fftf_00b.6i. Runs possessing an additional prefix of MDST2 or J13EVAP were done using the alternative input fluids described in Section 6.1.3. An additional run - hno3_j13.6i was done to test the buffering capacity of waste package degradation products. Runs were initially set up to model waste package degradation for 1,000,000 years. In a number of cases reaction was essentially complete before 100,000 years, and the calculation was stopped. Also in a few cases, the run was prematurely halted, due to numerical instability. A series of CSNF runs were done to test the effect of waste package component metal degradation rates on reaction paths. In these runs, metal rates were lowered from those listed in Table 2 by a factor of 10. These runs were labeled "L" (e.g., csnf_10L.6i). Lastly, a number of EQ3 runs were done to set up the initial waste package calculation and to calculate the solubility of nickel. The first file is named j13ref0c.3i. The latter are named ni_6.3i, ni_7.3i, ni_8.3i, and ni_9.3i, the number after the underscore referring to the pH of the solubility calculation.

6.2 RESULTS

The results of the EQ6 runs to test sensitivity to input solution composition are shown for CSNF and FFTF waste forms in Figures 1-2, respectively. Examination of the figures reveals that there are some minor differences with regard to the simulated pH profiles. However, given the compositional ranges observed in the figures, the sensitivity to input water composition to the output pH is insignificant compared to the effects of changing the water flux and/or the percentage of fuel exposed.

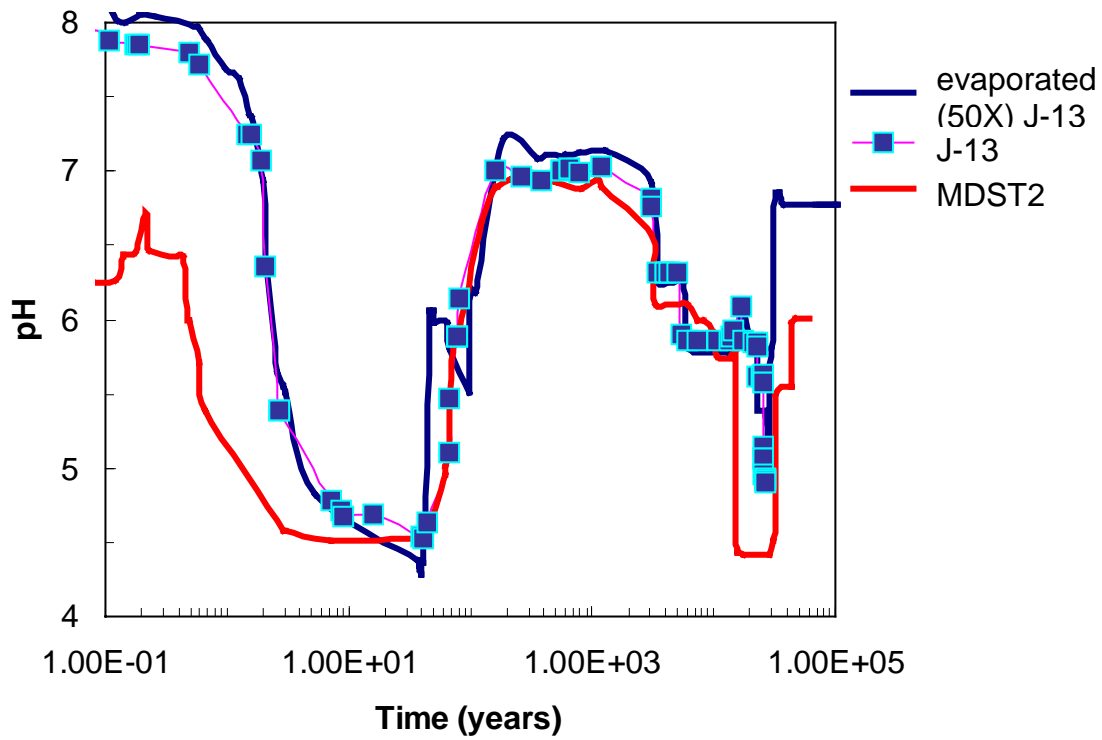


Figure 1. EQ6 Output Comparing the pH Profiles of J-13, 50X J-13, and MDST2 Solutions Reacted with CSNF

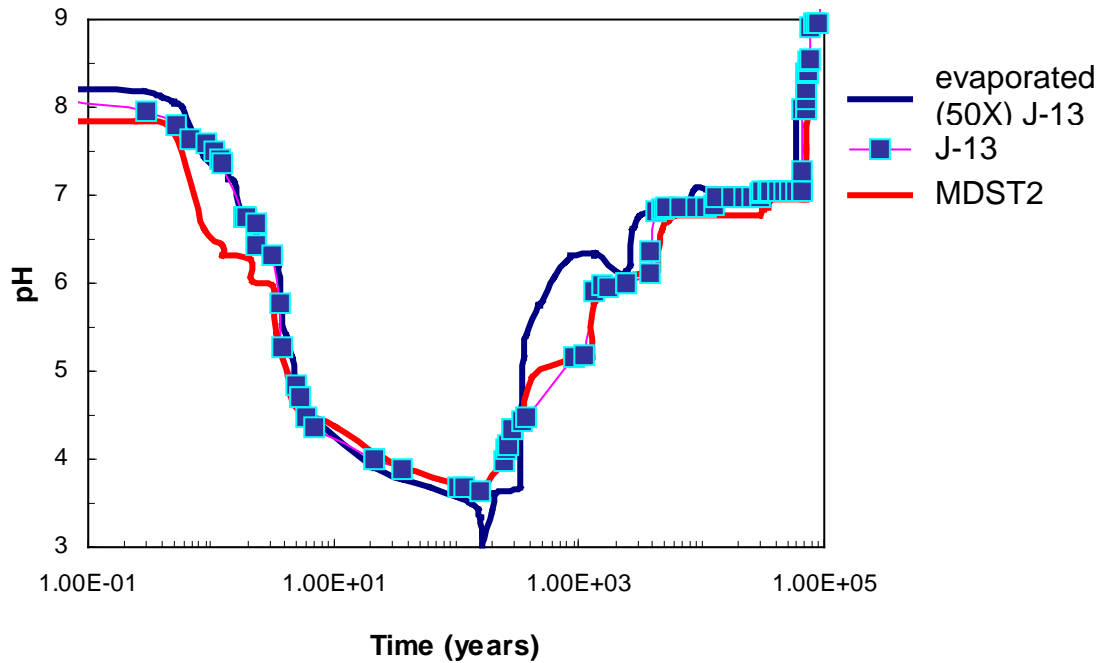


Figure 2. EQ6 Output Comparing the pH Profiles of J-13, 50X J-13, and MDST2 Solutions Reacted with an FFTF Waste Package

The mineralogy of waste packages degrading into repository level ambient fluids is predicted to be dominated by clay minerals, carbonates, and metal oxides. $\text{Fe}(\text{OH})_3$ and schoepite are the most abundant secondary phases in the CSNF runs. $\text{Fe}(\text{OH})_3$ and trevorite are most abundant in codisposal runs. $\text{Fe}(\text{OH})_3$ is the most common secondary phase in all runs. Maximum predicted accumulations of secondary phases occasionally exceed a liter of fluid suggesting a potential for self-sealing of the waste packages. Note though that there is a counteracting decrease in volume that is associated with the degradation of waste package components. For the purposes of establishing bounding limits of pH, Eh, alkalinity, etc., net changes are neglected in void volume caused by accumulation of secondary phases and degradation of waste package components.

