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

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## ACRONYMS

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
DOE	United States Department of Energy
DSNF	DOE spent nuclear fuel
DTN	data tracking number
FEP	features, events, and processes
FFTF	fast flux test facility
HLW	high-level waste
LLNL	Lawrence Livermore National Laboratory
M&O	Management and Operating Contractor
MOX	mixed oxide
NRC	Nuclear Regulatory Commission
OCRWM	Office of Civilian Radioactive Waste Management
ODE	ordinary differential equation
SCFT	solid-centered flow-through mode
SCM	Software Configuration Management
SCR	Software Change Request
SQR	Software Qualification Request
TBV	to be verified
TSPA-VA	Total Systems Performance Assessment - Viability Assessment
UOX	uranium oxide
WP	waste package

## 1. PURPOSE

As directed by written work direction (CRWMS M&O 1999d), this document examines 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 primary processes likely to control the major element chemistry of reacting in-package fluids 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 (WPs); dissolution of high-level waste (HLW) 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 Si levels, and ionic strength. Note that these all are likely to vary as a function of time. Timescales of interest begin with the first breach of the WP and often extend for at least 50,000 years, which is often the amount of time required for a substantial portion of the WP solids to react with incoming fluids. (In some cases, reactions approach completion much sooner; hence, runs are shorter. Also in a few cases, the run was prematurely halted, due to numerical instability). 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.

To perform such a calculation, termed a reaction-path simulation, requires a number of specific inputs, some of which are known only semi-quantitatively. 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 1992a). With a few exceptions (see Section 6.1.4), the alteration phase identities are calculated from the EQ3/6



database. The design information used for the calculation is EDA II. The results of the in-package chemistry AMR will not be affected by the changes in the EDA design announced on 1/21/00 (see Section 5. [#5.2]).

## 2. QUALITY ASSURANCE

The Quality Assurance (QA) program applies to this analysis. All types of waste packages were classified (per QAP-2-3) as Quality Level-1 in *Classification of the MGR Uncanistered Spent Nuclear Fuel Disposal Container System* (CRWMS M&O 1999a, p. 7). This analysis applies to all of the waste package designs included in the MGR Classification Analyses. Reference CRWMS M&O (1999a) is cited as an example. The development of this analysis is conducted under Activity Evaluation 1101213FM3 *Waste Form Analyses & Models - PMR* (CRWMS M&O 1999b) which was prepared per QAP-2-0. The results of that evaluation were that the activity is subject to the *Quality Assurance Requirements and Description* (DOE 1998b) requirements.

## 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 1992a). 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. Much of the thermodynamic data that is relied on in the present calculations was measured at 25°C (see Section 5. [#5.5] for further explanation). EQPT takes a formatted data file (a "data0" file, DTN: SN0001T0811199.006) 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 reactants, which react irreversibly. 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 (ODE) 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.

### **3.2 SOLID-CENTERED FLOW-THROUGH MODE**

EQ6 Version 7.2b, as distributed by LLNL, does not contain a solid-centered flow-through (SCFT) mode. A SCFT calculation much more closely mimics the likely path of WP alteration, and is therefore critical. To add this mode, it is necessary to change the EQ6 for source code and recompile the source. However, by using a variant of the special reactant type built into EQ6, it is possible to add the functionality of SCFT mode in a very simple and straightforward manner. 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).

The new mode is induced with a "special" reactant. The EQ6 input file nomenclature for this new mode is jcode=5; in the Daveler format, it is indicated by the reactant type DISPLACER. The jcode=5 is immediately trapped and converted to jcode=2, and a flag is set to indicate the existence of the DISPLACER reactant. Apart from the input trapping, the distinction between the DISPLACER and SPECIAL reactants is seen only in one 9-line block of the EQ6 FORTRAN source code (in the reacts subroutine), where the total moles of elements in the rock plus water system is adjusted by adding in the DISPLACER reactant and subtracting out a commensurate amount of the total aqueous elements.

### **3.3 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. 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, 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 WP 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. 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 (M&O) contractor QAP-SI.1Q procedure. 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.

#### **4. INPUTS**

The method used for this analysis involves the following steps:

- Use of the EQ3/6 software package (Section 6.2) for tracing the progress of reactions with evolution of the chemistry, which includes the estimation of the concentrations remaining in solution and the composition of the precipitated solids. EQ3NR is used to determine a starting fluid composition for EQ6 calculations [Section 3].
- Selection of dissolution rates and masses of waste package components (Section 6.1.1)
- Use of the SCFT mode in EQ3/6; in this mode, an increment of aqueous “feed” solution is added continuously to the WP system, and a like volume of the existing solution is removed, simulating a continuously-stirred tank reactor (Section 3.2)
- Determination of major element concentrations in solution as a function of time (from the output of EQ3/6 simulated reaction times greater than 50,000 years)
- Identification of solids (precipitated minerals or corrosion products [Section 6.1.4]).

#### **4.1 DATA AND PARAMETERS**

The primary data that are used in the calculation include the thermodynamic database for EQ3/6 (Data Tracking Number [DTN]: SN0001T0811199.006), WP component amounts (DTN: SN9911T0811199.003 and CRWMS M&O 1998b), surface areas (DTN: SN9911T0811199.003 and CRWMS M&O 1998b), degradation rates (DTN: SN9911T0811199.003 and DTN: LL981004451021.061), and fluid fluxes (a range of values were used to test the sensitivity of results to fluid flux).

#### **4.2 CRITERIA**

No specific criteria have been identified as applying to this work activity.

#### **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:

- 5.1 Aqueous solution filling all voids within WPs, and solutions that drip into the package for ~50,000 years will have the composition of J-13 well water. This composition is given in Table 2. The justification for the first part of this is that it provides the maximum degradation rate with the potential for the fastest flushing of radionuclides and is, thereby, conservative. The justification for the second part is that the groundwater composition is controlled largely by transport through the host rock, over pathways of hundreds of meters, and the host rock composition is not expected to change substantially over the next million years.
- 5.2 Water entering the waste package can be approximated by the J-13 well water. This means that the infiltrating water is envisioned to have only a minimal contact, if any at all, with metal (degraded or intact) and backfill before entering the breached WP. The justification for this is that water should move rapidly into the WP such that minimal time is available for reaction.
- 5.3 Water may circulate freely enough in the partially degraded WP so that all degraded solid products may 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 WP.
- 5.4 The existing database supplied with the EQ3/6 computer package is sufficiently accurate for the purposes of this calculation. The justification for this is that the data have been carefully scrutinized by many experts over the course of several decades and carefully selected by LLNL for incorporation into the database (Spahiu and Bruno 1995; Daveler and Wolery 1992; Wolery 1992b; Wolery and Daveler 1992). These databases are periodically updated and/or new databases added. The databases include references internally for the sources of the data. The reader is referred to this documentation, included in the electronic files labeled data0 (DTN: SN0001T0811199.006) that accompany this calculation (see Attachment I). Nevertheless, the quality of data needs to be verified in the future.
- 5.5 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 justification 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, hence the broad scale features of the output fluid compositions are deemed independent of temperature.

