OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT

MODEL COVER SHEET

Complete Only Applicable Items

1. QA: QAPage 1 of 113

2. Type of Mathematical Model

☐ Process Model☒ Abstraction Model☐ System Model

Describe Intended Use of Model:

The abstraction model will be used by the configuration generator model for calculating the probability of in-package criticality.

Technical Contact / Department:

Emma Thomas / Waste Form

3. Title:

Geochemistry Model Abstraction and Sensitivity Studies for the 21 PWR CSNF Waste Packages

4. DI (Including Rev. No. and Change No., if applicable):

MDL-DSU-MD-000001 REV 00

5. Total Attachments:

5

6. Attachment Numbers – No. of Pages in Each:

I-CD, II-2, III-9, IV-10, V-4

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13. Remarks:

Independence between originators and checkers was maintained throughout the checking process. The checkers did not check the sections that they originated. The details of who originated and who checked which sections are as follows:

Patricia Bernot originated Sections 1, 2, 4.2, 4.3, 6.1.1, 6.3, 6.4, 7, 8, 9; and checked pages 1-9, Sections 4.1.1, 4.1.2.1, 4.1.2.2, 4.1.2.3, 6.1.2, 5.1 through 5.4, and Attachment I, II, and III.

Susan LeStrange originated Sections 4.1.2.6, 6.1.3, 6.1.2.6, 6.2, 10, Attachment IV and V; and checked Sections 4.1.2.4 and 4.1.2.5.

Emma Thomas originated pages 1-9, Sections 3, 4.1.1, 4.1.2.1, 4.1.2.2, 4.1.2.3, 5.1 through 5.4, 6.1.2 (except 6.1.2.6), Attachment I, II, and III; and checked Sections 4.2, 4.3, 6.1.1, 6.2, 6.3, 6.4, 10, Attachment IV and V.

Kaveh Zarrabi originated Section 4.1.2.4 and checked Sections 1, 2, 3, 7, 8, 9.

Sara Arthur originated Section 4.1.2.5 and checked Sections 4.1.2.6, 6.1.3, "Limiting O₂ and CO₂ Sensitivity" in Section 4.1.1.7.

Geochemistry Model Abstraction and Sensitivity Studies for the 21 PWR CSNF Waste Packages

Mineral	Density (g/cm ³)	Hydrologic Mode of Formation	Mode of Formation Reference
Thomsonite	2.366	3b. contact metamorphic deposits 5. hydrothermal or hot spring deposits 6b. volcanic rock marine deposits	Iijima, 1980 (p. 2118) Iijima, 1980 (p. 2119) Boles, 1977b
*Wairakite	2.26	3a. burial metamorphic deposits 3b. contact metamorphic deposits 5. hydrothermal or hot spring deposits	Hay, 1978 Iijima, 1980 (p. 2118) Iijima, 1980 (p. 2119)
Wellsite	2.248 ^m		
Willhendersonite	2.20		
Yugawaralite	2.26	3b. contact metamorphic deposits 5. hydrothermal or hot spring deposits	Iijima, 1980 (p. 2118) Iijima, 1980 (p. 2119)

Source: Density values come from Roberts et al., 1990

NOTES: * signifies minerals that are in the Data0.ymp.R0 database

ⁿ signifies minerals that were added for the new database, Data0.ymp.R2

^m measured density (otherwise it is the calculated density)

The zeolites above that do not have any indication of their formational environment are rare and not expected to form in the WP. However, they are presented in the table for completeness.

7. VALIDATION

The validation approach uses two goodness of fit methods for the validation of the model abstraction: (1) the R^2 correlation figure of merit was used for the pH abstraction, for the HCO_3^- -drop abstraction, for the HCO_3^- concentration abstraction, and for the U-loss abstraction; and (2) the chi-squared was used to validate the boron abstraction (per the TWP BSC 2002b). The abstraction model will be used to calculate probability distributions that will *not* be used directly in performance assessment calculations, public safety related issues, or other LA design activities (BSC 2002b, C-2).

The acceptance level for the linear regressions was a value of $R^2 > 0.8$ and an F-statistic significance of less than 0.10. As can be seen in Table 47 below, all of the regression analyses fall above an R^2 of 0.8 and most fall above 0.9. The lowest values of R^2 occur for time intervals where the pH fluctuates greatly. For most cases, the greatest fluctuation of pH occurs early in the run while the A516 steel degrades rapidly. Drastic pH shifts also occur later in the run, when the last of a component (such as the slowly degrading neutronit or fuel) has completely degraded, and that component is no longer controlling the pH. The goodness of fit is also considered acceptable based on the significance of the F-statistic. A value of 0.01 for the significance of F-statistic indicates that there is a 99% chance that the relationship between the variables is significant and not merely due to chance. Therefore, based on the F-statistics in Table 47, all of the regressions listed have at least a 98% chance that the relationship between the variables is significant. Though many are much higher than this with a 99.9 to 100% chance.

Since the B release from the waste package is calculated using a formula based on simple mass balance, the chi-squared test was used for the validation. The acceptance level for the chi-squared test was a rejection probability of less than 10% (TWP, BSC 2002b). As mentioned before, B in the waste package depends solely on the corrosion rate of the neutronit and the flushing (drip) rate. With the current rates used in this abstraction, a set of six possible combinations were used to calculate the rejection probability. The chi-squared statistic (χ^2) for each of these cases is presented in "B-loss-validation.xls" in Attachment I. The χ^2 values show that in all cases, the B in the waste package predicted by the model presented in Section 6.2 shows less than a 0.5% rejection probability (Scheaffer and McClave, 1990, Table 6 of Attachment) of that predicted by EQ6.

Geochemistry Model Abstraction and Sensitivity Studies for the 21 PWR CSNF Waste Packages

Table 47. Goodness of Fit for Regression Analysis of the Base Case, "g7" Pore Water, and Limiting Oxygen Cases

Regression Goodness of Fit for Base Case			Regression Goodness of Fit for “g7” Pore Water		
pH			pH		
Interval	R ²	Significance of F-Statistic	Interval (Years)	R ²	Significance of F-Statistic
0-150 year	0.8668	9.89E-08	0-120	0.9475	3.44E-08
150-550 years (ss* < 0.5 μm/y)	0.9571	3.75E-05	120-500	0.9235	4.66E-08
150-550 years (ss > 1 μm/y)	0.9065	2.65E-04	500-3000	0.9250	4.05E-08
550–25K years	0.9592	7.65E-12	3000–12500	0.8091	4.03E-06
25K–50K years	0.9991	1.80E-17	12500-27500	0.9172	7.65E-09
			27500-50000	0.8735	1.37E-08
Regression Goodness of Fit for “g7” Pore Water					
Time to Beginning of U Loss , <i>T_U</i> (years)					
Case		R ²		Significance of F-Statistic	
Drip rate = 0.015 m ³ /y		0.8973		1.08E-03	
Regression Goodness of Fit for Reducing Conditions					
pH			Time to HCO ₃ ⁻ drop (years)		
Time interval	R ²	Significance of F-Statistic	Case	R ²	Significance of F-Statistic
0-300 year	0.8414	1.92E-02	ss = 0.1 μm/y	0.9513	9.03E-04
300 years to HCO ₃ ⁻ drop (ss = 0.1 μm/y)	0.9896	4.05E-05	ss = 1-2 μm/y	0.9614	2.92E-04
300 years to HCO ₃ ⁻ drop (ss = 1-2 μm/y)	0.9440	5.78E-03	HCO ₃ ⁻ Concentration		
HCO ₃ ⁻ drop to 50K years (ss = 0.1 μm/y)	0.9923	6.75E-04	Case	R ²	Significance of F-Statistic
HCO ₃ ⁻ drop to 25K years (ss = 1-2 μm/y)	0.9484	4.92E-03	300 years to HCO ₃ ⁻ drop (ss = 0.1 μm/y)	0.9753	2.30E-04
25K-50K years (ss = 1-2 μm/y)	0.9909	3.12E-05	300 years to HCO ₃ ⁻ drop (ss = 1-2 μm/y)	0.9448	5.60E-03

Note: * ss = stainless steel degradation rate

8. CONCLUSIONS

The CSNF geochemistry model abstraction, as directed by the TWP (BSC 2002b), was developed to provide regression analysis of EQ6 cases to obtain abstracted values of pH (and in some cases HCO_3^- concentration) for use in the Configuration Generator Model. The pH of the system is the controlling factor over U mineralization, CSNF degradation rate, and HCO_3^- concentration in solution.

The abstraction encompasses a large variety of combinations for the degradation rates of materials. The "base case" used EQ6 simulations looking at differing steel/alloy corrosion rates, drip rates, and percent fuel exposure. Other values such as the pH/ HCO_3^- dependent fuel corrosion rate and the corrosion rate of A516 were kept constant. Relationships were developed for pH as a function of these differing rates to be used in the calculation of total C and subsequently, the fuel rate.

An additional refinement to the abstraction was the addition of abstracted pH values for cases where there was limited O_2 for waste package corrosion and a flushing fluid other than J-13, which has been used in all EQ6 calculation up to this point. These abstractions also used EQ6 simulations with varying combinations of corrosion rates of materials to abstract the pH (and HCO_3^- in the case of the limiting O_2 cases) as a function of WP materials corrosion rates.

The goodness of fit for most of the abstracted values was above an R^2 of 0.9. Those below this value occurred during the time at the very beginning of WP corrosion when large variations in the system pH are observed. However, the significance of F-statistic for all the abstractions showed that the variable relationships are significant.

For the abstraction, an analysis of the minerals that may form the "sludge" in the waste package was also presented. This analysis indicates that a number a different iron and aluminum minerals may form in the waste package other than those described in the EQ6 output files which are based on the use of a thermodynamic database.

The output DTNs from this model abstraction are listed in Section 9.2.

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9.1 INPUT DTNS

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MO0109RIB00049.001. Waste Package Material Properties: Neutron Absorbing Materials. Submittal date: 09/17/2001.