Figures 3 and 4 show calculated waste package pHs over time for CSNF and codisposal packages.

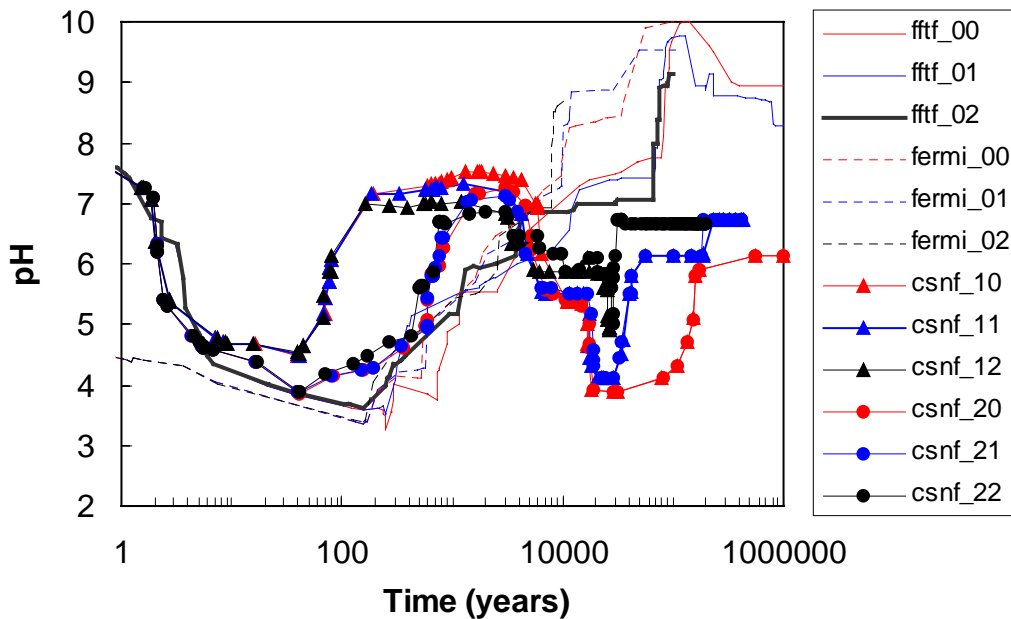


Figure 3. Predicted pHs for Waste Package Fluids (long time scale)

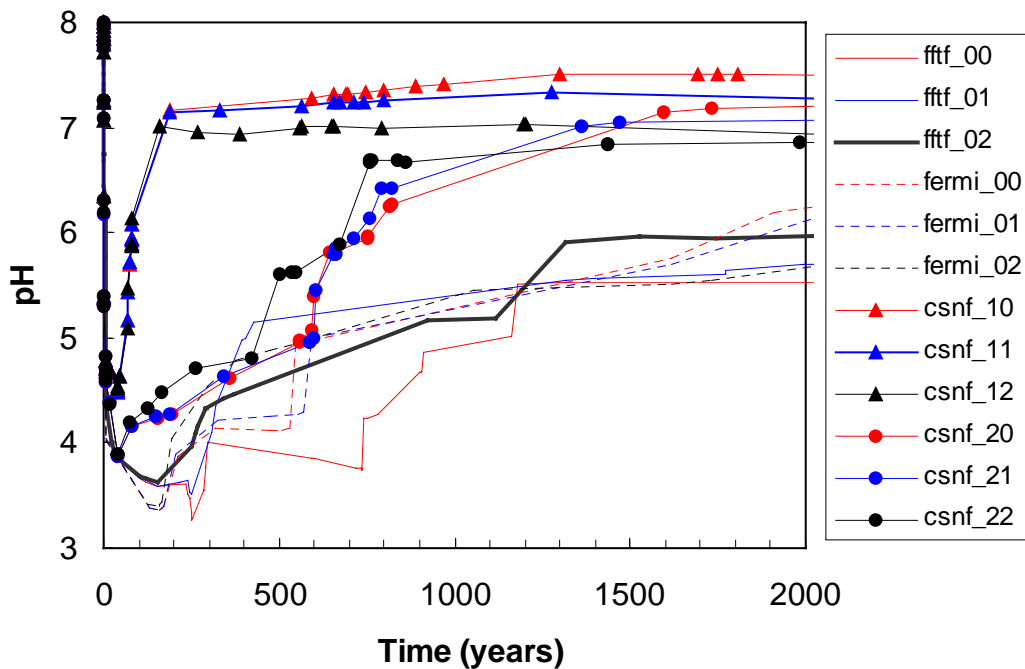


Figure 4. Predicted pHs for Waste Package Fluids (short time scale)

In all runs, the slightly alkaline pH of the input solution (pH ~ 8.1) prevails inside the waste package initially. In the CSNF runs, the system pH progresses towards a minimum between pH 4 and 5, primarily due to the oxidation of the A516 carbon steel. A second pH minimum is reached beyond 100,000 years due to the continued oxidation of 316 stainless steel. In between the two pH minima, the pH rises primarily due to dissolution of Al alloy and the influx of slightly alkaline influent solutions. Runs having 10% of the fuel exposed experience the pH minima earlier than runs having only 1% of the fuel exposed, pointing to an additional moderation of acid excursions by fuel degradation. pHs rise after the second minimum primarily because of alkaline fluid influx. The range of input fluid fluxes has a minor impact over the trajectory of pH curves. Runs done with input steel rates set at 1/10th of the values in Table 2 showed broadly similar pH trajectories, though the pH minima were less extreme due to the lower steel oxidation rates. pH trajectories likewise do not appear to be overly sensitive to minor variations in waste package component surface areas and masses.

The pH trajectories of codisposal waste packages follow paths very similar to one another. Specifically, there is an initial pH minimum at between 100 to 300 years that is caused by oxidation of A516 carbon steel followed by a steady rise in pH that is driven largely by waste glass dissolution. Along the latter pH upswing, degradation of other steel components tends to mitigate the shift to alkaline conditions. The latter becomes most extreme when the steels are exhausted. At very long times (>500,000 years) complete dissolution of the glass followed by influx of less alkaline solutions causes pHs to decrease somewhat. The range of input fluid fluxes has a minor impact over the trajectory of pH curves.

Table 3 summarizes the range of in-package fluid compositions predicted to occur for both the CSNF and codisposal waste packages. When fluid fluxes are low (0.15 L/yr), the ionic strengths

calculated for the codisposal packages occasionally exceed 10 M. This is a consequence of high degradation rates, minimal loss of dissolved salts through export, abstraction of water to form hydrated alteration phases, and the combination of high pH and the assumed fixed fugacity of carbon dioxide.