- 5.6 Gases in the solution in the WP remain in equilibrium with the ambient atmosphere outside the WP. In other words, contact of WP fluids with the gas phase in the repository is envisioned to be sufficient to maintain equilibrium with the CO<sub>2</sub> and O<sub>2</sub> present, whether or not this is the normal atmosphere in open air or rock gas that seeps out of the adjacent tuff. Moreover, the specific partial pressures of CO<sub>2</sub> and O<sub>2</sub> of the ambient repository atmosphere are set to, respectively, 10<sup>-3.0</sup> and 10<sup>-0.7</sup> atm (DOE 1998a). The oxygen partial pressure is equivalent to that in the atmosphere. The carbon dioxide pressure is somewhat higher and was chosen to reflect the observation that J-13 well water appears to be in equilibrium with above-atmospheric carbon dioxide levels. The gas phase equilibria at the repository horizon are expected to be similar to that prevailing in the open atmosphere.
- 5.7 Precipitated solids that are deposited remain in place and are not mechanically eroded or entrained as colloids in the advected water. This allows full simulation of likely fluid-solid interaction inside the WP.
- 5.8 Corrosion rates will not be significantly enhanced by microbial induced corrosion. The backfill will be inspected or treated to ensure no organic nutrients will be available for microbial induced corrosion.
- 5.9 Circulation and mixing of the water occurs inside the package. This allows complete exposure of WP components to incoming fluids, thereby maximizing the amount of WP degradation.
- 5.10 The reported alkalinity in analyses of J-13 well water corresponds to bicarbonate (HCO<sub>3</sub><sup>-</sup>) alkalinity (Harrar et al. 1990). Contributors to alkalinity in J-13 well water, in addition to bicarbonate, potentially include borate, phosphate, and silicate. However, at pH less than 9, the contribution of silicate will be small, and in any case the concentrations of all three of these components in J-13 well water are small. Fluoride ion will not contribute to a typical measured alkalinity because the titration will not be carried out to a sufficiently low pH for its influence to be detectable. Nitrate will likewise not contribute.
- 5.11 The rate of entry of water into, as well as the rate of egress from, a WP is equal to the rate at which water drips onto the package. 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.
- 5.12 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 WP components—in other words hundreds of years or less. The choice of minerals assumed to grow and dissolve in the calculation is justifiable because it is consistent with scientific fact.

The analysis begins with selection of data for compositions (moles), amounts (g), surface areas ( $\text{cm}^2$ ), and reaction rates ( $\text{mol}/\text{cm}^2\cdot\text{s}$ ) of the various components of CSNF and codisposal WPs. These quantities are then normalized to represent reaction of 1 liter of fluid. Given fluxes of J-13 well water into a WP, EQ3/6 estimates the compositions and amounts of solid products and of substances in solution as a function of time.

## 6. ANALYSIS/MODEL

### 6.1 CALCULATION INPUTS

#### 6.1.1 WP Materials and Performance Parameters

Waste packages considered include CSNF and codisposal wastes. CSNF WPs 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  $\text{GdPO}_4$ , and Zr-clad fuel rods. The chemical characteristics of each are outlined in Table 1. CSNF is primarily  $\text{UO}_2$ . The spent fuel composition used in the EQ6 runs and listed in Table 1 is for 10,000-year old, 4.9%  $^{235}\text{U}$ -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  $\text{NpO}_2$ ,  $\text{PuO}_2$ ,  $\text{BaO}$ ,  $\text{MoO}_3$ ,  $\text{Nd}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{Cs}_2\text{O}$ , and  $\text{CeO}_2$ .

Codisposal wastes cover a broad range of compositions (CRWMS M&O 1998d) but have in common the fact that the WPs will include a DSNF canister surrounded by 5 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]), the fast flux test facility (FFTF) WP was used as the DSNF component in all calculations. This is conservative because FFTF has a relatively high Pu content, as well as a potentially large Np source, relative to other DSNF sources. FFTF WPs are made up of six reactive components: A516 carbon steel; 316 stainless steel (with and without  $\text{GdPO}_4$  dopant); 304L low carbon steel; DHLWG; mixed oxide fuel (MOX)—made up of Pu, U, and Np oxide; and  $\text{UO}_2$  fuel (UOX).

The dissolution rate law for CSNF, UOX, and MOX was fit from  $\text{pH} < 9$  pH-dependent data ( $\text{P}_{\text{CO}_2} = 10^{-3.52}$ ;  $\text{P}_{\text{O}_2} = 10^{-0.68}$ ) from the literature (Grambow 1989):  $\log \text{Rate} (\text{mg}/\text{m}^2\cdot\text{d}) = 3.3 - 0.5\cdot\text{pH}$  and the high pH minimum rate of  $4.42\text{E}-14$ . [The rate law is converted to units of  $\text{mol}/\text{cm}^2\cdot\text{s}$  in Table 1 (CRWMS M&O 1998b)]. The dissolution rate of DHLWG is pH-dependent, increasing with increasing pH above pH 7 at  $25^\circ\text{C}$  and increasing with decreasing pH below pH 7. Dissolution rate constants in Table 1 come from fits to SRL-165 high level waste glass dissolution data DTN: LL981004451021.061. While the latter values are used to bound 'low' dissolution rates, 'high' rates are used that are 10 times the low values. The latter value represents the characteristic maximum spread that is typically observed in compilations of solid dissolution rates in the literature. Note though that use of the high DHLWG degradation rates

does not have a significant impact on the fluid chemistry values used in the TSPA-VA. Dissolution rates of the various steels come from DTN: SN9911T0811199.003.

Surface areas and moles of WP components were calculated from the geometries of the waste form components and come from DTN: SN9911T0811199.003 (codisposal) and CRWMS M&O (1998b) (CSNF). Each case assumed that the interior sleeve of the WP 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 WP 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 WP, 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  $[1/5807 \text{ l}][2\pi * 0.94 \text{ (m)} * 4.617 \text{ (m)} * 0.005 \text{ (m)} + 2 * \pi * (0.94)^2 * 0.01 \text{ (m)}] * 7980000 \text{ g m}^{-3} / 100 \text{ g mol}^{-1} = 26.35 \text{ mol/l}$ .