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9.2 OUTPUT DTNS

MO0210MWDLOG01.006 CSNF LogK Sensitivity study cases – CSNF_LogK

MO0210MWDRAD01.007 CSNF Radiolysis Sensitivity output files – CSNF_Radiolysis

MO0210MWEXCD01.008 CSNF results in Excel Spreadsheets – CSNF_Spreadsheets

MO0210MWDINP01.009 CSNF input files – CSNF_Input

MO0210MWDPWS01.010 CSNF Sensitivity Studies – Pore Water – CSNF_PWsens

MO0210MWDBAS01.011 CSNF Base Case – CSNF_BaseCase

MO0210MWDCO201.012 CSNF Limiting O2 and CO2 cases – CSNF_CO2_O2sens

MO0210MWDDBS01.013 CSNF Database Sensitivity cases – CSNF_DBsens

MO0210MWDPWG01.014 CSNF g7 Pore Water cases – CSNF_G7Abstract

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10. ATTACHMENTS

Attachment I. One Compact Disk

Attachment II. Listing of Files on Compact Disk

Attachment III. Pore Water Mineralization Plots

Attachment IV. Plots of U Loss for "g7" Pore Water Cases

Attachment V. Derivation of Equations for Boron Remaining in the Waste Package

ATTACHMENT I
ONE COMPACT DISK

ATTACHMENT II

LISTING OF FILES ON COMPACT DISK

This attachment contains the name and size of the zip file placed on the electronic media (Attachment I). Winzip 7.0 was used to compress the files.

Volume in drive F is MDL-DSU-MD-1Rev0
Volume Serial Number is 50CB-7848

Directory of f:\

```
10/23/02  09:49a      <DIR>          .
10/23/02  09:49a      <DIR>          ..
10/18/02  08:50a           14,488,559 CSNF_BaseCase.zip
08/21/02  11:19a           25,035,488 CSNF_CO2_O2sens.zip
10/18/02  10:40a           6,944,998 CSNF_DBsens.zip
09/24/02  02:52p           15,834,447 CSNF_g7Abstract.zip
10/18/02  10:43a           809,839 CSNF_Input.zip
10/18/02  09:41a           6,599,879 CSNF_LogK.zip
09/10/02  11:35a           14,321,346 CSNF_PWsens.zip
09/09/02  01:24p           6,356,670 CSNF_Radiolysis.zip
10/18/02  10:44a           22,837,773 CSNF_Spreadsheets.zip
09/24/02  02:54p           754,046 data0 files.zip
          12 File(s)      113,983,045 bytes

Total Files Listed:
          12 File(s)      113,983,045 bytes
                                0 bytes free
```

The zip files contain files of various types:

1. Excel files (extensions = xls).
2. EQ3/6 input files (extension = 3i or 6i).
ASCII text file: provides input parameters for EQ3/6.
3. EQ3/6 output files (extension = 3o or 6o).
ASCII text file: provides detailed information about the system at each print point, which is specified by the user in the input file.
4. EQ3/6 pickup files (extension = 3p or 6p).
ASCII text file: provides a description of the system at the end of that run to be used as an input file for a continuation run.
5. EQ6 Tab-delimited text files (extension = txt).
*.elem_aqu: total aqueous moles of elements.
*.elem_min: total moles of elements in minerals.
*.elem_tot: total moles of elements (aqueous + mineral).
*.min_info: moles of each mineral.
6. EQ6 binary output file (extension = bin).
Binary file: provides detailed information about the system at the full numerical precision for every time step.
7. EQ3/6 text data files used for the calculations, 'data0.ymd'.
8. Batch files (extension = bat) used to start EQ6 runs.
9. Winzip files (extension = zip).

ATTACHMENT III
PORE WATER MINERALIZATION PLOTS

Attachment III Figure 38: c111_g1a

Attachment III Figure 39: c111_g2a

Attachment III Figure 40: c111_g3a

Attachment III Figure 41: c111_g4a

Attachment III Figure 42: c111_g5a

Attachment III Figure 43: c111_g6a

Attachment III Figure 44: c111_g7a

Attachment III Figure 45: c111_g7c

Attachment III Figure 46: c331_g1a

Attachment III Figure 47: c331_g1c

Attachment III Figure 48: c331_g2a

Attachment III Figure 49: c331_g2c

Attachment III Figure 50: c331_g3a

Attachment III Figure 51: c331_g4a

Attachment III Figure 52: c331_g5a

Attachment III Figure 53: c331_g7a

ATTACHMENT IV

PLOTS OF U LOSS FOR "G7" PORE WATER CASES

Attachment IV Figure 54: pH, U in WP, and U loss for Case c112_g7

Attachment IV Figure 55: pH, U in WP, and U loss for Case c212_g7

Attachment IV Figure 56: pH, U in WP, and U loss for Case c312_g7

Attachment IV Figure 57: pH, U in WP, and U loss for Case c122_g7

Attachment IV Figure 58: pH, U in WP, and U loss for Case c132_g7

Attachment IV Figure 59: pH, U in WP, and U loss for Case c222_g7

Attachment IV Figure 60: pH, U in WP, and U loss for Case c232_g7

Attachment IV Figure 61: pH, U in WP, and U loss for Case c322_g7

Attachment IV Figure 62: pH, U in WP, and U loss for Case c332_g7

ATTACHMENT V

**DERIVATION OF EQUATIONS FOR BORON REMAINING
IN THE WASTE PACKAGE**

The waste package, as modeled by EQ6, can be thought of as a well-stirred reactor

The derivation starts with a mass balance on boron and eliminating terms that are zero:

$$\cancel{\frac{\text{moles in}}{t}}^0 = \frac{\text{moles out}}{t} + \cancel{\text{Disappearance by reaction}}^0 + \text{Accumulation}$$

The first and last terms on the right side of the equation are defined by

$$\frac{\text{moles out}}{t} = F_B = C_{B_f} v_{out}$$

$$\text{Accumulation} = \frac{dN_B}{dt}$$

where

$$N_B = C_{B_F} V_R + B_i - Dt \quad \text{Equation V-1}$$

Taking the derivative of N_B ,

$$\frac{dN_B}{dt} = V_R \frac{dC_{B_F}}{dt} + C_{B_F} \frac{dV_R}{dt} - D \quad \begin{matrix} \nearrow 0 \text{ (constant volume of 1L)} \\ \searrow \end{matrix}$$

Substituting into the original mass balance equation

$$0 = F_B + 0 + \frac{dN_B}{dt}$$

$$0 = C_{B_F} \nu + V_R \frac{dC_{B_F}}{dt} - D$$

While neutronit is
degrading.

After neutronit has finished
degrading (D=0)

$$\frac{1}{V_R} dt = \frac{1}{(D - C_{B_F} \nu)} dC_{B_F}$$

$$\frac{\nu}{-V_R} dt = \frac{1}{C_{B_F}} dC_{B_F}$$

$$\frac{1}{V_R} \int_0^t dt = \left(\frac{1}{D - C_{B_F} \nu} \right) \int_0^{C_{B_F}} dC_{B_F}$$

$$\frac{\nu}{-V_R} \int_{t_f}^t dt = \int_{C_f}^{C_{B_F}} \left(\frac{1}{C_{B_F}} \right) dC_{B_F}$$

$$\left[\frac{t}{V_R} \right]_0^t = \left[\frac{\ln(D - C_{B_F} \nu)}{-\nu} \right]_0^{C_{B_F}}$$

$$\frac{-\nu(t - t_f)}{V_R} = \ln \left(\frac{C_{B_F}}{C_f} \right)$$

$$\frac{t}{V_R} = \frac{1}{-\nu} (\ln(D - C_{B_F} \nu) - \ln(D - \nu(0)))$$

$$C_{B_F} = C_f e^{\frac{-\nu(t-t_f)}{V_R}} \quad \text{Equation V-2}$$

While neutronit is degrading (continued):

$$\frac{tv}{V_R} = \ln\left(\frac{D}{D - C_{B_F} v}\right)$$

$$e^{\frac{tv}{V_R}} = \frac{D}{D - C_{B_F} v}$$

$$D - C_{B_F} v = D e^{-\frac{tv}{V_R}}$$

$$C_{B_F} = \frac{D \left(1 - e^{-\frac{tv}{V_R}}\right)}{v}$$

Equation V-3

When neutronit is fully degraded, the equation for boron in the waste package (Equation V-1) reduces to

$$N_B = C_{B_F} V_R$$

Equation V-4

Substituting Equation V-2 into Equation V-4 results in

$$N_B = C_f e^{-\frac{v(t-t_f)}{V_R}} V_R$$

Equation V-5

C_f is the concentration of boron when the neutronit has just finished degrading. Therefore, Equation V-3 is substituted into Equation V-5, with the substitution of $C_{B_F} = C_f$ and $t = t_f$. The result is the equation for the quantity of boron in the waste package after neutronit has degraded:

$$N_B(t > t_f) = \frac{V_R D}{v} e^{-\frac{v(t-t_f)}{V_R}} \left(1 - e^{-\frac{t_f v}{V_R}}\right)$$

Substituting Equation V-2 into Equation V-1 for N_B results in the final equation for boron remaining in the waste package while neutronit is still degrading:

$$N_B(t \leq t_f) = \frac{V_R D}{v} \left(1 - e^{-\frac{tv}{V_R}}\right) + B_i - Dt$$

4.1.2.6 Limiting O₂ and CO₂ Conditions

Table 26 lists the results from the cases with limited O₂ and CO₂. The fuel remaining was higher than the base cases (Table 19), indicating that the fuel degraded at a lower rate. The rate was lower since the rate is a function of pH and HCO₃⁻, which are affected by reduced O₂ and CO₂. Figure 19 (which focuses on the first 10,000 years in order to show detail) shows that the pH is significantly lower for the case with fixed O₂ and CO₂ than the case with limited O₂ and CO₂. Figure 20 shows the degradation rate for case c30y111, with limited O₂ and CO₂, compared with the base case. Figure 20 covers the first 50,000 years, which is the time interval covered by the abstraction. The degradation rate for the case with limited O₂ and CO₂ ranges from 5 to 33 times lower than the rate for the base case. This decrease in degradation rate matches rates observed experimentally. Two studies measured dissolution rates of spent fuel under anoxic conditions and found that, compared to rates under aerated conditions, the rates under anoxic conditions were reduced by a factor of 10 in one study (Werme et al. 1990, p. 10) and reduced by about 2 orders of magnitude in another study (Tait and Luht 1997, p 15).