Table 3. Range of In-Package Fluid Compositions (mol/l except for pH and Eh)

| Variable | CSNF | Codisposal |
|------------|-----------|------------|
| pH | 3.9-8.1 | 3.3-10.0 |
| Eh (volts) | 0.6-1.0 | 0.6-1.1 |
| I | 0.001-0.6 | 0.002-12 |

Although the carbon dioxide fugacity was set to 10^{-3} atm in the calculations above, there is the possibility that this number may vary over the lifetime of the repository. Specifically, microbial activity might lead to higher carbon dioxide levels than modeled here. One EQ6 run (input file csnf_00_co2.6i) was done using a carbon dioxide fugacity of 10^{-2} atm to bound the effect. Although relatively low pHs are observed for the high carbon dioxide runs, pHs soon approach one another. Although high carbon dioxide levels would tend to favor increased CSNF dissolution and heightened U solubility, the lowering of pH tends to more than compensate. The net effect is that higher carbon dioxide levels actually decrease dissolved levels, at least in the two runs compared.

6.2.1 Radiolysis

Radiolytic conversion of gas phase nitrogen and oxygen to NO_2 might cause accumulation of nitric acid and ferric chloride, which in combination might corrode. Radiolysis-induced clad breakdown is considered in detail in Attachment II.

6.2.2 Bypass Flow

The assumption that the waste packages are instantaneously filled and that subsequent inputs equal outputs is obviously a limiting case for what is likely to actually occur upon waste package breach. In reality, reaction might involve intermittent or discontinuous wetting of waste package components. If wetting of waste package components were complete, but void filling were not, this might be reflected in the calculation by decreasing the fluid/solid ratio. This would tend to maximize the amount of dissolved solids in the effluent. Alternatively, incomplete filling of voids along with incomplete wetting of waste package components would probably not result in significantly different effluent compositions as the fluid/solid ratio would not change.

It is easy to envision fluids flowing through and reacting with only selected portions of breached waste packages. Nevertheless, the waste package degradation described above assumes that all waste package components are in communication with fluids that completely fill the waste package. This approach is a reasonable approximation of a complex process and provides a conservative bounding estimate of fluid chemistries. To begin with, radionuclide release from the waste package requires a sequence of four steps to occur: ingress of fluid, degradation of fuel covering (e.g., clad), dissolution of fuel into solution, and egress of fluid from the waste package. Heterogeneous flow, which implies the bypassing of waste package components, also implies bypassing of critical reaction steps and a diminished contact time with waste package

components. Although bypassing of specific waste package components might lead to anomalous waste package fluid compositions, it also would lead to limited reaction with those components and possibly not all of the reaction steps needed to cause radionuclide release. Lastly, because waste package components (steels, fuel elements, etc.) are distributed in a reasonably homogeneous fashion throughout the waste package, only reaction paths involving exposure of all waste package components can be justified. In other words, homogeneous flow, as modeled above, is conservative because it involves complete reaction and maximal release of radionuclides. Increasing the maximum seepage value above the range considered here would cause output pHs and solution compositions to more closely resemble those of the input solutions. In essence, higher fluid fluxes would lead to more limited output fluid compositions.

6.2.3 Alternative Fluid Inputs

Fluids having compositions substantially different from those used as inputs in the calculations above are likely to occur intermittently throughout the proposed repository. Prior interaction of incoming fluids with rock bolts and/or cementitious materials might affect the makeup of the fluids that ultimately encounter the interiors of breached waste packages. The first might increase Fe levels in solution while locally depleting O₂. The second would cause a shift to higher pH. These specific effects were neglected as being second-order relative to similar reactions that will occur inside the waste package. Interaction with steel components inside the waste package as modeled above is likely to have a far more profound effect on fluid chemistry than any prior encounter with rock bolts. Moreover, interaction of water with DHLWG in codisposal waste packages is likely to lead to sharper rises in pHs than similar encounters with local deposits of cementitious materials.

Evaporation of incoming fluids during the thermal pulse is likely to leave scales of calcium carbonate, calcium sulfate, and other evaporite minerals on the drip shield and possibly on the outer shell of the waste packages themselves. The residual fluids would tend to be alkaline, in some cases due to stripping of CO₂ during boiling, and in part due to mineral-fluid reactions that occur during evaporation (CRWMS M&O 2000c, Section 6). Note first of all that such fluids are by their very nature relatively small in volume. Secondly, while high pHs would favor the formation of soluble actinide complexes, the presumed lack of carbonate alkalinity in the most extreme, CO₂-stripped solutions would work against increased radionuclide solubilities. Such anomalous fluid compositions are likely to be transient, due for example to readsorption of CO₂, and subsequent post-thermal pulse contact with dilute solutions. Natural alkaline fluids persist only where evaporative conditions and inputs of dissolved salts can be maintained indefinitely. In the post-thermal pulse time span that is the focus of the present AMR, the more likely input is believed to be dilute.

In summary, solution pH in each run represents a dynamic balance between proton-producing reactions—dissolution of stainless steels, and proton-consuming reactions—dissolution of Al alloy and high-level waste glass and input of ambient alkaline fluids. Early dissolution of steel causes low initial pHs. Glass degradation (in the case of codisposal waste packages) and fluid influx cause a general increase in pH with time.

6.2.4 Sensitivities and Conservatism

A number of conservatisms are explicit in the calculations described above. In general, bounding assumptions were made in input parameters that err on the side of maximizing radionuclide transport. The primary conservatisms involve the assumed redox state of the system, glass degradation rates, and in-package transport. Later efforts will consider the actual (versus conservative) inputs describing fuel and steel dissolution.

Oxygen Fugacity—The current in-package chemistry models assume that all of the waste package pore space is filled with water and the solution inside of a waste package is in equilibrium with oxygen at its atmospheric value ($10^{0.7}$ bar). Under this oxidizing condition, uranium and plutonium tend to form soluble carbonate complexes and are, thus, available for transport out of a waste package—a conservative assumption. However, taking into consideration the expected failure mode of a waste package and the strong affinity of the steel components of the waste package to react with oxygen to form ferric-oxy-hydroxides, it is more probable that the redox environment inside of a waste package will be reducing.

Stress corrosion cracking is seen as the most likely form of early failure in waste packages. In this mode of failure the small aperture of the cracks limits the avenue for oxygen to enter a waste package. Thus, oxygen availability will be limited to diffusion through these small aperture cracks and further through the solution filling the waste package. In later stages of waste package corrosion, when penetrative patches may be present, the availability of oxygen may approach that of atmospheric values. Therefore, a range of oxygen fugacities should be used in the simulation of in-package chemistry. Ideally, it would be desirable to implement oxygen fugacity as a function of diffusion area to parallel the development of cracks and patches in the waste package.