Table 1. Chemical Characteristics of CSNF and Codisposal WP Components

Material	Formula	Amount (mol/l)	Degradation Rate (mol/cm <sup>2</sup> ·s); 25°C	<sup>a</sup> Surface Area (cm <sup>2</sup> )
<b>CSNF WP Parameters</b>				
Al alloy	<sup>a</sup> Al <sub>0.9757523</sub> Mg <sub>0.0112008</sub> Si <sub>0.0058174</sub> Fe <sub>0.0034132</sub> Cu <sub>0.0011786</sub> Ti <sub>0.0008528</sub> Zn <sub>0.0010414</sub> Mn <sub>0.0007435</sub>	<sup>a</sup> 2.36	<sup>g</sup> 2.28E-13	<sup>a</sup> 96.424
A516	<sup>b</sup> Fe <sub>1.760435</sub> Mn <sub>0.001902143</sub> S <sub>0.001091499</sub> P <sub>0.001129989</sub> Si <sub>0.01032561</sub> C <sub>0.02331196</sub>	<sup>c</sup> 11.948	<sup>b</sup> 2.487E-11 (hi) <sup>b</sup> 8.706E-12 (low)	<sup>a</sup> 504.160
316 SS	<sup>b</sup> Fe <sub>1.169177</sub> Cr <sub>0.3269746</sub> Ni <sub>0.2044646</sub> Mn <sub>0.03640464</sub> Si <sub>0.03560556</sub> Mo <sub>0.02605795</sub> C <sub>0.00249771</sub> N <sub>0.00713942</sub> P <sub>0.001452843</sub> S <sub>0.0009355704</sub>	<sup>d</sup> 23.75	<sup>b</sup> 2.528E-13 (hi) <sup>b</sup> 2.528E-14 (low)	<sup>d</sup> 52.500
316 SS/B	<sup>a</sup> Fe <sub>0.5699404</sub> B <sub>0.0623405</sub> Cr <sub>0.1924212</sub> N <sub>0.1210848</sub> Mn <sub>0.0191</sub> Mo <sub>0.0137216</sub> N <sub>0.0037597</sub> S <sub>0.0004942</sub> Si <sub>0.0140616</sub> P <sub>0.0016906</sub> C <sub>0.013154</sub>	<sup>a</sup> 7.856	<sup>a</sup> 1.169E-13 (hi) 1.169E-14 (low)	<sup>a</sup> 156.010
CSNF	<sup>a</sup> U <sub>0.315799</sub> O <sub>0.660284</sub> Np <sub>0.000623109</sub> Pu <sub>0.00205439</sub> Mo <sub>0.00280144</sub> Nd <sub>0.00230907</sub> Zr <sub>0.00356548</sub> Cs <sub>0.00117321</sub> Ba <sub>0.00162654</sub> Ce <sub>0.00141261</sub>	<sup>a</sup> 27.21	<sup>e</sup> 4.420E-14 + 10 <sup>-10.59-0.5<sup>pH</sup></sup>	<sup>a</sup> 96200
<b>Codisposal WP Parameters</b>				
304L	<sup>b</sup> Fe <sub>1.218418</sub> Cr <sub>0.365412</sub> Ni <sub>0.1703868</sub> Mn <sub>0.03640464</sub> Si <sub>0.02670417</sub> N <sub>0.00713942</sub> C <sub>0.00249771</sub>	26.384 (gpc) 20.065 (ident)	22.516E-13 (hi) 22.516E-14 (low)	2150.804 (gpc) 26.661 (ident)
A516		<sup>b</sup> 10.140		<sup>b</sup> 129.615
DHLWG	<sup>b</sup> Si <sub>0.7820395</sub> Na <sub>0.3766185</sub> B <sub>0.2980151</sub> Li <sub>0.2134365</sub> Fe <sub>0.1327982</sub> Al <sub>0.0867235</sub> K <sub>0.07670634</sub> Mg <sub>0.03405157</sub> Mn <sub>0.0284515</sub> Ti <sub>0.01250704</sub> U <sub>0.007914684</sub> S <sub>0.004051165</sub> Cl <sub>0.00328077</sub> Cu <sub>0.002410401</sub> F <sub>0.001682371</sub> Cr <sub>0.001593477</sub> Ba <sub>0.00082583</sub> P <sub>0.0004554802</sub> Pb <sub>0.0002952349</sub> Pu <sub>0.00006241702</sub> Np <sub>0.000004031999</sub> O <sub>2.807943</sub>	<sup>b</sup> 24.821	<sup>f</sup> 1.983E-19(H <sup>+</sup> ) <sup>-0.4721</sup> + 6.144E-12(H <sup>+</sup> ) <sup>0.6381</sup> (low)  1.983E-18(H <sup>+</sup> ) <sup>-0.4721</sup> + 6.144E-11(H <sup>+</sup> ) <sup>0.6381</sup> (hi)	<sup>b</sup> 1915.142
316 SS	can assembly pins sleeve	<sup>b</sup> 0.946 <sup>b</sup> 20.573 <sup>b</sup> 0.423 <sup>d</sup> 26.35		<sup>b</sup> 24.134 <sup>b</sup> 27.267 <sup>b</sup> 257.913 <sup>d</sup> 56.5
316 SS/ GdPO <sub>4</sub>	<sup>b</sup> Fe <sub>1.13167</sub> Cr <sub>0.3164594</sub> Ni <sub>0.1979051</sub> Mn <sub>0.03523682</sub> Si <sub>0.03446337</sub> Mo <sub>0.02522204</sub> N <sub>0.006910394</sub> P <sub>0.01412484</sub> S <sub>0.0009055582</sub> Gd <sub>0.0127186</sub> O <sub>0.0508744</sub>	<sup>b</sup> 0.653	<sup>b</sup> 2.528E-14	<sup>b</sup> 16.732
UOX	<sup>b</sup> U <sub>0.370332</sub> O <sub>0.7406648</sub>	<sup>b</sup> 0.018	<sup>e</sup> 4.420E-14 + 10 <sup>-10.59-0.5<sup>pH</sup></sup>	<sup>b</sup> 72.072
MOX	<sup>b</sup> U <sub>0.2746725</sub> Pu <sub>0.09407909</sub> Np <sub>0.001101603</sub> O <sub>0.7397063</sub>	<sup>b</sup> 0.393	<sup>e</sup> 4.420E-14 + 10 <sup>-10.59-0.5<sup>pH</sup></sup>	<sup>b</sup> 1559.382

<sup>a</sup> CRWMS M&O (1998b)<sup>b</sup> DTN: SN9911T0811199.003<sup>c</sup> Originally from CRWMS M&O (1998b), recalculated to a MW = 100 g/mol<sup>d</sup> See preceding paragraph<sup>e</sup> Grambow (1989)<sup>f</sup> DTN: LL981004451021.061. gpc = glass pour canisters. All moles and surface area values truncated three digits right of the decimal point for clarity. The molecular weights of all components is 100 g/mol, except for borated 316 SS: MW = 52.49 g/mol<sup>g</sup> ASM (1987)<sup>h</sup> normalized to a liter of solution



Note that uncertainty in the dissolution rates of the various WP materials is dealt with by using a range of high and low values. By the same token, uncertainties in the actual fluid inputs are dealt with by using a range of values (Section 6.1.2).