The degradation rate equation, presented in Table 5, was based on equations for CSNF degradation from CRWMS M&O 2000a (Equations 16 and 18, p. 82) that include a term dependent on the fugacity of O₂ (fO₂). Figure 19 shows that the value of fO₂ drops dramatically from 0.2 to 10⁻⁷³ at 300 years when the system changes from fixed fO₂ to diffusion-controlled O₂. To determine the sensitivity of the degradation rate to levels of fO₂ observed in the EQ6 runs, the degradation rate was calculated using a range of values of fO₂ (spreadsheet "CSNF Fuel Model Abstraction.xls", Attachment I, worksheet "Rates"). The rate constants calculated for fO₂ of 10⁻⁷³ were 2.14E-34 for the low pH leg of the equation and 7.76E-37 for the high pH leg of the equation. If EQ6 runs had been done using these small rate constants, the fuel degradation rate would be essentially zero. Case c30y302 covers the case of fuel that does not degrade.

The volumes of solids formed in these runs were considerably lower than for the base case runs (Table 26). All of the runs with limited O₂ and CO₂ were run out to 100,000 years without exceeding the 60% full value of 1133 cm³ (file "CSNF WP Model Abstraction.xls", worksheet "Volumes and Surface Areas"). Figure 21 shows the major minerals formed in Case c30y111 during the second stage in the first 10,000 years. All the iron released during the first stage is precipitated as hematite. As the second stage progresses, hematite becomes unstable and magnetite (Fe₃O₄) is the main Fe-bearing mineral. Smaller amounts of iron are contained in trevorite (NiFe₂O₄). The aluminum is contained in gibbsite (Al(OH)₃), uranium in uraninite (UO₂), chromium in eskolaite (Cr₂O₃), and manganese in tephroite (Mn₂SiO₄) and Mn (OH)₂ (am). The complete listing of minerals present in the waste package are found in Attachment I in "c30y111f.min_info.txt".

Geochemistry Model Abstraction and Sensitivity Studies for the 21 PWR CSNF Waste Packages

Table 26: Percent Remaining for Limiting O₂ and CO₂ Conditions

	Years	pH	Vol Solids (cm ³)*	Fuel Intact (moles)	Percent Remaining in Waste Package						
					B	Gd	Np	Pu	Ru	Tc	U
c30y111f	297	4.21	724	22.82	100	100.00	100.00	100.00	100.00	100.00	100.00
	100,180	9.11	871	21.55	0	100.00	100.00	100.00	100.00	99.95	100.00
c30y112f	297	4.21	724	22.82	100	100.00	100.00	100.00	100.00	100.00	100.00
	100,160	8.21	885	21.32	0	99.97	99.99	100.00	100.00	99.61	100.00
c30y121f	288	4.47	767	21.06	100	100.00	100.00	100.00	100.00	100.00	100.00
	100,310	9.23	873	9.15	0	100.00	100.00	100.00	100.00	99.54	100.00
c30y122f	288	4.47	767	21.06	100	100.00	100.00	100.00	100.00	100.00	100.00
	100,150	8.24	888	1.86	0	99.98	100.00	100.00	100.00	96.17	100.00
c30y131f	288	5.63	946	13.71	100	100.00	100.00	100.00	100.00	100.00	100.00
	100,300	7.99	878	0.00	0	99.96	100.00	100.00	100.00	95.19	100.00
c30y132f	288	5.63	946	13.71	100	100.00	100.00	100.00	100.00	100.00	100.00
	100,140	8.20	893	0.00	0	99.60	100.00	100.00	100.00	68.45	100.00
c30y211f	305	5.71	770	23.00	100	100.00	100.00	100.00	100.00	100.00	100.00
	100,410	11.21	1,119	22.25	0	100.00	100.00	100.00	100.00	99.98	100.00
c30y221f	292	5.71	785	22.40	100	100.00	100.00	100.00	100.00	100.00	100.00
	100,260	11.22	1,120	15.44	0	100.00	100.00	100.00	100.00	99.85	100.00
c30y222f	292	5.71	785	22.40	100	100.00	100.00	100.00	100.00	100.00	100.00
	100,150	11.33	1,128	17.47	0	99.98	100.00	100.00	100.00	98.76	100.00
c30y231f	286	5.73	922	16.73	100	100.00	100.00	100.00	100.00	100.00	100.00
	100,210	11.22	1,122	0.00	0	99.96	100.00	100.00	100.00	97.65	100.00
c30y232f	286	5.73	922	16.73	100	100.00	100.00	100.00	100.00	100.00	100.00
	100,140	11.33	1,131	0.00	0	99.61	100.00	100.00	100.00	82.66	100.00
c30y311f	308	5.58	771	23.04	100	100.00	100.00	100.00	100.00	100.00	100.00
	100,490	11.21	1,119	22.23	0	100.00	100.00	100.00	100.00	99.99	100.00
c30y331f	283	5.58	894	17.99	100	100.00	100.00	100.00	100.00	100.00	100.00
	100,230	11.21	1,122	0.00	0	99.93	100.00	100.00	100.00	98.93	100.00
c30y302f	286	5.46	771	23.10	100	100.00	100.00	100.00	100.00	100.00	100.00
	100,150	11.33	1,126	23.10	0	100.00	100.00	100.00	100.00	100.00	100.00

Note: *The volume of solids and moles of fuel are normalized values. Multiply by the void volume (4685 liters) to get true values. One mole of fuel is defined to be 100 g.

NOTE: Case c30_111a has fixed O_2 and CO_2 fugacities. Case c30(xy)111f has fixed O_2 and CO_2 fugacities for the first 300 years, followed by diffusion-limited O_2 and CO_2 limited to the amount in the in-dripping water.

Figure 19. Reduced O_2 and CO_2 Impacts on Fugacity and pH

Figure 20. CSNF Degradation Rate for Base Case and Limited O₂ and CO₂ Case

 Figure 21. Minerals Formed with Limited O₂ and CO₂, Case c30y111

4.2 CRITERIA

There are no criteria for this model in any project-requirements documents. This model provides input to the Configuration Generator model, which is a requirement listed in Section 3.6 of the Topical Report (YMP 2000). The Configuration Generator model also addresses NRC KTI agreement CLST.5.04. Per the TWP (BSC 2002b), this model will meet the level of detail and quality of fit needed to support License Application (LA) as defined by the *Yucca Mountain Review Plan (YMRP)(NUREG-1804)* (NRC 2002) in general and specifically Section 4.2.1.3 of YMRP, *Review Plan for Safety Analysis Report*.

The validation of this report is discussed in Appendix C of the TWP (BSC 2002b, p. C-2). The TWP states that "the anticipated acceptance level for the goodness of fit criteria will be a correlation figure of merit, for example, of 0.9 for R^2 measures or a rejection probability of less than 10% for a Chi-squared test." Instead of using $R^2=0.9$ as the acceptance level (which was provided only as an example), a value of $R^2=0.8$, combined with a significance of the F-statistic of less than 0.1 was used as the acceptance criteria in the model. The confidence level assigned for this model is low (the repository design or performance is relatively insensitive to the model output and associated uncertainties).

4.3 CODES AND STANDARDS

The following standards were used in this model for material compositions and densities:

ASME (American Society of Mechanical Engineers) 1998. *1998 ASME Boiler and Pressure Vessel Code*. 1998 Edition with 1999 and 2000 Addenda.

ASTM A 887-89 (Reapproved 2000). 2000. *Standard Specification for Borated Stainless Steel Plate, Sheet, and Strip for Nuclear Application*.

ASTM G 1-90 (Reapproved 1999). 1999. *Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens*.

No codes were used in this model.

5. ASSUMPTIONS

All assumptions are for preliminary design. Assumptions in Section 5.1 through 5.4 are used as input to the EQ6 runs (Section 4.1.1). Assumptions in Section 5.3 are used in Section 6 of this report.

5.1 INCOMING WATER

- a. It is assumed that the solutions that drip into the WP will have the major ion composition of J-13 well water as given in DTN: MO0006J13WTRCM.000. It is also assumed that the solutions will have the dissolved oxygen content of J-13 well water as given in Harrar (5.6×10^{-6} g oxygen/gram water, Harrar 1990). The rationale for this assumption is that the groundwater composition is controlled largely by transport through the host rock, which is not expected to change substantially over 10^6 years. This assumption was used in Table 17 in calculating the change of oxygen concentration.
- b. It is assumed that the reported alkalinity in analyses of J-13 well water corresponds to bicarbonate (HCO_3^-) alkalinity. The rationale for this assumption is that the concentrations of the other alkalinity contributors: borate, phosphate, silicate and fluoride are small and their effect is not significant at moderate pHs. The same assumption is implicitly made in DTN: MO0006J13WTRCM.000. The calculated electrical neutrality based on this assumption is zero, which is within the analytical uncertainty.
- c. It is assumed that the density of J-13 well water is 1.0 g/cm^3 . The rationale for this assumption is that in dilute solutions, the density is extremely close to that for pure water and that any differences are insignificant with respect to other uncertainties in the data and calculations. Moreover, this number is used only initially in EQ3/6 to convert concentrations of dissolved substances from mg/L to molality.
- d. It is assumed that the aqueous compositions of several pore waters used in this calculation (listed in Table 12, based on BSC 2001g and BSC 2001h) are representative of solutions that may be exposed to the WP. The rationale for this assumption is that they account for grout seepage interaction, which is an important consideration in the WP.
- e. It is assumed that the CO_2 and O_2 gases in the WP solution remain in equilibrium with the ambient atmosphere outside the WP. The specific partial pressures of CO_2 and O_2 of the ambient repository atmosphere are set to $10^{-3.0}$ and 0.2 atm respectively ($\log f\text{O}_2 = -0.7$ and $\log f\text{CO}_2 = -3$). The rationale for the oxygen partial pressure is that it is equivalent to that in the atmosphere (Weast 1977, p. F-210). The rationale for choosing the carbon dioxide pressure to be somewhat higher than atmospheric is that ambient fluids drawn from boreholes near the repository horizon appear to be in equilibrium with above-atmospheric carbon dioxide levels (Yang et al. 1996, Table 8).
- f. It is assumed that the drip rate into the WP varies from 1.5 to 150 l/y. The drip rate is taken from a correlation between percolation flux and drip rate, also called mean seep flow rate (CRWMS M&O 2000c, Figure 3.2-15). The drip rates selected were: 0.0015, 0.015, and $0.15 \text{ m}^3/\text{year}$, corresponding to percolation fluxes ranging from about 10 mm/year to 80