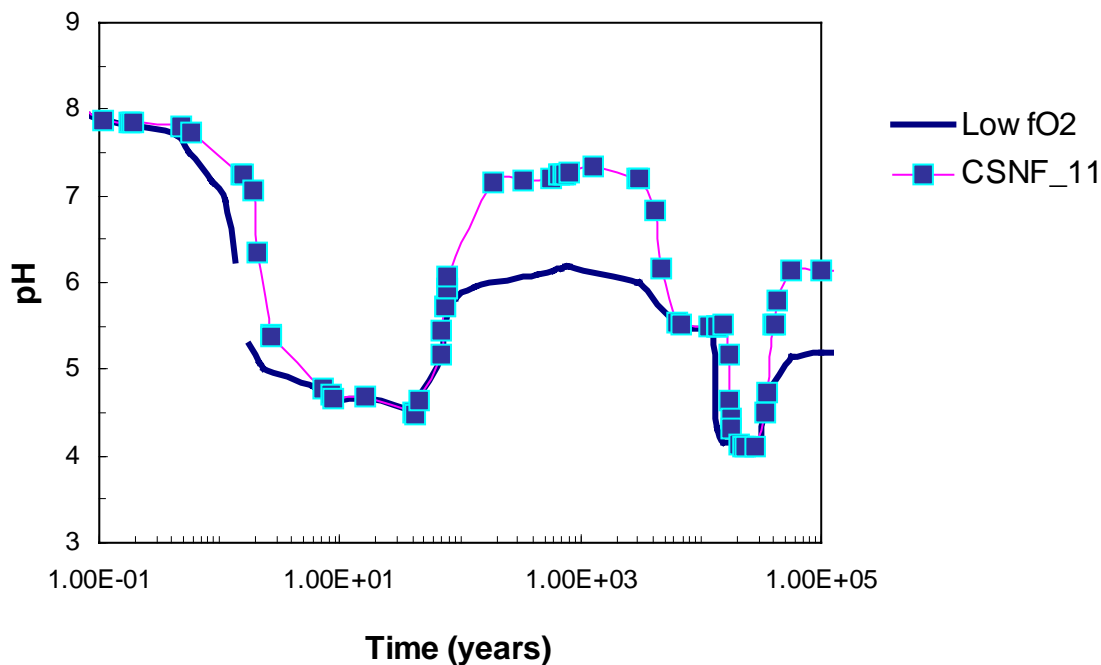


Figure 5. Effect of Lowered Oxygen Fugacity on In-Package Chemistry

Figure 5 shows the minor effect that lower oxygen fugacities (in this case, $10^{-3.5}$ atm) have on waste package pHs. Although the effect of oxygen fugacity is minor in this case, its effect on radionuclide solubility is expected to be much larger.

Glass Degradation—The glass degradation rate used until now is conservative as it probably represents the maximum rate at which waste glass can dissolve. Minerals and glasses are observed to degrade under long-term geologic conditions at rates that tend to be orders of magnitude less than that observed in short-term laboratory conditions. Active sites tend to dissolve away with time. Secondary phases can accumulate and passivate a surface. Chemical "poisons" can inhibit dissolution as well. A more reasonable parameterization of glass degradation that would be consistent with geologic observations would entail consideration of dissolution rates at least a factor of 1000 less than those used at present. The pH and temperature dependence of the rates are not believed to be overly conservative as modeled presently.

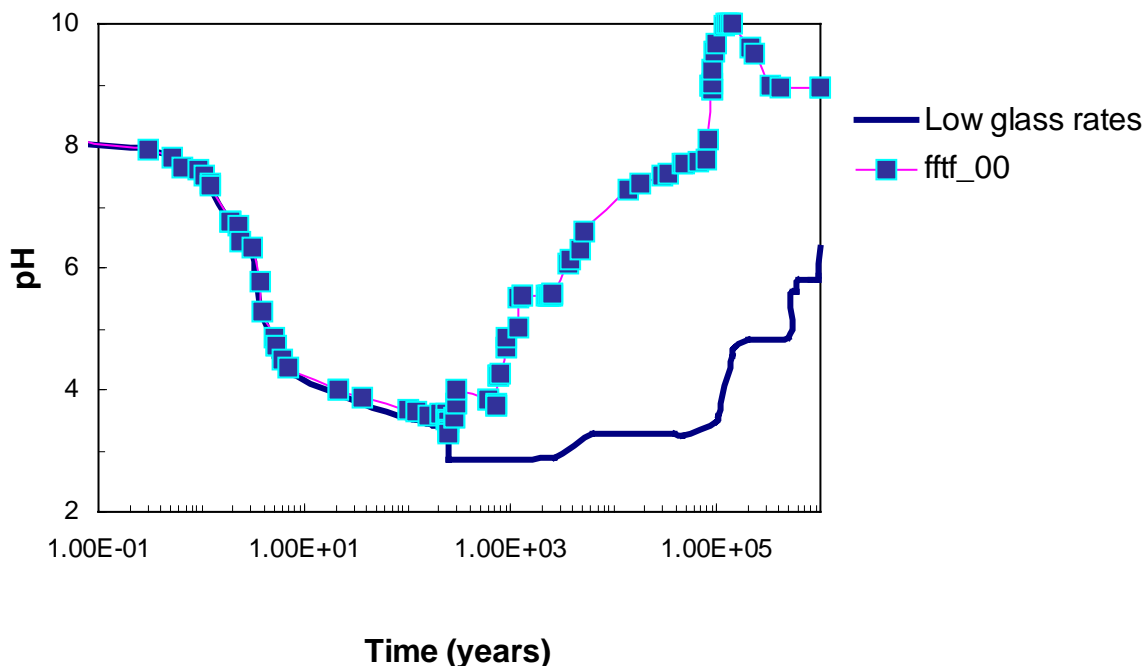


Figure 6. Effect of Lowered Glass Dissolution Rate on In-Package Chemistry

Figure 6 shows the dramatic effect that lower glass rates have on waste package pHs. The "low glass rates" curve was calculated using as input glass rates that had been lowered by a factor of 1000 under the low-flow scenario for the FFTF waste package. (This scenario, FFTF_00, maximizes the impact of glass degradation on waste package pHs.) Diminished proton consumption due to lower glass rates prevents high pH excursions.

In-Package Transport—The present conceptual model envisions a water-filled waste package in which every waste package component is fully exposed to fluid at all steps of the degradation process. This is clearly a bounding approximation of what is expected to actually occur. Specifically, waste package components are likely to be differentially wet depending upon the temporal variation in water ingress and egress. Moreover, secondary degradation phases (primarily, fe-hydroxides and clays) are expected to accumulate and to block some portion of the waste package component surfaces that would otherwise be able to dissolve. Indeed waste package component surfaces will probably provide the primary nucleation sites needed for mineral growth. The net effect is that waste package component degradation rates are, collectively, expected to be orders of magnitude less than those used at present.

6.2.5 Nickel Solubility

An additional concern that must be addressed is Ni solubility. Previous calculations of bounding dissolved concentration limits assumed equilibrium with bunsenite (NiO). A more conservative approach is to assume equilibrium with respect to Ni(OH)₂. J-13 well water was used as input and EQ3NR calculated Ni solubilities as a function of pH at 25°C, assuming the carbon dioxide fugacity was 0.001 atm. At pH 9 Ni solubility is 0.52 ppm; at pH 8, 43.87 ppm; at pH 7, 16,205

ppm. EQ3NR does not converge at pHs lower than 7 due to the extreme solubility of $\text{Ni}(\text{OH})_2$. At low pH, Ni concentrations are likely to instead be inventory limited.