### 6.1.2 Chemical Composition of J-13 Well Water

The water composition entering the waste package is assumed to be J-13 well water (Assumption 5.1). This composition is reproduced in Table 2 (from DTN: LL980711104242.054—see subsequent text for exceptions)

Table 2. Composition of Input

Component	Molarity	Component	Molarity
O	5.55E+01	Mg	8.27E-05
Ag	1.00E-16	Mn	3.05E-16
Al	2.55E-08	Mo	1.00E-16
Am	1.00E-16	N	1.42E-04
B	1.24E-05	Na	1.99E-03
Ba	1.00E-16	Nd	1.00E-16
Ca	3.24E-04	Ni	1.00E-16
Cl	2.01E-04	Np	1.00E-16
Cr	1.00E-16	Pb	1.00E-16
Cu	1.00E-16	Pd	1.00E-16
Eu	1.00E-16	Pr	1.00E-16
F	1.15E-04	Pu	1.00E-16
Fe	3.60E-12	Rb	1.00E-16
Gd	1.00E-16	Rh	1.00E-16
H	1.11E+02	Ru	1.00E-16
C	2.09E-03	S	1.92E-04
Cs	1.00E-16	Si	1.01E-03
Ce	1.00E-16	Sm	1.00E-16
P	1.26E-06	Am	1.00E-16
K	1.29E-04	Sn	1.00E-16
La	1.00E-16	Tc	1.00E-16
Li	6.92E-06	Ti	1.00E-16
Zn	1.00E-16	U	1.00E-16
Zr	1.00E-16	Y	1.00E-16

Any element whose concentration is listed as 1.00E-16 M is one that has not actually been detected in J-13 well water, but was initially included in the calculation since EQ6 occasionally requires a token amount of each element to be present in solutions. The molarity cutoff value for trace elements in Table 2 is  $10^{-12}$  mol/L, and including the trace elements would be below the noise level of calculation accuracy. Note that a number of the trace elements in Table 2 were subsequently deleted in the actual calculation in the interest of computational efficiency. This was solely for those elements that are not present in the WP solids and have not been actually detected in J-13 well water (e.g., Tc).

### 6.1.3 Drip Rate of J-13 Well Water into a WP

It is assumed (Assumption 5.12) that the drip rate onto a WP is the same as the rate at which water flows through the WP. The drip rate is taken from a correlation between percolation rate and drip rate (CRWMS M&O 1998c). Specifically, percolation rates of 40 mm/year and 8 mm/year correlate with drip rates onto the WP of 0.15 m<sup>3</sup>/year and 0.015 m<sup>3</sup>/year, respectively. The choice of these particular percolation and drip rates is discussed in detail in CRWMS M&O (1998c).

### 6.1.4 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<sub>2</sub>SiO<sub>4</sub>, 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<sub>3</sub> was prevented because of suspicions about data quality. Quartz growth was suppressed because J-13 well water is supersaturated with respect to quartz, suggesting that if it is growing near the repository horizon, it is doing so slowly. CaZrO<sub>3</sub> was suppressed because it is not known to form at low temperature.

## 6.2 EQ3/6 CALCULATIONS AND SCENARIOS MODELED

The primary uncertainties involved in the WP degradation calculation are the drip rate, the degradation rates of the various alloys in the WP, and the degradation rate of the HLW glass, and the degree of clad coverage. These parameters were varied widely to examine wide-range variations in major-element chemistry. All of the runs were named A\_XYZb.6i:

A = csnf (CSNF runs); A = cdsp (codisposal runs)

X = 0 (0% clad coverage); X = 1 (99% clad coverage); X = 2 (20% clad coverage) for CSNF runs only; for codisposal runs only; X = 0 (low HLW glass degradation rate) or 1 (high HLW glass degradation rate)

Y = 0 (low steel degradation rates) or 1 (high alloy degradation rates)

Z = 0 (0.0015 m<sup>3</sup>/yr H<sub>2</sub>O flux into the WP), 1 (0.015), or 2 (0.15)

b, if present, denotes a run that was restarted.

For example, the file csnf\_010.6i represents input for the CSNF WP where the low glass degradation rate is used, high alloy degradation rates are used, and a fluid flux of 0.0015 m<sup>3</sup>/yr is used. The file cdsp\_010.6i represents input for the codisposal WP where no credit is taken for cladding, high alloy degradation rates are used, and a fluid flux of 0.0015 m<sup>3</sup>/yr is used.

An additional calculation was done to test the specific effect of S content in the A516 steel on an early acid pulse observed for the low clad failure case. Decreasing the sulfur content by an order of magnitude causes the minimum pH to increase by roughly one unit and the onset and duration of the pulse to be smeared out.

## 6.3 RESULTS

Reaction of the WPs with incoming fluids results in dramatic changes in solution chemistry and in the solids likely to grow over time. These are both discussed separately below. Particular attention is paid though to solution chemistry, particularly actinide solubilities.

### 6.3.1 Solids

The mineralogy of WPs degrading into repository level ambient fluids is predicted to be dominated by clay minerals and a number of oxides. Specifically, a complex sequence of the following minerals is predicted to grow over time, including combinations of (for codisposal WPs):

- Copper minerals—brochantite and tenorite
- Silicates—nontronites, montmorillonites, microcline, mesolite, and petalite
- Oxides—hematite, diaspore, rutile, chalcedony,  $\text{BaCrO}_4$ , crocoite,  $\text{CeO}_2$ ,  $\text{PuO}_2$ , lopezite, and pyrolusite
- Carbonates—calcite, witherite, siderite, cerrusite, and  $\text{NaNpO}_2\text{CO}_3 \cdot 3.5\text{H}_2\text{O}$
- Borates—hydroboracite, and boric acid
- Phosphates, sulfates, and fluorides—fluorapatite, hydroxyapatite, rhabdophane, Cu-phosphate, Ni-phosphate, barite,  $\text{GdPO}_4 \cdot \text{H}_2\text{O}$ , pyromorphite,  $\text{CaF}_2$ , and  $\text{MgF}_2$
- Uranium minerals— $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ , soddyite,  $\text{CaUO}_4$ , U-phosphate, and haiweeite.

For CSNF WPs the minerals formed include:

- Copper minerals—brochantite and tenorite
- Silicates—nontronites, montmorillonites, beidellites, saponites, mesolite, and stilbite
- Oxides—hematite, diaspore, rutile, chalcedony, trevorite, baddeleyite,  $\text{BaCrO}_4$ ,  $\text{NpO}_2$ ,  $\text{NpOHCO}_3$ ,  $\text{CeO}_2$ ,  $\text{PuO}_2$ , hydrozincite, and pyrolusite
- Carbonates—calcite, magnesite, rhodochrosite, witherite, siderite, and smithsonite
- Phosphates, sulfates, and fluorides—fluorapatite, U-phosphate, barite, REE solid solutions with phosphate and fluoride
- Uranium minerals— $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ , soddyite,  $\text{CaUO}_4$ , saleeite, and haiweeite.