mm/year. The value of 10 mm/year corresponds to a high infiltration rate for the present-day climate. Eighty mm/year corresponds to about twice the high infiltration rate for the glacial-transition climate (CRWMS M&O 2000c, Table 3.2-2), which gives values of net surface infiltration rate, rather than percolation flux; however, they are equal at the potential repository level. (CRWMS M&O 2000c, Section 3.2.3.4, p. 3-33).

5.2 DEGRADATION MODEL

- a. It is assumed that the corrosion rates used in this calculation encompass rates for microbially assisted degradation, but that these rates are not controlled principally by bacteria (DOE 1998, p. 3-84). The rationale for this assumption is that steel corrosion rates measured under environmental conditions inherently include exposure to microbes.
- b. It is assumed that only the inside surface area of the 316NG inner shell is exposed to degradation within the WP. The rationale for this assumption is that the gap between the 316NG liner and the Alloy 22 outer liner is too small for significant water to accumulate (0.5 cm, see Attachment III of BSC 2002a).
- c. It is assumed that the outer shell of the WP (Alloy 22) is inert. The basis for this assumption is that Alloy 22 corrodes very slowly compared to other reactants in the WP. The probability of Alloy 22 corroding quickly is very low, as shown in Figure 51 of CRWMS M&O 2000b (p. 109).
- d. It is assumed that aqueous solution drips onto the upper surface of the WP and penetrates it. The solution then accumulates inside the WP, filling all the voids, circulating freely, dissolving and flushing the dissolved material from the WP. The rationale for this assumption is that it is conservative for criticality, providing the maximum degradation rates of WP components with the potential for precipitation of radionuclides within the WP or the flushing of radionuclides from the WP.
- e. It is assumed that sufficient decay heat causes convective circulation and mixing of the water inside the WP. The study that serves as the rationale for this assumption is discussed in CRWMS M&O 1996 (Attachment VI).
- f. It is assumed that once the volume of solids in the WP exceeds two thirds of the total volume of the WP itself (due to the expansion of the corrosion products) this model no longer holds true. The rationale for this assumption is that at this point, only one third of the volume is taken up by aqueous solution, which no longer allows for thorough mixing.
- g. It is assumed that when precipitated solids are deposited, they remain in place and are not mechanically eroded or entrained as colloids in the advected water, and the most insoluble solids form for fissile radionuclides. The rationale for this assumption is that it is conservative for internal criticality to assume that any fissile material (U or Pu) remains inside the WP. (Though transport by colloids is possible (DOE 1998, Sections. 3.5), it is not considered in this report).
- h. In general it is assumed that chromium and molybdenum will oxidize fully to chromate (or dichromate) and molybdate, respectively. Based on the available thermodynamic data

("data0.ymf", DTN: MO0009THERMODYN.001), the chromium and molybdenum would both oxidize to the VI valence state in the presence of air. The rationale for this assumption is that it is conservative for criticality because the oxidation lowers the pH, which provides a broader range of pH conditions modeled in the WP. A broader range of pH can influence the WP chemistry, since the pH is an important parameter in determining the solubility of minerals and the types of dissolved species that are formed (for example, Figure 13.4 and Figure 13.5 in Langmuir 1997)

5.3 THERMODYNAMIC DATA

- a. It is assumed that the EQ3/6 results generated using the B-dot activity model for solutions with ionic strength greater than 1 molal are sufficiently accurate for the current calculation. (It is already accepted that the B-dot activity model is accurate for ionic strengths *less* than 1 molal.) The rationale for this assumption is that experimental data (in sulfate, nitrate, and chloride solutions) shows that EQ3/6 results using the B-dot activity model can be used qualitatively up to an ionic strength of about 4 molal to indicate the general nature of the reactions that would actually occur (CRWMS M&O 1997b, Appendix D).
- b. It is assumed that data in the 25°C thermodynamic database (data0.ymf.R0, DTN: MO0009THERMODYN.001) can be used for the calculation. The rationale for this assumption is that the WP temperatures are likely to be close to 25°C at times > 25,000 years, even though the initial breach of the WP may see temperatures ~ 50°C (DOE 1998, Figures 3-20 through 3-22). The database is discussed in more detail in Section 4.1.1.4
- c. It is assumed that any error in the densities used to calculate the molar volumes for the following minerals: CaUO_4 , Cr-ettringite, $\text{Cu}_3(\text{PO}_4)_2$, GdOHCO_3 , KNpO_2CO_3 , $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$, $\text{Ni}_3(\text{PO}_4)_2$, and α -uranophane, will not negatively impact the calculation. The rationale for this assumption is that the density is only used to calculate the volume of minerals in the WP, and these minerals make up less than 0.1% of the total moles. The values of molar volumes were originally added to "data0.ymf" to more accurately estimate the volume of the solids produced in the WP. However a qualified source is not available in the Technical Information Center to corroborate the values.
- d. It is assumed that all of the rare earth elements (REE) in the fuel can be modeled as Gd, since the database contains the most data available for this element. It is also assumed that the logK for GdOHCO_3 is the same as the logK for NdOHCO_3 (as given in DTN: MO0009THERMODYN.001). The rationale for this assumption is that all rare earth elements are chemically similar.

5.4 CSNF FUEL

- a. It is assumed that the B&W 15x15 assembly design with the mass of type MK-B2 is the most conservative PWR fuel assembly design. The basis for this assumption is that the MK-B2 design contains the greatest mass of U per assembly (CRWMS M&O 1998b, p. 26), and the B&W 15x15 fuel assembly is one of the most reactive (B&W Fuel Company 1991, p. II 6-6). It is further assumed that the characteristics of the PWR fuel listed in Table 8 and Table 9

(based on BSC 2001c, p. 44; Punatar 2001, p. 2-5) are conservative and representative of PWR fuel. The rationale for this assumption is that this is the most recent and reliable data.

- b. It is assumed that the structural components (non-fuel materials) of the fuel assembly are inert. The rationale for this assumption is that the zircaloy is very non-reactive, and the amount of non-zircaloy materials in the fuel assembly (such as the 304L springs) is negligible when compared to the total volume of the WP.
- c. It is assumed that the displaced volume of a PWR assembly is 0.081 m³ (CRWMS M&O 1997a, Table 4.1-1, p. 6). The rationale for this assumption is that this is the value reported in the 1997 calculation, and the dimensions of the PWR assembly have not changed since then. This assumption is used in the calculation of the void volume ("CSNF WP Model Abstraction.xls," Attachment I).
- d. It is assumed that the sketch SK-0219 Rev 02 (Attachment III of BSC 2002a), which is more recent than the baseline drawing (BSC 2001j) is also representative of the CSNF WP. The basis for this assumption is that the sketch gives more detail about the WP interior used in this calculation. Furthermore, the height of the inner shell was taken from the sketch and not the drawing, but the difference is so small (1.3 cm), that it is not expected to impact the results of this calculation.
- e. There were several assumptions made about the geometry of the fuel basket assembly for simplification. The rationale for these assumptions is that any error associated with the simplification is minimal when compared to geometry of the whole WP. These assumptions are stated in "CSNF WP Model Abstraction.xls" (Attachment I) and were used in the calculation of the moles and surface areas of the neutronit, the A516 and the A1-6061.

5.5 MODEL ABSTRACTION

- a. It is assumed that the pH of the system can be used to calculate the amount of fuel degrading at a given time. The basis for this assumption is that the fuel degradation rate calculated using the pH, and the pH of the system controls all other chemical variables such as total carbon, U mineral precipitation, and fuel degradation rate.
- b. The time intervals used in the abstraction represent time after waste package breach when fluids are able to enter the internal spaces of the WP. The basis for this assumption is that prior to WP breach, there is no water in the WP, which is needed for component interactions and degradation and to serve as a moderator.
- c. The Uranium loss for the base case (Section 6.1.1), the limiting O₂ and CO₂ (Section 6.1.3), and the low drip rate cases from the pore water abstraction (Section 6.1.2) were assumed to be negligible (less than 0.04%) and were not included in Section 6.1.2.6. In the medium drip rate cases of Section 6.1.2, the U loss is not considered to occur until the point when 2% has been lost.

6. MODEL DISCUSSION

The CSNF geochemistry model abstraction seeks to simplify the complex, time-dependent chemistry into time intervals. The average pH values for each interval (and in some cases the HCO_3^-) are then used for the generation of multi-variable formulas using waste package component degradation rates to solve for the dependent variable, pH. The abstracted values will then be used in the Configuration Generator Model to predict CSNF degradation. The discussion that follows outlines the chemical parameters that are considered in the abstraction and the methods/reasoning used in the abstraction for the CSNF WPs.