7. CONCLUSIONS

Corrosion of waste package components into ambient fluids by dissolution under a wide variety of conditions is expected to cause relatively large changes in waste package effluent chemistry. In CSNF waste packages, relatively low pHs are expected to occur, at least initially, due to the production of protons associated with corrosion of steel components. Large-scale release of U into solution will ultimately drive pHs to near neutral. High pHs (pH ~10) and ionic strengths will occur if ambient fluids degrade codisposal canisters containing defense high-level waste glass and DOE spent nuclear fuel. Effluent Eh and alkalinity are expected to be controlled by free oxygen and carbon dioxide levels that are near to atmospheric.

Two data packages were generated from the output of this work, (1) Table 3, the summary of fluid composition ranges, and (2) a spreadsheet containing all of the fluid composition outputs ELEM_AQU.xls (DTN: SN0009T0811199.008). Additionally, the data0.pvb file was updated (DTN: SN0011T0811199.010).

Although the results of the calculations presented may be considered a partial validation of the model, they collectively do not constitute full model validation - the latter is an ongoing process. This model and model results may change upon model validation.

This document may be affected by technical product input information that requires confirmation. Any changes to the document that may occur as a result of completing the confirmation activities will be reflected in subsequent revisions. The status of the technical product input information quality may be confirmed by review of the DIRS database.

8. INPUTS AND REFERENCES

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8.2 CODES, STANDARDS, REGULATIONS, AND PROCEDURES

Procedures listed below are retrievable from the OCRWM Program Documents database contained in Lotus Notes 4.6 and the BSC INTRANET.

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8.3 SOURCE DATA

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MO0009THERMODYN.001. Input Transmittal for Thermodynamic Data Input Files for Geochemical Calculations. Submittal date: 09/20/2000.

SN0009T0811199.009. Revised Thermodynamic Database for Waste Package Degradation. Submittal date: 09/28/2000.

SN9911T0811199.003. Calculations of Physical and Chemical Properties of Fast Flux Test Facility (FFTF) Waste Package. Submittal date: 11/15/99.

8.4 OUTPUT DATA

SN0009T0811199.008. Revised Range of Waste Package Effluent Compositions. Submittal date: 09/28/00.

SN0011T0811199.010. Updated Thermodynamic Database for Waste Package Degradation. Submittal date: 11/29/00.

ATTACHMENT I
COMPUTER FILES

ATTACHMENT I COMPUTER FILES

Attachment I contains a list of compressed EQ6 input files for each run (*.6i). Each of the prefixes for the files are labeled by the nomenclature outlined in Section 6.2. The aqueous concentration outputs are collected in the file ELEM_AQU.xls. EQ3 input files (described in Section 6.2) are also included. There is one data0 file - data0.pvb in the archive that contains the thermodynamic data used for the calculation. All of the actual files are on a read-only compact disc (CD) (Attachment III).

AI.1 LIST OF FILES ON CD

| Name | Size(bytes) | Date | Time |
|---------------------|-------------|----------|--------|
| fftf_02.6i | 49,280 | 9/25/00 | 5:58a |
| fftf_01.6i | 49,278 | 9/25/00 | 5:57a |
| fftf_01b.6i | 34,133 | 10/22/00 | 4:39p |
| fftf_00.6i | 49,278 | 9/25/00 | 5:57a |
| fftf_00b.6i | 34,379 | 10/23/00 | 7:28a |
| csnf_02b.6i | 30,583 | 9/26/00 | 4:04p |
| MDST2_csnf_12.6i | 37,476 | 10/23/00 | 6:19p |
| csnf_00.6i | 39,936 | 9/25/00 | 6:00a |
| csnf_00b.6i | 35,880 | 9/25/00 | 6:01a |
| csnf_01.6i | 39,934 | 9/25/00 | 6:03a |
| j13evap_fftf_02b.6i | 33,261 | 10/23/00 | 9:57p |
| j13evap_fftf_02.6i | 46,987 | 10/23/00 | 9:21p |
| MDST2_FFTF_02.6i | 46,218 | 10/23/00 | 6:47p |
| Csnf_20.6i | 40,088 | 10/26/00 | 10:41a |
| csnf_00_co2.6i | 39,999 | 9/25/00 | 6:01a |
| csnf_12c.6i | 30,501 | 10/3/00 | 5:15p |
| csnf_12b.6i | 32,346 | 10/3/00 | 4:53p |
| csnf_12.6i | 39,940 | 10/3/00 | 3:40p |
| csnf_12d.6i | 30,583 | 10/3/00 | 6:10p |
| csnf_12e.6i | 30,583 | 10/3/00 | 9:00p |
| csnf_12f.6i | 30,583 | 10/4/00 | 5:43a |
| csnf_12g.6i | 30,583 | 10/4/00 | 6:06a |
| csnf_11b.6i | 32,346 | 10/22/00 | 4:07p |
| csnf_11.6i | 39,940 | 9/25/00 | 6:06a |
| csnf_10.6i | 39,934 | 10/22/00 | 3:35p |
| csnf_02c.6i | 30,583 | 9/26/00 | 4:31p |
| csnf_02.6i | 39,938 | 9/25/00 | 6:04a |
| csnf_02_co2.6i | 39,933 | 9/25/00 | 6:04a |
| csnf_01_co2.6i | 39,934 | 9/25/00 | 6:04a |
| j13evap_b.6i | 32,091 | 10/23/00 | 4:22p |
| j13evap_Csnf_12.6i | 38,257 | 10/23/00 | 6:12p |
| CSNF_22L.6i | 40,014 | 10/3/00 | 3:16p |
| csnf_22lb.6i | 36,434 | 10/3/00 | 4:01p |
| Csnf_20L.6i | 40,088 | 10/22/00 | 2:35p |
| CSNF_21L.6i | 40,088 | 10/22/00 | 2:48p |
| Csnf_12L.6i | 40,014 | 10/26/00 | 12:13p |
| Csnf_11L.6i | 40,014 | 10/3/00 | 1:44p |

| | | | |
|-------------------|-----------|----------|--------|
| Csnf_10L.6i | 40,047 | 10/3/00 | 2:36p |
| CSNF_22.6i | 39,940 | 10/3/00 | 8:01a |
| csnf_22b.6i | 28,816 | 10/22/00 | 2:22p |
| Csnf_21.6i | 40,088 | 10/3/00 | 12:13p |
| fermi_02.6i | 43,048 | 9/25/00 | 5:55a |
| fermi_01.6i | 43,048 | 9/25/00 | 5:55a |
| fermi_01b.6i | 39,478 | 10/23/00 | 8:53p |
| fermi_00.6i | 43,048 | 9/19/00 | 6:35p |
| mdst2_fermi_00.6i | 39,700 | 10/23/00 | 2:54a |
| data0.pvb | 2,717,112 | 9/25/00 | 5:54a |
| J13ref0c.3i | 11,510 | 6/14/00 | 5:56a |
| ni_6.3i | 11,553 | 7/30/00 | 10:39a |
| ni_7.3i | 11,553 | 7/30/00 | 10:46a |
| ni_8.3i | 11,553 | 7/30/00 | 10:40a |
| ni_9.3i | 11,553 | 7/30/00 | 10:44a |
| ELEM_AQU.xls | 4,562,432 | 10/26/00 | 1:32p |