Growth of hematite and  $\text{UO}_3 \cdot 2\text{H}_2\text{O}$  for CSNF runs are volumetrically the dominant secondary phases. Maximum predicted accumulations of secondary phases are ~1.6 liters (per liter of fluid). There may, therefore, exist a potential for self-sealing of the WPs in some cases. Note though that there is a counteracting decrease in volume that is associated with the degradation of WP 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 WP components.

### 6.3.2 Solutions

Figures 1, 3, 4, and 5 illustrate typical calculated changes in fluid composition as J-13 well water reacts with WP components over time. Figure 2 shows calculated changes in dominant solid composition over time. (Only the most abundant phases formed are shown.) Note that the presence of WP components, particularly A516 carbon steel, is directly linked to sharp changes in solution composition.

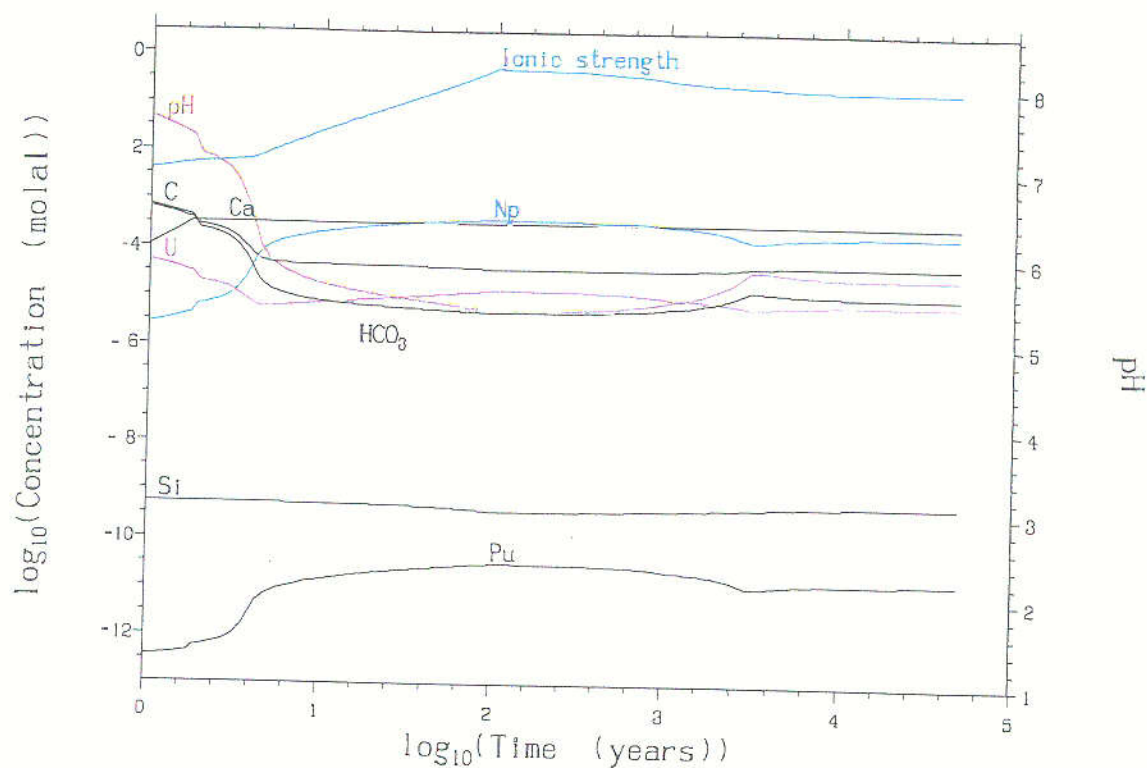


Figure 1. Predicted Changes in Fluid Composition for Case csnf\_000 (0% cladding coverage; low steel degradation; fluid flux = 0.0015 m<sup>3</sup>/yr)

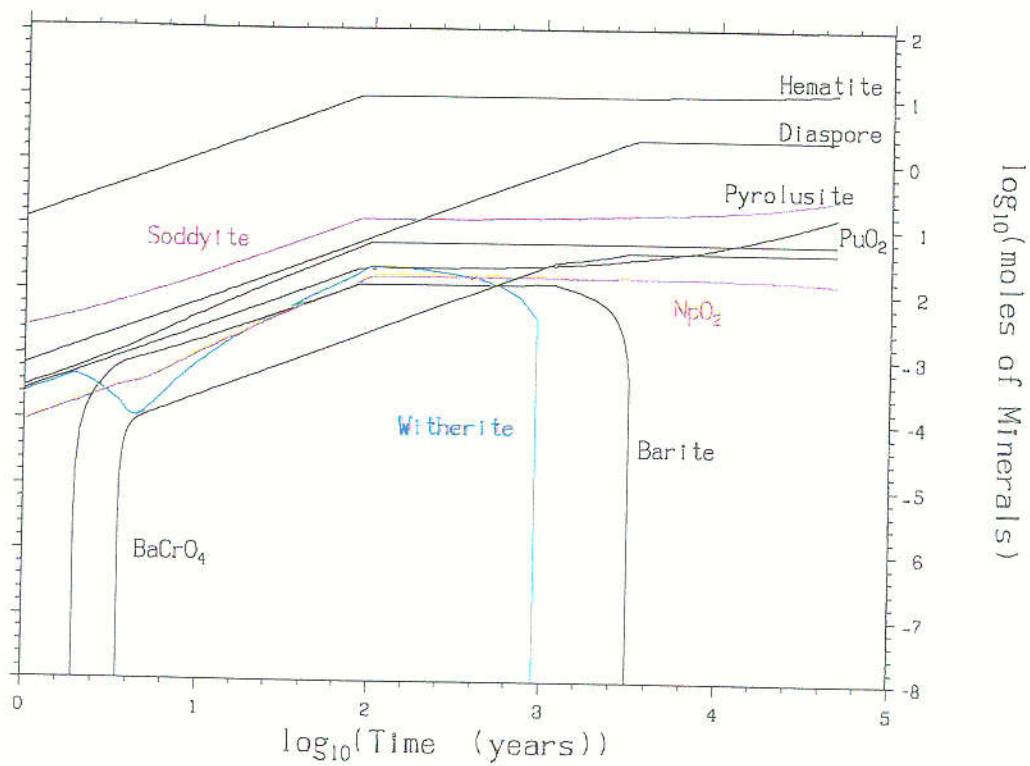


Figure 2. Predicted Changes in Selected Solid Abundances for Case csnf\_000 (0% cladding coverage; low steel degradation; fluid flux =  $0.0015 \text{ m}^3/\text{yr}$ )