6.1 FUEL ABSTRACTION

The pH of the aqueous system is the most important in-package parameter. The pH of the system controls the mineralization of uranium (as shown in the previous EQ6 calculation, BSC 2002a), the total carbonate of the system, and the dissolution rate of the CSNF fuel (the equation for the fuel is written in terms of pH). Therefore, the amount of uranium in the system at a given time can be predicted using the pH, with some exceptions (see Section 6.1.3). This model abstraction develops equations to estimate the pH at a given time, and then uses that pH to calculate the fuel remaining at a given time. A matrix of runs varied the neutronit / 316NG degradation rates, percentage fuel exposure, and drip rates. The resulting pHs were then abstracted. The degradation of the A516 carbon steel lowers the pH to a minimum early in the runs. After the A516 is completely corroded, the pH recovers to near neutral conditions, held steady by the corrosion of steel WP components and the movement of water through the system. Then, as steel components fully degrade, the pH increases. The step-like behavior of the pH is modeled by calculating an average pH for distinct "time intervals" for any case. Time intervals are defined as the stretch of time where the pH behavior is distinctly different from other times and dependent on different parameters than that of another zone.

6.1.1 Base Case

6.1.1.1 0 to 150 years

Because the pH from 0 to 150 years fluctuates so much, this time interval was selected as the first time interval of interest. The pH values for the first 150 years of the EQ6 runs from the CSNF calculation are shown in Figure 22.

Figure 22: pH versus Time, Base Case, 0-150 Years

In the first 150 years, the pH drops from 8.1 (the pH of the incoming water) to below 6 due to the rapid corrosion of the A516 which releases sulfur (S). The degradation of the neutronit and 316NG also contribute to a lower pH, but they do not degrade as quickly as the A516. As the A516 degrades, its effect on the pH is countered by the fuel degradation (the fuel releases alkali elements causing the pH to increase). The percentage of fuel exposed limits the pH plunge during this early period. A high drip rate (the flushing rate of fluids through the WP), can help moderate the pH over time by flushing the ions and complexes from the system. But, for the first 150 years, the drip rate does not significantly affect the pH because of how rapidly the A516 is degrading. The only moderating effect on the pH at this point in the run is the degradation of the fuel.

The Al-6061 does not help to control the pH; even though it degrades quickly, the mass of the aluminum relative to the A516 is not great enough to counteract the effect the A516 has on the pH.

The spreadsheet "pH-plots.xls" (Attachment I) shows how each individual component can effect the system pH when all other parameters are kept constant. This, as well as those components shown to control pH in the abstraction, helps to demonstrate which components are responsible for affecting the pH in the different time intervals.

6.1.1.2 150 to 550 years

The pH values for the first 550 years in the EQ6 runs from the CSNF calculation are shown in Figure 23.

Figure 23: pH versus Time, Base Case, 0-550 Years

By 150 years, the initial pH low begins to rise because the A516 has fully degraded. As shown in Figure 23, the cases with the higher neutronit / 316NG degradation rates (1 and 2 $\mu\text{m}/\text{year}$) recover quickly from the initial pH low. The lower neutronit / 316NG degradation rate (0.1 $\mu\text{m}/\text{year}$) takes more time to stabilize, and the pH for these cases rises steadily until 550 years. Since the low neutronit / 316NG rate cases behave so differently, another rate of 0.5 $\mu\text{m}/\text{year}$ was simulated to observe the effects (Attachment I). The pH values for these cases are plotted in Figure 24, and show that the behavior of the system with 0.5 $\mu\text{m}/\text{year}$ neutronit / 316NG degradation rate is more similar to the low rate of 0.1 $\mu\text{m}/\text{year}$.

The second time interval selected was from 150 years to 550 years (when the pH of lowest neutronit / 316NG rate case has stabilized). For this time interval, two separate abstractions were performed: one for the high neutronit / 316NG rates and one for the low neutronit / 316NG rates, since the effects on the system are quite different.

Figure 24. pH Versus Time, Base Case, 0-550 Years, Stainless Steel Degradation = 0.5 $\mu\text{m}/\text{year}$

6.1.1.3 550 to 25,000 years and 25,000 to 50,000 years

Figure 25 shows the last two time intervals taken into consideration in the pH abstraction.

Figure 25: pH versus Time, Base Case, 550 to 50,550 Years

From 550 to 50,000 years, the pH of the system is controlled by the corrosion of neutronit / 316NG and the flushing rate. The entire time frame is divided into two time intervals because the 316NG has fully degraded shortly after 25,000 years in those cases with the 2 $\mu\text{m}/\text{year}$ rate. Once the neutronit / 316NG is gone, the pH of the system increases until it stabilizes at the pH of the incoming water.

The abstraction ends at 50,000 years, which is when the neutronit fully degrades with the lowest rate (49,670 years at a corrosion rate of 0.1 $\mu\text{m}/\text{year}$, Attachment I of BSC 2002a). Once the neutronit has degraded, the boron (neutron absorber) leaves the waste package (see Section 6.2).

For all time intervals, the average pH is used in the abstraction for the dependent variable ("pHabstract.xls"). These values were used along with different combinations of fuel exposure (%), neutronit / 316NG rate ($\mu\text{m}/\text{year}$), and drip rate (m^3/year) to obtain regression data in Microsoft Excel (outputs in Attachment I). The matrix for the regression analysis is presented in Table 27.

Table 27. CSNF Matrix of Average pH and Degradation Rates of CSNF WP Internals

Case	Average pH				"fuel exposure" % cladding failure	drip rate (m ³ /year)	Neutroxit / 316NG Rate	Al-6061 rate
	0-150 years	150 - 550 years	550-25000 years	25K-50K years			μm/year	
c30_111	3.7561	4.4879	5.6821	5.6651	1	0.0015	0.10	2.953
c30_112	3.7951	5.0745	6.0212	6.0169	1	0.015	0.10	2.953
c30_121	4.1202	4.7296	5.6970	5.6754	10	0.0015	0.10	2.953
c30_122	4.1694	5.1566	6.0277	6.0200	10	0.015	0.10	2.953
c30_131	4.8216	5.6537	5.7040	5.6748	100	0.0015	0.10	2.953
c30_132	4.8427	5.8072	6.0297	N/A	100	0.015	0.10	2.953
c30_411	3.8293	4.9564	5.5007	5.5936	1	0.0015	0.5	2.953
c30_412	3.8832	5.2966	5.8719	5.9424	1	0.015	0.5	2.953
c30_421	4.2142	5.0533	5.5026	5.5931	10	0.0015	0.5	2.953
c30_422	4.2612	5.3388	5.8805	5.9425	10	0.015	0.5	2.953
c30_431	4.8375	5.6898	5.5054	5.5931	100	0.0015	0.5	2.953
c30_211	5.0771	5.6860	5.4157	5.4716	1	0.0015	1.0	29.53
c30_222	5.4610	5.7536	5.8081	5.8356	10	0.015	1.0	29.53
c30_231	5.4801	5.6955	5.4131	5.4733	100	0.0015	1.0	29.53
c30_232	5.5109	5.7658	5.8043	N/A	100	0.015	1.0	29.53
c30_212	5.1095	5.7527	5.8015	5.8355	1	0.015	1.0	29.53
c30_302	5.5810	5.4997	5.7160	N/A	0	0.015	2.0	295.3
c30_311	5.8671	5.5538	5.3045	N/A	1	0.0015	2.0	295.3
c30_331	6.0928	5.5527	5.2994	N/A	100	0.0015	2.0	295.3

Table 28 provides the equations from the regression analysis that bound the pH parameter for the CSNF base case. Those marked with an N/A are to have a value of zero since their effect on the abstracted value is negligible (see "pHabstract.xls", "Summary" tab).

Table 28. Regression Analysis Parameters for the CSNF WP

$pH = y_0 + a(\text{fuel exposure, \%}) + b(\text{drip rate, m}^3/\text{year}) + c(\text{neutronit rate, } \mu\text{m/year}) + d(\text{AI-6061 rate, } \mu\text{m/year})$						Regression	
Interval	y_0	a	b	c	d	R^2	Significance of F-Statistic
0-150 year	3.8306	0.0070	N/A (0)	0.9430	N/A (0)	0.8668	9.89E-08
150-550 years (ss < 0.5 $\mu\text{m/y}$)	4.5386	0.0086	27.7308	0.6536	N/A (0)	0.9571	3.75E-05
150-550 years (ss > 1 $\mu\text{m/y}$)	5.9261	N/A (0)	N/A (0)	-0.1953	N/A (0)	0.9065	2.65E-04
550-25K years	5.6076	N/A (0)	27.1925	-0.1871	N/A (0)	0.9592	7.65E-12
25K-50K years	5.6545	N/A (0)	26.0800	-0.2129	N/A (0)	0.9991	1.80E-17

Due to the simplicity of the mathematical expressions used to calculate pH, it is possible to calculate unrealistic pH values. For this reason, it was necessary to set bounds on the parameters used to calculate pH, specifically the drip rate. Taking the maximum rates for the other parameters, the maximum drip rates for use in the abstraction are presented in Table 29 (calculated in "phabstract.xls"). Those values with a "*" next to them are for cases in which the drip rate has negligible effect on the abstracted value. In "pHabstract.xls", in the worksheets ending with "-drip", a drip rate was calculated to see how high it had to be to affect the system. As can be seen, these drip rates are ≥ 2 orders of magnitude above those used in the abstraction showing that drip rate must be high to affect the system pH. These rates are also higher than the glacial transition rates presented in CRWMS M&O 2000c, so are extremely unlikely to occur in the CSNF WPs.

Table 29. Maximum Drip/Flushing Rates for Degrading CSNF WPs

	Neutronit / 316NG Rate	AI-6061 Rate	Fuel exposure
Max for parameter	2 or 0.5 $\mu\text{m/y}$	295.3 $\mu\text{m/y}$	100%
Interval	Calculated Max Drip rate		
0 – 150 years	3.4129 m^3/year *		
150-550 years (2 max)	0.0856 m^3/year		
150-550 years (0.5 max)	1.4679 m^3/year *		
550-25K years	0.1054 m^3/year		
25K-50K years	0.1101 m^3/year		

NOTES: "*" Indicates the cases in which the drip rate has negligible effect on the abstracted value
 The above maximum drip rates were calculated taking into account the fact that in the system of the "base case", the pH will never be above 8.1 (the pH of the fluid entering the WP).