ATTACHMENT II
ACID CORROSION OF CLADDING FROM RADIOLYSIS–YMP NO. 2.1.02.15.00

ATTACHMENT II
ACID CORROSION OF CLADDING FROM RADIOLYSIS - YMP NO. 2.1.02.15.00

YMP Primary Features, Events, and Processes (FEP) Description: Gamma radiolysis has the potential to convert nitrogen and oxygen in air to NO₂, which could dissolve in water on cladding surfaces to form nitric acid. Although Zircaloy cladding is resistant to direct attack by nitric acid, this might indirectly destabilize the cladding by allowing the buildup of metal-halide complexes in solution that can promote corrosion. This in turn could cause release of radionuclides from spent fuel at an earlier time and in greater concentrations than would be expected if radiolysis were ignored. Another potentially corrosive radiolytic product is hydrogen peroxide. It can be shown, however, that conditions that must exist for appreciable accumulation of nitric acid and halides in waste package fluids are unlikely to occur, and sufficiently high concentrations of hydrogen peroxide to attack Zircaloy cladding are unlikely to be produced.

Screening Decision: Exclude for general acid corrosion based on low consequence. Include for local suppression of pH resulting in local corrosion.

Related Primary FEPs:

| <u>YMP No.</u> | <u>Topic</u> |
|----------------------|---|
| YMP No. 2.1.02.16.00 | Localized Corrosion (including Pitting) of Cladding |
| YMP No. 2.1.02.17.00 | Localized Corrosion (Crevice Corrosion) of Cladding |

IRSR: CLST1, CLST3, TSPA13, TSPA14

Screening Argument: General acid corrosion is omitted on the basis of low consequence for general acid corrosion. An unlikely set of conditions must be maintained within the waste package for long periods of time in order for gamma radiolysis to produce acidic conditions on the cladding surface and, thereby, contribute to cladding failure. A delicate balance among continually changing water influxes, heat loads, and diffusive driving forces would have to be sustained over long periods in order for acidic conditions to be produced that could have any effect on the cladding.

The specific sequences of reaction paths that are needed to link radiolysis with cladding degradation are coupled and self-canceling. Radiolysis has the potential to produce chemical species that may not otherwise be anticipated in the repository. One example is the production of nitric acid as a result of the radiolytic reaction between nitrogen and oxygen. Another example is the production of hydrogen peroxide.

Following a breach, the expected environment inside waste packages for most of the containment period is an air-water vapor mixture, with liquid water dripping into some waste packages, at temperatures ranging from 27°C to 250°C and a total pressure of close to one atmosphere. Under these conditions, the key radiolytic products are (1) nitrogen fixation products: nitrogen acids, nitrogen oxides, and ammonia; (2) hydrogenous species: atomic and molecular hydrogen; and (3) oxygen-containing oxidizing species: oxy-radicals, ozone, and hydrogen peroxide (Reed and Van Konynenburg 1991, p. 1397). In the irradiated air-water vapor system, the nitrogen

oxides are rapidly converted to nitrogen acids by the OH radical generated from water vapor. Nitric acid is the predominant product because nitrogen dioxide is more stable in the irradiated system and persists at a higher concentration in the gas phase than nitric oxide. Hydrogen peroxide is generated as a molecular product as a result of secondary reactions of the oxy-radicals OH and HO₂. However, yields are low, and the concentration does not build up with absorbed dose (Reed and Van Konynenburg 1991, p. 1401). The predominant effect is to contribute to the nitrogen fixation process and production of nitrogen acids.

In addition to considerations of acid production per se, it should be noted that zircaloy is used for fuel cladding because of its high resistance to corrosion in high radiation fields. Yau and Webster (1987, p. 710) note that zircaloy has excellent corrosion resistance to nitric acids. The effect of nitric acid is indirect in that nitric acid stabilizes the formation of metal-halide complexes that control corrosion of the cladding. They also report that zircaloy does not corrode in concentrated hydrogen peroxide.

Corrosion of zircaloy occurs in the presence of fluoride and chloride ions at low pHs, or when ferric or cupric ions are present with chloride ions. Thus, when there is no dripping of groundwater into waste packages, the requisite halide ions are not present, and zircaloy is essentially inert to the nitric acid and hydrogen peroxide produced by radiolysis. When groundwater containing halide ions drips into the waste packages, conditions may exist for corrosion of the cladding. However, the resulting solutions will contain bicarbonates from the groundwater (in addition to dissolution of CO₂ from the air) and Fe(OH)₃ formed through waste package degradation; such solutions possess a considerable buffering capacity. Lastly, even if the pH of water films on the cladding is sufficiently low for corrosion to occur, the corrosion rate will be severely limited by the low fluoride content of the groundwater. It is ultimately the halide concentration of the water films that determines the corrosion rate, so if the influx of groundwater dripping into waste packages is low, sufficient fluoride ion concentration does not build up to enhance corrosion of the cladding, regardless of the extent of acid production from radiolysis.

While acid corrosion of cladding from radiolysis has been screened out as a significant bulk process at YMP, it has not been ruled out as one of the possible contributors to local suppression of pH resulting in local corrosion of cladding and is, thus, included in the local corrosion model. On the scale of the repository model, acid corrosion of cladding from radiolysis is included for in-package chemistry. It is included as a specific feature in the local corrosion model where acid corrosion might be the cause of localized corrosion.

TSPA Disposition: Local suppression of pH resulting in local corrosion of cladding is included in the local corrosion model (CRWMS M&O 2000c) as a specific feature where acid corrosion might be the cause of localized corrosion.

Basis For Screening Decision: It is recognized that radiolysis may create various chemical species that may not otherwise be expected in the repository. Examples are the production of nitric acid as a result of the radiolytic reaction between nitrogen and oxygen and the formation of hydrogen peroxide. In either case, accelerated corrosion of Zircaloy would not be predicted in the absence of irradiation since zirconium alloys have been shown to be relatively inert in both media as discussed in Yau and Webster (1987) and CRWMS M&O (2000a, Sections 6.1.6 and

II.4). As one example, zirconium equipment is used in the chemical processing industry where peroxide strengths of 90% are used. The service life has been increased by an order of magnitude compared to graphite components previously used, which were generally considered to be very inert. In nitric acid, zircaloy and its alloys are inert up to acid concentrations of 65%. The effect of nitric acid is indirect in that nitric acid stabilizes the formation of metal-halide complexes, which control corrosion of the cladding. Provided radiolysis does not produce nitric acid at greater concentrations, there will be no impact on the uniform corrosion rate as a result of nitric acid production from radiolysis in the absence of halide ions.