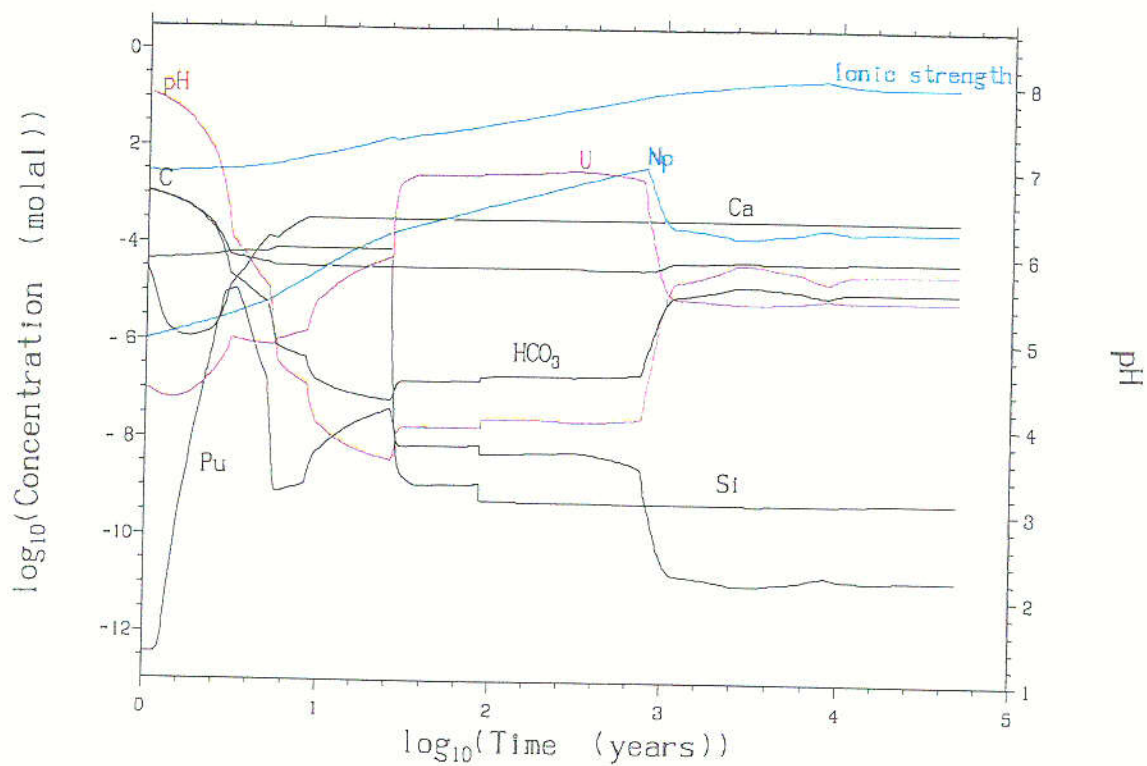


Figure 3. Predicted Changes in Fluid Composition for Case csnf\_100 (99% cladding coverage; low steel degradation; fluid flux =  $0.0015 \text{ m}^3/\text{yr}$ )

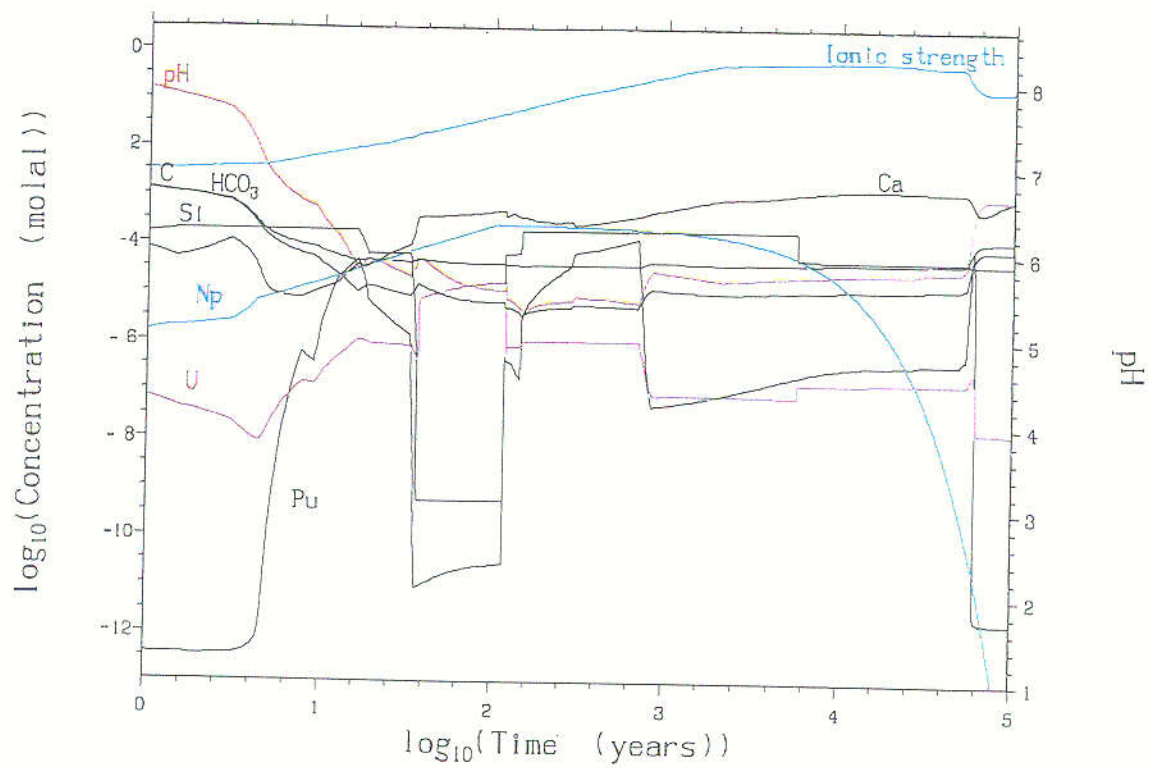


Figure 4. Predicted Changes in Fluid Composition for Case cdsp\_000 (low glass dissolution; low steel degradation; fluid flux =  $0.0015 \text{ m}^3/\text{yr}$ )