If the flushing rate is kept constant during the entire duration of the case, the maximum drip rate for those cases with a neutronit / 316NG rate $0.5 \mu\text{m}/\text{year}$ would be $0.0856 \text{ m}^3/\text{year}$ and those with neutronit / 316NG rates of $\geq 1 \mu\text{m}/\text{year}$ would have a maximum rate of $0.1054 \text{ m}^3/\text{year}$. If the drip rate varies during the case, then the maximum drip rate for any interval of time is presented in Table 29. When the drip rates are above those values presented in Table 29, the pH will remain constant at the pH of the flushing fluid, in this case, J-13 well water with a pH of 8.1.

6.1.1.4 Use of abstracted pH

Once the pH of the case has been established, then this can be used to calculate the total carbon of the system and the degradation rate of the fuel during the time interval for which the pH was calculated.

BSC 20011 (Section 6.2) gives an expression for calculating the total carbon of the system as a function of pH and CO_2 fugacity.

$$\text{Total C} = F_{\text{CO}_2(\text{g})}(10^{-1.47} + 10^{(\text{pH} - 7.82)} + 10^{(2\text{pH} - 18.15)})$$

This stems from the following relationships between the carbonate species in an open system.

- 1) $\text{Total C} = [\text{CO}_2(\text{aq})] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$
- 2) $\text{CO}_2(\text{g}) \leftrightarrow \text{CO}_2(\text{aq})$ $\log K = -1.47$
- 3) $\text{CO}_2(\text{aq}) + \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{HCO}_3^-$ $\log K = -6.35$
- 4) $\text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-}$ $\log K = -10.33$

Substituting and rearranging the above equations as a function of pH and CO_2 fugacity

- 5) $[\text{CO}_2(\text{aq})] = F_{\text{CO}_2(\text{g})} \cdot 10^{-1.47}$
- 6) $[\text{HCO}_3^-] = (F_{\text{CO}_2(\text{g})} \cdot 10^{-1.47} \cdot 10^{-6.35}) / 10^{-\text{pH}}$
- 7) $[\text{CO}_3^{2-}] = \{(F_{\text{CO}_2(\text{g})} \cdot 10^{-1.47} \cdot 10^{-6.35}) / 10^{-\text{pH}}\} 10^{-10.33} / 10^{-\text{pH}}$

Substituting Equations 5 through 7 into Equation 1 gives the total carbon equation above as a function of CO_2 fugacity and pH.

The CSNF fuel degradation rate used in the EQ6 simulations of CSNF WP degradation, calculated in "CSNF Fuel Model Abstraction.xls" (Attachment I), based on CRWMS M&O 2000a, was of the form:

$$2.14\text{E-}11 \times [\text{H}^+]^{0.41} + 7.76\text{E-}14 \times [\text{HCO}_3^-]^{0.12} \quad (\text{moles}/\text{cm}^2 \cdot \text{s})$$

Total C is used in place of HCO_3^- in the above rates since HCO_3^- will be the dominant species in the system below a pH of 10. Using the pH abstracted and the equations presented in

Table 28 with the total carbon calculated with Equation 1, the fuel rate for the time interval can be calculated keeping in mind the relationship:

$$[H^+] = 10^{-pH}$$

Once the fuel degradation rate has been calculated. The amount of fuel still intact can be calculated through the equation

$$\begin{array}{ccccccc} \text{Initial mass} & & \text{Fuel Degradation} & & \text{Time} & & \text{Surface} & & \text{Intact fuel left} \\ \text{of fuel} & - & \text{Rate} & * & \text{(seconds)} & * & \text{area} & = & \text{in WP} \\ \text{(moles)} & & \text{(moles/cm}^2\cdot\text{s)} & & & & \text{(cm}^2\text{)} & & \text{(moles)} \end{array}$$

NOTE: the moles of intact fuel are normalized. To convert to grams, you must multiply by the normalization factor (4,685) and the molecular weight of the fuel (100 grams/mole).

For each subsequent time interval, the initial mass of fuel will be that left at the end of the previous time interval. If interested in a time over 25,000 years, all 4 pH abstractions will need to be used in compilation.

In BSC 2002a, the most U lost from the WP for the base case is 0.04%. Therefore, for the purposes of this abstraction it is assumed that all the U that is released from the fuel is taken up into various U minerals. These minerals include schoepite ($\text{UO}_3 \cdot 2\text{H}_2\text{O}$), $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$, uranophane- α ($\text{Ca}(\text{UO}_2\text{SiO}_3\text{OH})_2 \cdot 5\text{H}_2\text{O}$), and CaUO_4 .

For each equation, the confidence limits on the true value of pH, given a specific set of inputs, can be calculated based on the method provided in Draper and Smith (1966, p. 121). The inputs required for the method include (1) all the data used to create the regressions, which are provided in Table 27 and also provided in "pHabstract.xls" (Attachment I), (2) the residual mean square (MS) for each regression, which is provided in "pHabstract.xls", and (3) a Student t-distribution table.

6.1.2 "g7" Pore Water Abstraction

The following sub-sections (6.1.2.1-6.1.2.5) contain the pH abstraction for the pore water cases during each time interval. The time intervals for the "g7" pore water matrix are slightly different than the base case, due to the pH of the incoming "g7" pore water, which strongly affects the fuel degradation rate. Figure 26 shows the moles of CSNF remaining over time for the matrix of runs.

Section 6.1.2.6 contains an abstraction related to U loss from the WP. In some "g7" pore water cases, unlike the base case, an appreciable amount of U is lost from the WP (Table 20). Therefore, one cannot assume that all the U released from the fuel is contained in minerals. For the medium drip rate cases, all of the U precipitates initially, while the pH is low. After awhile, however, the pH increases and U-minerals dissolve and U no longer precipitates in minerals. The abstraction for "Time to U loss", represented by T_U , (Section 6.1.2.6) determines the time at which U loss begins for each case. Attachment IV presents plots of U in aqueous, U in minerals, U in fuel, and U loss for all the cases with U loss.

Figure 26: "g7" Pore Water: CSNF Moles Remaining

6.1.2.1 0-120 Years

Figure 27: "g7" Pore Water Abstraction: pH from 0-120 Years

As shown in Figure 27, the pH drops in the first 100 years due to the degradation of the A516 (which degrades by 70 years) and the degrading neutronit and 316NG. By 120 years, the initial drop has leveled off for all cases, with the high fuel exposure cases leveling off first. The drip rate does not have a dramatic effect during this time interval, as seen by comparing cases 111 with 112, or 121 with 122. The pH in the lower drip rate cases drop slightly slower than the higher drip rate cases. The two higher neutronit / 316NG rate cases show the pH dropping much faster than the low rates.

6.1.2.2 120-500 Years

Figure 28: "g7" Pore Water Abstraction: pH from 120-500 Years

As shown in Figure 28, between 120 and 500 years, the pH for the cases with low neutronit / 316NG have leveled off and the degradation of the steels are buffered by the degradation of the fuel. The pH for the higher neutronit / 316NG rate cases continues to drop.

6.1.2.3 500-3,000 Years

Figure 29: "g7" Pore Water Abstraction: pH from 500-3,000 Years

By 500 years, the pH for the high neutronit / 316NG rate cases has finally leveled off. The higher drip rate cases show the pH stabilizing at a slightly higher pH (due to the pH of the incoming water, ~ 11.22). The fuel exposure has very little effect during this time interval; as seen in Figure 29, where the pH curves for the different fuel exposure cases overlap each other for each of the neutronit / 316NG and drip rate cases.

6.1.2.4 3,000 to 12,500

Figure 30: "g7" Pore Water Abstraction: pH from 3,000-12,500 Years

As shown in Figure 30, for the high drip, high neutronit / 316NG rate cases, the pH climbs abruptly at 3,000 due to the complete degradation of the Neutronit (which occurs at 2,500 years). This pH climb for the medium neutronit / 316NG cases occurs around 5,000 years, corresponding to the finished degradation of the neutronit. For the corresponding cases with a low drip rate, the climb is not so evident, since the drip rate is not fast enough to elevate the pH. Again, the fuel exposure is not a significant contributor to the pH at this point, as seen by the three fuel exposure pH curves overlapping one another for each neutronit / 316NG and drip rate cases.

6.1.2.5 12,500-50,000 Years

Figure 31: "g7" Pore Water Abstraction: pH from 12,000-52,000 Years

As shown in Figure 31, the effect of the drip rate is obvious between 12,000 and 50,000 years, with the lower drip rate keeping a low pH, depending only on the neutronit / 316NG rate, and the high drip rate case shows the pH climbing, and leveling out at values dependant on the fuel exposure. The cases with the higher neutronit / 316NG rate show the pH increasing around 30,000 years, which is just after the 316NG has finished degrading (~27,000 years). The pH jump for the medium neutronit / 316NG rate cases correspond to the final degradation of the fuel (which varies depending on the case).