Radiolysis was reviewed in detail in the IAEA 1993 report (pp. 82-92). Specifically the topic of radiolysis of “thick oxide film effects” was discussed. The report noted (IAEA 1993, p. 91) that “the radiation enhancement of Zircaloy corrosion in the aqueous phase arises from the synergistic interaction of radiation and water chemistry. It has been recognized that in the early stages of Zircaloy corrosion the acceleration by reactor radiation, which is usually observed in oxygenated water, is suppressed in the presence of excess hydrogen in the aqueous phase, but that beyond the threshold oxide thickness Zircaloy specimens exposed to low-oxygen water corrode at accelerated rates under irradiation as if they were immersed in oxygenated water.” The report concluded that, under the worst conditions of high radiation levels and excess oxygen ions, the corrosion rate is only accelerated by a factor of three. Further support for this position can be obtained from Hillner et al. (1998, p. 12). On page 12, it is stated that “the corrosion rate of Zircaloy in water is limited by the slowest of the basic corrosion steps: dissociation of water into oxygen and hydrogen ions, diffusion of oxygen ions through the oxide film, oxidation of the Zr metal, diffusion of electrons through the oxide, and hydrogen-ion reduction by the electrons at the water-to-oxide interface. At temperatures for current testing, that is, above about 230°C, diffusion of oxygen ions through the oxide film is rate limiting. In extrapolating to lower temperatures, one of the other basic steps could become rate limiting, which would decrease the corrosion rate to less than predicted by the extrapolation.” In summary, if corrosion is controlled by the oxygen ion diffusion rate, the presence of peroxide would have no effect on Zircaloy corrosion, and the corrosion rate would be expected to be that of uniform corrosion.

Yau and Webster (1987, pp. 707-721) review the corrosion of zircaloy under various chemical environments for commercial applications (corrosion rates and time scales of interest for industrial applications, not for repository time scales). Zircaloy is resistant to corrosion from HCl to temperatures well above boiling (Yau and Webster 1987, p. 710). Yau and Webster (1987) report no corrosion in seawater, brackish water, and polluted water. Zircaloy is resistant to corrosion from sulfuric acids in concentrations less than 20 percent and corrodes slowly in terms of commercial applications (not repository time scales) in sulfuric acid solutions below 65 percent.

Van Konynenburg et al. (1998, p. 7-17) performed container material scoping tests using Zircadyne 702 (a zircaloy-hafnium alloy) in 0.01 mol/L each of sodium formate (NaCOOH), nitric acid (HNO₃), NaCl, H₂O₂, and 0.02 mol/L sodium oxalate (Na₂C₂O₄), with an initial pH of approximately 4, temperature of 90±5 °C, and typical test duration of 96 hours. The test solution was designed to represent highly concentrated forms of acids formed by radiolysis. Formic acid, a potential pH buffer, was not present in the Zircadyne 702 test. They report a final pH of 4.26 and corrosion rate of 50 μm/yr for zircaloy in the acid solution.

In basic solutions, Hansson (1984, summary page) measured corrosion of Zircaloy 2 in anaerobic cement pore solutions of pHs of 12.0 to 13.8. She concludes that “active corrosion of Zircaloy 2 in anaerobic concrete will not occur and by comparison with measurements on steel, it is likely that the passive corrosion rates will be even lower in concrete than those measured in the synthetic pore solution.” The duration of highly alkaline conditions in an emplacement drift depends on the assumed use of concrete. If concrete (emplacement drift liner material) is not used, the duration of highly alkaline conditions in the emplacement drift is less than 5000 years, with the long-term pH at about 8. If concrete material is used in the liner, the expectation is that the pH in the emplacement drift will be quite basic for the first 10,000 years.

Radiolysis might indirectly destabilize cladding by allowing the buildup of ferric chloride in solution. Above pH 3, ferric ions tend to form insoluble ferric hydroxides. Note that a number of waste package components are able to buffer nitric acid formation. In particular, influent bicarbonate and ferric hydroxides formed through waste package degradation possess a considerable acid-buffering capacity. For radiolysis to have an impact on cladding stability any nitric acid that is formed must come into contact with Fe-containing minerals. Although such contact will add iron to solution, where it might combine with halides, it will also tend to anchor the pH to values above pH 3. In other words, the specific sequences of reaction paths that are needed to link radiolysis with cladding degradation are coupled and self-canceling. This is illustrated schematically in Figure II-1 where nitric acid reacted at an arbitrary rate with the degradation product $\text{Fe}(\text{OH})_3$.

Nitric acid levels caused by radiolysis will depend upon the makeup and relative volumes of the gas and aqueous phases, the wetted surface area of the waste package interior, the time of breach (which determines the radiation level), and the gamma dose. Note again that Zircaloy cladding is resistant to direct attack by nitric acid. It is through stabilization of soluble metal-halide complexes by low pHs that nitric acid production can promote cladding corrosion. The important point to Figure II-1 is that sub-pH 3 conditions may entail dissolution of large amounts of waste package degradation products. While $\text{Fe}(\text{OH})_3$ dissolution provides dissolved iron, it consumes acid, making it difficult to envision a scenario that favors chemical corrosion of the cladding.

It is accepted that corrosion degradation of Zircaloy fuel cladding does not begin until the waste package is breached (typically 10,000 years or more after emplacement). Once a waste package is breached, water may enter the waste package as water vapor or as drips. The waste package and fuel will have cooled down by that time to an extent that will allow a water film to form on the fuel cladding (either by flowing liquid, as bulk condensation, or as adsorbed water) that is thick enough to support corrosion reactions.