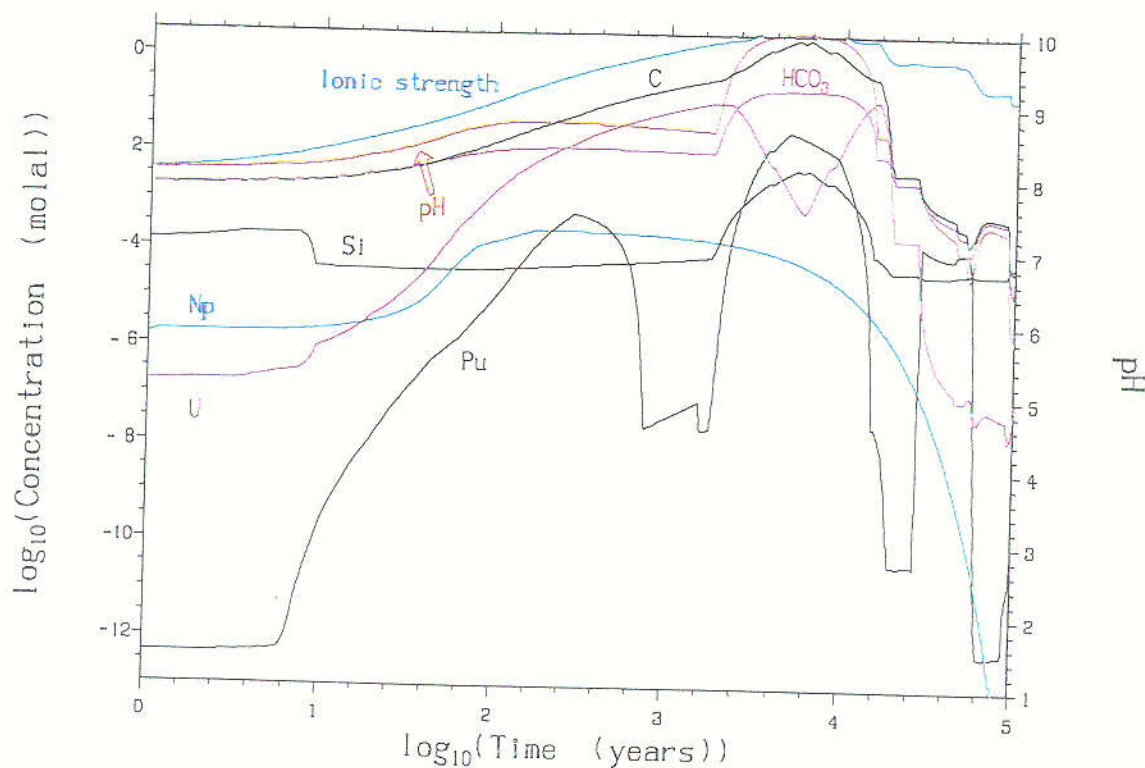


Figure 5. Predicted Changes in Fluid Composition for Case cdsp\_100 (high glass dissolution; low steel degradation; fluid flux = 0.0015 m<sup>3</sup>/yr)

In all runs, the slightly alkaline pH of the input solution (pH ~ 8.1) prevails inside the WP initially. Then the system pH progresses towards a minimum, primarily due to the oxidation of the A516 carbon steel. The high specific rate and relatively high surface area of the latter mean that its dissolution tends to dominate the whole reaction path, at least as long as it remains. Oxidation of sulfur in the steel to sulfate is the primary proton-producing reaction. pHs as high as 10 were predicted for codisposal WPs under conditions of high glass dissolution. Low flow rates also tend to drive pHs high. Dissolution of base cation-containing DHLW glass leads to the accumulation of alkalinity, the accumulation being most significant when fluid influx is least.

Solution ionic strength varies between 0.003 and ~5.8 mol/l. The higher values are associated with low fluid fluxes and/or elevated glass degradation rates. The latter are specific to codisposal WPs. Ionic strengths of CSNF WP effluents never exceed 1.7 and the primary dissolved salts are Ni and Cr. Note that solutions having ionic strengths exceeding ~1.0 M are probably not accurately described by the calculation approach in EQ3NR. The primary elements that contribute to the high ionic strength were ions of Cr and Na. The predicted accumulation of Cr may be somewhat dubious as it arises from the lack of Cr(VI)-bearing solids in the thermodynamic database. The predicted presence of Na<sup>+</sup> is probably real though as it is the inevitable consequence of Na-B waste glass dissolution. Na<sup>+</sup> levels occasionally exceed 1M and must be considered when considering the solubility of actinide-bearing phases that also contain Na (e.g. NaNpO<sub>2</sub>CO<sub>3</sub>).



Table 3 summarizes the range of in-package fluid compositions predicted to occur for both the CSNF and codisposal WPs.

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

Variable	CSNF	codisposal
pH	3.6-8.1	4.8-10.0
Eh (volts)	0.7-1.0	0.6-0.9
I	0.003-1.7	0.003-5.8
Ca	3.9E-6 - 0.00032	3.0E-7 - 0.02
C	2.8E-5 - 0.002	3.5E-5 - 0.5
Pu	0 - 5.6E-9	0-1.0E-4
Si	3.7E-10 - 1.9E-4	5.3E-10 - 1.9E-4
U	0 - 5E-3	0 - 1.1E-3

In summary, solution pH in each run likely represents a dynamic balance between proton-producing reactions—dissolution of stainless steels, and proton-consuming reactions—dissolution of uranium oxide fuels, Al alloy, and HLW glass. Relatively high rates of the first leads to transiently low pH. Relatively high rates for the latter causes solution pHs to be transiently high. Complete dissolution of either group would likewise lead to sharp shifts in pH.

The assumption that the WPs are instantaneously filled and that subsequent inputs equal outputs is obviously a limiting case for what is likely to actually occur upon WP breach. In reality, reaction might involve intermittent or discontinuous wetting of WP components. If wetting of WP components was complete, but void filling was 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 WP components would probably not result in significantly different effluent compositions as the fluid/solid ratio would not change.

Linkages between in-package chemistry and degradation of Zircaloy cladding must be considered. Zr alloys are chosen for their extreme resistance to corrosion, and general corrosion by influent solutions is not expected to be an overwhelming source of clad failure (clad-covered spent fuels that have been in wet storage for 40 years show no signs of clad degradation). Nevertheless, there are a number of specific in-package scenarios that might lead to accelerated degradation of Zr clad inside a breached WP. Note first of all that Zr degradation is synonymous with oxidation to  $ZrO_2$ . Dissolution of Zr oxide alteration products (by e.g. fluoride ion) would leave void spaces in the original clad surface. Clad thinning through wet oxidation of Zr has been estimated to be between 4 and 53 microns after 10,000 years at 180°C (Rothman 1984). Note that the thinnest clad expected in the repository (Westinghouse W1717WL) is 570 microns thick and that the temperature and F levels of the solution contacting the clad in a breached WP after 25,000 years will be substantially less than respectively 180°C and 100 ppm (recall that fluoride levels in J-13 well water are ~2.4 ppm). Pre-evaporation of influent solutions would be required to raise F levels.

The combination of high F contents and low pH (pH 3.2 and below) cause relatively rapid dissolution of Zr. To begin with, in-package pHs are not estimated to get this low (see Table 3), and high F levels depend on a pre-evaporation step, suggesting that high fluoride-low pH corrosion is not likely to be consequential. To confirm this, the decrease in clad thickness that

might occur if the reaction depends solely on the availability of F can be estimated (dissolution rates are therefore assumed to be exceedingly fast). Setting J-13 well water (and F) influxes to maximal levels of  $0.15 \text{ m}^3/\text{yr}$ ; assuming combination of 4 F atoms with one Zr atom, and using a clad surface area of  $420 \text{ m}^2/\text{WP}$ , suggests F-limited corrosion rates of 15 microns per hundred thousand years. This is conservative partly because it assumes complete stripping of F from solution, which certainly exaggerates the amount of Zr corroded.