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Table 30: "g7" Pore Water Matrix of Average pH and Degradation Rates of CSNF WP Internals

Years	0-120	120 - 500	500-3,000	3,000-12,500	12,500-27,500 *	27,500-50,000 *	% Fuel Exposure	Neutronit / 316NG	Al-6061	Drip Rate
Case (_g7)	Average pH						Cladding Failure	(m ³ /year)		μm/year
c111	9.0384	8.2045	8.0983	6.8320	6.5653	6.5653	1	0.10	2.953	0.0015
c112	9.2173	8.2653	8.3113	9.2386	9.4766	9.4766	1	0.10	2.953	0.015
c121	8.8119	8.2171	7.3221	6.8497	6.5787	6.5787	10	0.10	2.953	0.0015
c122	8.9037	8.2879	8.2867	8.3498	8.4568	8.4568	10	0.10	2.953	0.015
c131	8.1343	7.3316	7.1781	6.9151	6.5683	6.5683	100	0.10	2.953	0.0015
c132	8.2582	7.3766	7.3709	7.3691	8.4298	8.4298	100	0.10	2.953	0.015
c211	8.2762	7.0017	5.5209	5.3951	5.5624	5.5624	1	1.0	29.53	0.0015
c212	8.2925	8.0253	6.7162	7.7930	9.2524	9.2524	1	1.0	29.53	0.015
c221	8.2703	6.7259	5.5193	5.3947	5.5627	5.5627	10	1.0	29.53	0.0015
c222	8.2865	7.7976	6.5893	7.0945	8.2033	8.2033	10	1.0	29.53	0.015
c231	7.8422	6.2460	5.5309	5.3940	5.5629	5.5629	100	1.0	29.53	0.0015
c232	7.9649	7.1503	6.6539	7.0946	8.0283	8.0283	100	1.0	29.53	0.015
c311	7.9809	6.0268	5.2922	5.3051	5.3569	N/A	1	2.0	295.3	0.0015
c312	8.1226	6.6141	5.8110	7.9963	8.0946	N/A	1	2.0	295.3	0.015
c321	7.9705	5.9704	5.2840	5.2985	5.3576	N/A	10	2.0	295.3	0.0015
c322	8.0923	6.3898	5.8225	7.1028	7.1425	N/A	10	2.0	295.3	0.015
c331	7.2970	5.8368	5.2674	5.3002	5.3583	N/A	100	2.0	295.3	0.0015
c332	7.6645	6.0796	5.8609	7.1072	7.1435	N/A	100	2.0	295.3	0.015

NOTES: * For the high rate cases, all of the reactants have fully degraded by 27,000 years, so there are no parameters by which to abstract a pH.

Table 30 gives the average pH values for each time interval with the various parameters that were used to develop the regression analysis. Table 31 gives the output of the regression analysis which gives equations for calculating the average pH.

Table 31. Regression Analysis Parameters for the "g7" Pore Water for the CSNF WP

pH = y ₀ +a(fuel exposure)+b(neutronit/316NG rate)+c(Al-6061 rate)+d(drip rate)						Regression	
Interval (Years)	y ₀	a	b	c	d	R ²	Significance of F-Statistic
0-120	8.9384	-0.0062	-0.6772	0.0014	9.7185	0.9475	3.44E-08
120-500	8.0085	-0.0066	-0.9455	N/A	36.4267	0.9235	4.66E-08
500-3000	7.5119	N/A	-2.0245	0.0056	52.7555	0.9250	4.05E-08
3,000-12,500	6.3131	N/A	-0.6411	N/A	135.4863	0.8091	4.03E-06
12,500-27,500	6.2517	N/A	-0.6677	N/A	179.0514	0.9172	7.65E-09
27,500-50,000	5.7807	N/A	N/A	N/A	190.7022	0.8598	1.42E-05

Source: "Pore Water pH and Fuel Abstraction.xls" in Attachment I

6.1.2.6 Time to U loss Abstraction

For low drip rate cases, all of the U is retained in the waste package as U-minerals (see Table 21). For the medium drip rate cases, the U loss begins after the pH reaches a value of about 8.4. From the plots in Attachment IV and spreadsheet "PW U loss.xls", the time at which the U loss begins for each run (T_U) was tabulated. A linear regression was performed relating the log of the stainless steel degradation rate and the log of the fuel exposure to T_U . The abstracted values of T_U are presented in Table 32 and the regression parameters are presented in Table 33.

Table 32. "g7" Pore Water Matrix of T_U and Degradation Rates for CSNF WP Internals

Case* (_g7)	T_U Time to U loss	% Fuel Exposure	Log (% Fuel Exposure)	Neutronit / 316NG Rate (m ³ /year)	Log (Neutronit/ 316NG Rate)	Predicted T_U based on Abstraction
	year	Cladding Failure				year
112	5,200	1	0	0.1	-1	3,305
122	8,500	10	1	0.1	-1	9,921
132	17,900	100	2	0.1	-1	16,538
212	12,700	1	0	1	0	20,762
222	30,300	10	1	1	0	27,378
232	31,200	100	2	1	0	33,995
312	29,000	1	0	2	0.30103	26,017
322	37,500	10	1	2	0.30103	32,634
332	37,500	100	2	2	0.30103	39,250

NOTE: *The cases with a low drip rate did not lose any U from the WP and therefore are not included in this table. In the cases that do lose U, the loss is not considered to occur up until the point when 2% has been lost.

Table 33. Regression Analysis Parameters for T_U for the "g7" Pore Water

$T_U = y_0 + a(\log(\text{fuel exposure})) + b(\log(\text{neutronit}/316\text{NG rate}))$			Regression	
y_0	a	b	R ²	Significance of F-Statistic
20761	6616	17457	0.8992	0.001022

Source: "PW U loss.xls" in Attachment I

6.1.2.7 Use of "g7" Pore Water Abstracted pH and T_U

The use of the "g7" pore water abstracted pH to calculate the quantity of fuel intact as a function of time is the same as for the base case (Section 6.1.1.4).

The following steps are used to determine the amount of U in minerals at time = t :

- (1) Calculate the moles of fuel intact at time= t , following Section 6.1.1.4
- (2) Calculate the moles of U in fuel intact by multiplying the moles of fuel calculated in step (1) by 0.3617 moles U per mole of fuel (Table 9)
- (3) Calculate T_U using the regression in Table 33 if the case of interest has a medium drip rate. If the drip rate is low, skip this step
- (4) Calculate moles of U in minerals by subtracting the U in fuel calculated in step (2) from initial U in fuel. For a case with a medium drip rate, t must be less than T_U , or the quantity of U in minerals will be overestimated. After $t = T_U$, dissolved U is lost from the WP in the effluent. Attachment IV shows U loss versus time for each medium drip rate case used in the abstraction.

6.1.3 Limited O₂ and CO₂ Abstraction

6.1.3.1 Abstraction of pH and HCO₃⁻

Figure 21 shows that essentially all of the elements of interest in the fuel remain in the WP as the materials degrade. As the fuel degrades, the elements precipitate as minerals that remain in the WP. In order to know the quantity of U in fuel versus U in minerals, the quantity of fuel intact as a function of time is needed. The degradation rate of the fuel is a function of pH and HCO₃⁻, which are functions of time. Therefore, if the pH and HCO₃⁻ variations with time are abstracted from the EQ6 results, then the degradation rate as a function of time can be calculated. Once the degradation rate versus time is known, then the fuel intact versus time can be calculated.

Average values of pH and HCO₃⁻ concentration for different time intervals were calculated. The time intervals chosen were (1) 0 to 300 years, (2) 300 years to the time of the drop in the HCO₃⁻ concentration (referred to as the HCO₃⁻-drop), (3) the time of the HCO₃⁻-drop to 25,000 years, and (4) 25,000 to 50,000 years. The "HCO₃⁻-drop" refers to the drop in the HCO₃⁻ concentration that each run experiences at some point during the run. The HCO₃⁻-drop is shown in Figure 32 for low neutronit / 316NG and Al-6061 degradation rates and in Figure 33 for medium and high rates.

6.1.3.2 0 to 300 years

The first 300 years occur during the first stage when the WP is filling and the fugacities of O₂ and CO₂ are controlled at 0.2 atm and 10⁻³ atm, respectively. For each run, the values of pH, that are plotted in Figure 34, were averaged over this interval. The average pH values, fuel exposure, neutronit degradation rate, and Al-6061 degradation rate for each run for the first 300 years are listed in Table 34.

The HCO₃⁻ concentration for the first 300 years is calculated from the equations relating pH and fugacity of CO₂(g) to total dissolved carbonate of the system (Section 6.1.1.4). At pH values between 7 and 10, the HCO₃⁻ concentration is approximately equal to the total dissolved carbonate (Langmuir 1997, Figure 6.12, p. 212). The equation for total dissolved carbonate can only be used for the first 300 years of the limited O₂ and CO₂ cases, because that is the only time interval during which the fugacity of CO₂(g) is held constant.

Figure 32. HCO_3^- Concentration for Low Steel and Al-6061 Degradation Rates

Figure 33. HCO_3^- Concentration for Medium and High Steel and Al-6061 Degradation Rates

Figure 34. pH From 0 to 300 Years After Breach

Table 34. Average pH and Degradation Rates for 0 to 300 Years

Case	Average pH	Fuel Exposure (% cladding failure)	Neutronit / 316NG Rate ($\mu\text{m}/\text{y}$)	Al-6061 Rate ($\mu\text{m}/\text{y}$)
c30x112	3.8317	1	0.10	2.953
c30x122	4.1944	10	0.10	2.953
c30x132	5.2170	100	0.10	2.953
c30x212	5.3627	1	1.00	29.53
c30x222	5.4546	10	1.00	29.53
c30x232	5.5248	100	1.00	29.53
c30x312	5.6970	1	2	295.3
c30x332	5.7686	100	2	295.3
c30x302	5.4064	0	2	295.3

6.1.3.3 300 to 50,000 years

The average pH and HCO_3^- concentration after 300 years are listed in Table 35 and Table 36. The time of HCO_3^- -drop for each run is also listed in Table 36. The values of pH are plotted for the low neutronit / 316NG and Al-6061 degradation rates in Figure 35 and for the medium and high rates in Figure 36.