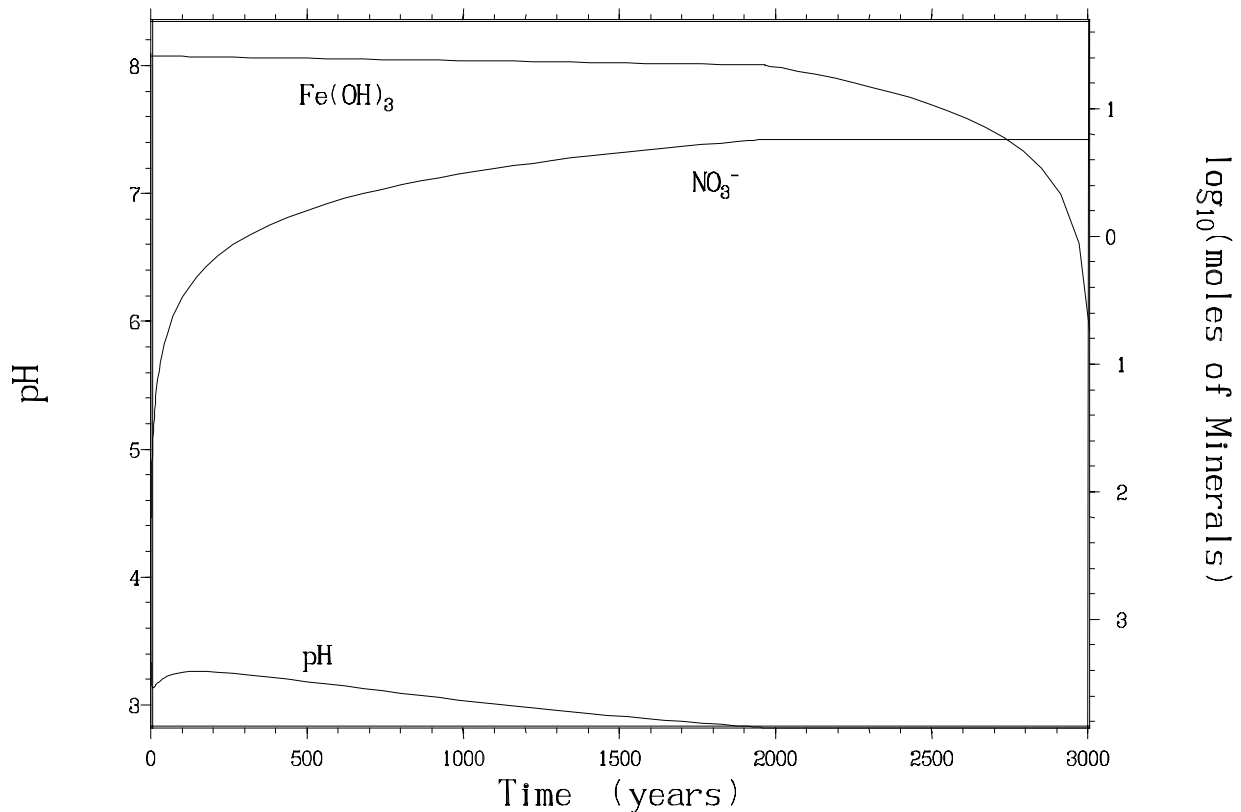


Figure II-1. Reaction of Nitric Acid with $\text{Fe}(\text{OH})_3$

Ahn (1997) conjectures that gamma radiolysis of the nitrogen/oxygen mixture in air and subsequent transport of the nitric acid generated to the water on the cladding surface could result in the formation of sufficiently acidic conditions to enhance cladding corrosion. The bases for that conjecture are examined here. Assumptions that are part of that conjecture include: (1) One liter of water per waste package is assumed to cover all 1-mm spent fuel particles in a 21-PWR spent fuel assembly, resulting in a water layer thickness of $\sim 4 \mu\text{m}$ (Ahn 1997, p. 4). (2) At relative humidity of 80%, 5 – 10 monolayers of water will be condensed at outdoor temperatures; therefore, the 4- μm water layer is likely to be aqueous (Ahn 1997, p.4). Ahn (1997, p.5) uses Equation 1 from Burns et al. (1982, p. 262) to predict the amount of nitrogen fixation due to gamma radiolysis at the cladding surface:

$$N = 2C_o R \{1 - \exp(-1.45 \times 10^{-5} G D t)\} \quad (\text{Eq. 1})$$

where

- N = concentration of HNO_3 in water [mol/L];
 C_o = initial concentration of N_2 in air [mol/L];

| | | |
|-----|---------------------------------------|-----------------------------|
| R | = ratio of air volume to water volume | [1]; |
| G | = yield | [molecules produced/100eV]; |
| D | = dose rate | [Mrad/hr]; |
| t | = time. | [hrs]. |

For time intervals of water drip (1 year and 3.5 days), with 4 μm water film thickness, a dose rate of ~ 50 rad/hr within 5000 years, and $G = 1.9$ (Burns et al. 1982, p. 263), Ahn (1997, p. 5) believes that the water film is likely to be acidic.

Inspection of Equation 1 indicates that, for large times, the concentration of HNO_3 approaches an asymptotic limit. The limiting value, $2C_oR$, should be that due to the net available inventory of nitrogen in the appropriate control volume. The presence of the term R within the limiting value for N suggests the possibility for extremely high concentrations (acidic conditions) in the water. If Equation 1 is evaluated for the time, t , it takes for the exponent to increase to unity (i.e., $N = 2C_oR\{1-1/e\}$), t (converted to years) is 8.29×10^4 years. Thus, the time required to reach a significant fraction of C_oR is of the order of tens of thousands of years. The form of this equation depends on an assumption that the water-air system is closed. It is not credible that the system would likely close again after being breached for water entry. Furthermore, the accumulation of significant amounts of nitric acid is not possible if water is constantly dripping onto the cladding surface, thus flushing away any HNO_3 absorbed in the water.

High acid concentrations could be achieved only if the volume of water held up in the waste package were very small (say, 1 L). This is readily achievable when no groundwater drips into the waste package, but then the absence of halide precludes significant corrosion of cladding. If dripping water simply flows *through* the waste package, acid is not able to accumulate, and the concentrations will remain low. In order for high acid concentrations to develop, a small amount of water must flow into the waste package early on and not accumulate, or else it must flow in at a rate that is minutely greater than the evaporation rate. In order for halide ions to accumulate, thereby enhancing corrosion of the cladding, water must flow in more or less continuously but only accumulate at a very slow rate. While accumulating water at low rates is physically possible, it seems improbable that a narrow range of net water influxes will prevail over long periods of time and be dispersed throughout a waste package, regardless of the drip rate. If inflowing water is not widely dispersed, the small pool of water will remain weakly acidic, since acid production will continue throughout a waste package, rather than being concentrated in the pool. Although halides may concentrate in a pool, the pH will remain too high for corrosion to be enhanced.

Films of water forming on the interior of the upper walls of the waste package and dripping onto the fuel rods have been considered. Thermodynamically, condensation is extremely unlikely since the outside surfaces of the packages are cooler than the inside surfaces. Thus a scenario where acidic vapors condense and 'rain' down on the cladding with dissolved HNO_3 and metal-halide complexes is excluded based on lack of credibility.

In order for nitric acid alone to corrode Zircaloy cladding, the concentration must be greater than about 65%, as stated previously. This is equivalent to 14.2 mol/L. Although it is at least physically possible for sufficiently high nitric acid concentrations to be obtained to corrode Zircaloy cladding with no halide ions present, during the 10,000 years required for such acid concentrations to be reached, the more readily-corroded components of the waste package would scavenge any acid produced. So it is unlikely that such quantities of acid would accumulate. On the other hand, during the 10,000 years required for such acid concentrations to be reached, the more readily-corroded components of the waste package would scavenge any acid produced, so it is unlikely that such quantities of acid would accumulate.

To summarize, in order for gamma radiolysis to produce acidic conditions on the cladding surface and thereby contribute to cladding failure, an unlikely set of conditions must be maintained within the waste package for long periods of time. Namely, the cladding surface must be continually wetted with groundwater containing fluoride and chloride ions while at the same time sufficient evaporation takes place to concentrate and accumulate solutes to provide the source of halides needed to enhance the corrosion rate for long time periods. This scenario is not credible. Higher water influx rates—enough to cause a steady flow of water through a waste package—would dilute any acid that is produced, raising the pH to levels where halides are ineffective in enhancing corrosion. The waste package must be sufficiently breached and under groundwater drips to allow water to flow in, but not be so open as to allow NO_2 or HNO_3 produced in the gas phase to diffuse out of the waste package before dissolving in water films on the cladding. A delicate balance among continually changing water influxes, heat loads, and diffusive driving forces would have to be sustained over long periods in order for acidic conditions to be produced that could have any effect on the cladding. Such conditions appear not to be credible.

ATTACHMENT III
COMPACT DISC (information is on a compact disc)