Other than fluoride, dissolved ferric iron is the only other solution component that might accelerate degradation of Zr cladding. Although there will be no shortage of ferric iron in breached WPs due to the oxidation of WP components, the vast bulk of this material will not be dissolved. Typically pHs less than 3 are needed for substantial quantities of ferric iron to be maintained in solution. Note that these pHs are not predicted to occur.

### 6.3.3 Features, Events, and Processes

The present analysis has been linked with the following 14 features, events, and processes (FEPs) listed. A brief detailing of any effects of the present calculations on the specific FEP is also provided in Table 4. The FEPs in Table 4 come from the FEPs database.

Table 4. Affected FEPs

FEP Title	Disposition
Diffusion in backfill	Present analysis assumes no diffusion gradients in breached, saturated WP.
Radionuclide transport through backfill	Radionuclide fluxes into the backfill can be estimated from the present analysis.
Degradation of invert and pedestal	Will not affect results of present analysis unless degradation leads to early breaching and/or modification of input solutions.
Floor buckling	Outside scope of present analysis.
Pathways for unsaturated flow and transport in the waste and Engineered Barrier System (EBS)	Present analysis assumes that all flow is saturated in the WP. No assumptions are made for transport in the EBS.
In-drift sorption	Sorption is ignored in present analysis. See Section 1.
Chemical gradients / enhanced diffusion in waste and EBS	Present analysis assumes no diffusion gradients in breached, saturated WP.
Complexation by organics in waste and EBS	Organic complexation is ignored in the present analysis as organic components of WP and influent solutions are minor.
Suspensions of particles larger than colloids	Particle transport from the breached WPs is ignored in the present analysis.
Differing thermal expansion of repository components	Outside of the scope of the present analysis.
Thermal effects on diffusion (Soret effect) in waste and EBS	Temperature gradients in the degrading WPs are not envisioned to exist in the present analysis.
Gas generation	Not considered in the present analysis.
Gas transport in waste and EBS	Not considered in the present analysis.
Radioactive gases in waste and EBS	Not considered in the present analysis.

## 7. CONCLUSIONS

Corrosion of WP components into ambient fluids by dissolution under a wide variety of conditions is expected to cause relatively large changes in WP effluent chemistry. In CSNF WPs, 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 ( $I > 4$  M) will occur if ambient fluids degrade codisposal canisters containing defense high-level waste glass and defense fuel. Effluent Eh and alkalinity are expected to be controlled by free oxygen and carbon dioxide levels that are near to atmospheric. The relatively high ionic strengths observed in a number of the simulations prevents exact calculation of secondary mineral solubilities with the existing EQ3/6 platform. In other words, the simulations become less defensible once ionic strengths approach, and subsequently exceed, approximately 1 M. Because the solubilities of many minerals do not appear to depend strongly on ionic strength at and above this range, the lack of exactness does not prevent the results from providing useful bounding ranges of fluid chemistry.

Two data packages were generated from the output of this work, (1) Table 3, the summary of fluid composition ranges and (2) all of the simulation outputs. The fluid composition ranges in Table 3 are cited in the Process Model Report and used in the Total System Performance Assessment to explicitly define the composition range over which dissolved phase radionuclide concentrations are estimated. This was done first by using the output fluid chemistries produced in the present calculations to abstract functional relations between the major element parameters in Table 3. These relationships which link, e.g., pH and total carbon (C), in WP effluents will then be used in the TSPA to define the range of compositions likely to prevail in WP effluents. The same abstraction of WP effluent chemistry is then used to calculate radionuclide solubilities for the range of waste form degradation scenarios.

This document and its conclusions may be affected by technical product input information that requires confirmation. Any changes to the document or its conclusions that may occur as a result of completing the confirmation activities will be reflected in subsequent revisions. The status of the input information quality may be confirmed by review of the Document Input Reference System database (DIRS).

In particular, the input surface areas, WP component dissolution rates, and thermodynamic database have yet to be verified. The input surface areas multiplied by specific component dissolution rates provide estimates of overall WP component degradation. The results presented in Table 3 are not expected to change substantially after confirmation because, for one, the original calculations considered a range of input WP component degradation rates, they implicitly account for any variation in the input surface areas and specific degradation rates. Moreover, any changes in the thermodynamic database are expected to reflect fine-scale upgrading of thermodynamic parameters, not wholesale modification of the relevant reactions involved. Because the outputs in Table 3 represent major-element trends, these values are not expected to depend strongly on minor changes in database values.

## 8. INPUTS AND REFERENCES

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## 8.2 DATA

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### **8.3 PROCEDURES**

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## ATTACHMENT I

Attachment I contains a list of compressed EQ6 output files for each run (\*.6t) that provide aqueous elemental totals as a function of reaction time and echo the original input files. The echoed inputs provide a means for reproducing the results of individual reaction path calculations. Each of the prefixes for the files are labeled by the nomenclature outlined in Section 6.2. The outputs provide the fine-scale detail of specific reaction path calculations. There are 2 data1 files (data1.pvb and data1.pds) in the archive. The latter was used for the 20% cladding CSNF runs; the former was used for all others. All of the actual files are on a read-only CD archive (CRWMS M&O 2000).

### LIST OF FILES ON CD

File	Size (bytes)	Date	Time
cdsp_000.6t	136,331	10/15/99	12:35p
cdsp_111.6t	202,827	10/15/99	11:37p
cdsp_100.6t	199,803	10/15/99	6:21p
cdsp_102.6t	387,114	10/15/99	7:29p
cdsp_110.6t	47,058	10/18/99	7:16a
cdsp_002.6t	590,993	10/15/99	2:28p
cdsp_001.6t	201,742	10/15/99	1:03p
cdsp_010.6t	141,508	10/15/99	2:42p
cdsp_012.6t	319,938	10/15/99	3:56p
cdsp_011.6t	181,293	10/15/99	3:07p
cdsp_101.6t	197,383	10/15/99	6:41p
cdsp_112a.6t	62,847	10/5/99	7:13a
cdsp_112b.6t	71,072	10/18/99	8:00a
csnf_102.6t	65,542	10/16/99	5:39p
csnf_101.6t	0	10/18/99	10:24a
csnf_112.6t	127,139	10/18/99	10:07a
csnf_111.6t	130,568	10/16/99	11:10a
csnf_110.6t	141,922	10/16/99	10:53a
csnf_011.6t	130,606	10/16/99	11:59a
csnf_000.6t	108,428	10/16/99	7:25a
csnf_002.6t	79,454	10/18/99	9:04a
csnf_001.6t	127,550	10/16/99	1:52p
csnf_010.6t	137,965	10/16/99	11:43a
csnf_100.6t	145,512	10/16/99	12:53p
CSNF_212.6T	66,639	10/21/99	10:57a
CSNF_210.6T	137,427	10/18/99	1:33p
CSNF_202.6T	155,031	10/18/99	1:07p
CSNF_201.6T	124,297	10/18/99	12:37p
CSNF_200.6T	116,605	10/18/99	11:36a
data1.psd	794,017	9/27/99	11:44a
data1.pvb	794,896	12/21/99	7:09p