Table 35. Average pH and Degradation Rates After 300 Years

Case	Average pH				Fuel Exposure (% cladding failure)	Neutronit / 316NGRate (μm/y)	Drip Rate (m ³ /year)
	300 y to before HCO ₃ -drop	Low Degradation Rates	Medium and High Degradation Rates				
		HCO ₃ -drop to 50,000 y,	HCO ₃ -drop to 25,000 y	25,000- 50,000 y			
c30y111	8.4306	8.3798	N/A	N/A	1	0.10	0.0015
c30y112	8.9987	9.4871	N/A	N/A	1	0.10	0.015
c30y121	8.4992	8.6154	N/A	N/A	10	0.10	0.0015
c30y122	9.0524	9.5366	N/A	N/A	10	0.10	0.015
c30y131	8.4693	9.1180	N/A	N/A	100	0.10	0.0015
c30y132	9.0709	10.2163	N/A	N/A	100	0.10	0.015
c30y211	8.0555	N/A	8.5754	8.6270	1	1.00	0.0015
c30y221	8.1082	N/A	8.5944	8.6525	10	1.00	0.0015
c30y222	8.2523	N/A	8.9667	9.1159	10	1.00	0.015
c30y231	8.1423	N/A	8.6515	8.6674	100	1.00	0.0015
c30y232	8.3120	N/A	9.1262	9.1758	100	1.00	0.015
c30y311	7.8725	N/A	8.5588	8.6700	1	2	0.0015
c30y331	8.0693	N/A	8.6013	a	100	2	0.0015
c30y302	8.0471	N/A	8.7823	a	0	2	0.015

Source: Spreadsheet "pH low o2.xls"

Notes: ^aValues not used in regression in order to achieve a good fit. Not included because the purpose of the regression is to calculate pH and then calculate the amount of fuel remaining and (1) the fuel is completely degraded by 25,000 years in c30y331 and (2) the fuel is not allowed to degrade in c30y302.

Table 36. Time to HCO₃-Drop and HCO₃⁻ Concentration

Case	Time to HCO ₃ -drop (years)	Average HCO ₃ Concentration Before HCO ₃ -drop (mole/kg)	LOG of HCO ₃ Concentration Before HCO ₃ -drop
c30y111	6599	1.57E-06	-5.8044
c30y112	8088	5.17E-06	-5.2867
c30y121	10838	1.10E-06	-5.9567
c30y122	13271	5.47E-06	-5.2621
c30y131	30457	1.37E-06	-5.8625
c30y132	38635	6.12E-06	-5.2134
c30y211	1691	4.36E-06	-5.3603
c30y221	1740	5.23E-06	-5.2817
c30y222	1743	6.27E-06	-5.2024
c30y231	2395	8.73E-07	-6.0592
c30y232	2388	2.02E-06	-5.6947
c30y311	1018	2.67E-06	-5.5730
c30y331	1271	7.97E-07	-6.0987
c30y302	986	3.34E-06	-5.4762

Source: Spreadsheet "HCO3 abs.xls"

Figure 35. pH for Low Steel and Al-6061 Degradation Rates

Figure 36. pH for Medium and High Steel and Al-6061 Degradation Rates

6.1.3.4 Regressions

For the abstraction of pH and HCO_3^- concentrations, linear regressions were performed in Excel. Average pH, HCO_3^- concentrations, and the time to HCO_3^- drop were the dependent variables. The factors that had an influence on pH and HCO_3^- and also were different in each run (fuel exposure, drip rate, neutronit / 316NG rate, Al-6061 rate) were the independent variables. The regression statistics are provided in spreadsheet "pH low o2.xls". For each time interval, all variables were included at first in the regression. If the p-value of the t-statistic for any of the independent variables was above 0.1, indicating less than 90% chance that the variable has a significant impact on the pH, then the variable was eliminated, and the regression was performed without that particular variable.

The results of the regressions, the multiple correlation coefficient, R^2 , and the significance of the F-statistic are presented in Table 37 for the pH, Table 38 for the time to HCO_3^- drop, and in Table 39 for the HCO_3^- concentration. The R^2 represents the linear relationship between the variables. The closer the R^2 is to 1.0, the better the fit. The F statistic, calculated from the degrees of freedom and the R^2 value is used to measure the significance of the entire fit of the data to the regression equation. For example, a value of 0.01 for the significance of the F-statistic indicates that there is a 99% chance that the relationship between the variables is significant and not merely due to chance. Therefore, based on the significance of the F-statistic listed in the following tables, all of the regressions listed below have at least a 98% chance that the relationships between the variables are significant.

Table 37. Regression Analysis Parameters for pH for Reducing Conditions

pH = $y_0 + a(\text{fuel exposure}) + b(\text{drip rate}) + c(\text{neutronit/316NG rate}) + d(\text{Al-6061 rate})$						Regression	
Time interval	y_0	a	b	c	d	R^2	Significance of F-Statistic
0-300 year	4.1011	5.3658E-03	0	1.2669	-4.0352E-03	0.8414	1.92E-02
300 years to HCO_3^- drop (ss = 0.1 $\mu\text{m/y}$)	8.4026	0	4.2539E+01	0	0	0.9896	4.05E-05
300 years to HCO_3^- drop (ss = 1-2 $\mu\text{m/y}$)	8.2019	1.1516E-03	1.1144E+01	-1.5562E-01	0	0.9440	5.78E-03
HCO_3^- drop to 50K years (ss = 0.1 $\mu\text{m/y}$)	8.3270	7.0693E-03	7.7205E+01	0	0	0.9923	6.75E-04
HCO_3^- drop to 25K years (ss = 1-2 $\mu\text{m/y}$)	8.6425	1.2103E-03	2.6851E+01	-9.8486E-02	0	0.9484	4.92E-03
25K-50K years (ss = 1-2 $\mu\text{m/y}$)	8.5996	0	3.6416E+01	0	0	0.9909	3.12E-05

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Table 38. Regression Analysis Parameters for Time to HCO₃⁻-Drop for Reducing Conditions

Time to HCO ₃ ⁻ drop (years) = $y_0 + a(\text{fuel exposure}) + b(\text{drip rate}) + c(\text{neutronit/316NG rate}) + d(\text{AI-6061 rate})$						Regression	
						R ²	Significance of F-Statistic
Case	y ₀	a	b	c	d		
ss = 0.1 μm/y	8.1874E+03	2.6470E+02	0	0	0	0.9513	9.03E-04
ss = 1-2 μm/y	2.5935E+03	5.4325	0	-8.4236E+02	0	0.9614	2.92E-04

Table 39. Regression Analysis Parameters for HCO₃⁻ Concentration for Reducing Conditions

HCO ₃ ⁻ Concentration = $10^{[y_0 + a(\text{fuel exposure}) + b(\text{drip rate}) + c(\text{neutronit/316NG rate}) + d(\text{AI-6061 rate})]}$						Regression	
Case	y ₀	a	b	c	d	R ²	Significance of F-Statistic
300 years to HCO ₃ -drop (ss = 0.1 μm/y)	-5.9435	0	4.5961E+01	0	0	0.975328	2.30E-04
300 years to HCO ₃ -drop (ss = 1-2 μm/y)	-5.0920	-5.9804E-03	1.2295E+01	-2.4822E-01	0	0.9448516	5.60E-03
0-300 years	Use Equation for Total C						
After HCO ₃ -drop	1E-21						

6.1.3.5 Use of Abstracted pH and HCO_3^- for Reducing Conditions

The abstracted pH and HCO_3^- values can be used to calculate the fuel remaining as a function of time as follows:

- (1). Specify fuel exposure (1 to 100%), drip rate (0.0015 to 0.15 m^3/year), neutronit / 316NG rate (0.1 to 2 $\mu\text{m}/\text{year}$, and Al-6061 rate (2.953 to 295.3 $\mu\text{m}/\text{year}$).
- (2). Calculate pH for 0-300 years using regression in Table 37.
- (3). Calculate HCO_3^- concentration (assumed the same as Total C) for 0-300 years based on equation presented in Section 6.1.1.4.
- (4). Calculate CSNF degradation rate for 0-300 years using equation from Section 6.1.1.4.
- (5). Calculate fuel remaining at 300 years using
$$\text{Moles fuel remaining} = (\text{initial moles fuel}) - (\text{degradation rate of fuel, mol/cm}^2/\text{s}) \times (\text{time interval, years}) \times (\text{surface area of fuel, } 4860 \text{ cm}^2) \times (\text{percent fuel exposure}/100) \times (\text{sec/year, } 3.16\text{E}+7).$$
- (6). Calculate time to HCO_3^- -drop using regression in Table 38.
- (7). Calculate pH for 300 years to time of HCO_3^- -drop using regression in Table 37.
- (8). Calculate HCO_3^- concentration for 300 years to time of HCO_3^- -drop using regression in Table 39.
- (9). Calculate degradation rate for 300 years to time of HCO_3^- -drop using equation from Section 6.1.1.4.
- (10). Calculate fuel remaining at the time of HCO_3^- -drop using
$$\text{Moles fuel remaining} = (\text{moles fuel at beginning of time interval}) - (\text{degradation rate of fuel, mol/cm}^2/\text{s}) \times (\text{time interval, years}) \times (\text{surface area of fuel, } 4860 \text{ cm}^2) \times (\text{percent fuel exposure}/100) \times (\text{sec/year, } 3.16\text{E}+7).$$
- (11). Calculate pH for time of HCO_3^- -drop to 50,000 years using regression in Table 37.
- (12). Obtain HCO_3^- concentration for time of HCO_3^- -drop to 50,000 years from Table 39
- (13). Calculate CSNF degradation rate for time of HCO_3^- -drop to 50,000 years using equation from Section 6.1.1.4.
- (14). Calculate fuel remaining at 50,000 years using
$$\text{Moles fuel remaining} = (\text{moles fuel at beginning of time interval}) - (\text{degradation rate of fuel, mol/cm}^2/\text{s}) \times (\text{time interval, years}) \times (\text{surface area of fuel, } 4860 \text{ cm}^2) \times (\text{percent fuel exposure}/100) \times (\text{sec/year, } 3.16\text{E}+7).$$

To convert moles of fuel (which have been normalized based on a 1-liter system) to kg of fuel, multiply moles of fuel by the normalization factor (4685 true moles per normalized mole), multiply by 100 g per mole, and divide by 1000 g per kg.

For each abstraction equation, the confidence limits on the true value of the dependent variable (such as pH), given a specific set of inputs, can be calculated based on the method provided in

Draper and Smith (1966, p. 121). The inputs required for the method include (1) all the data used to create the regressions, which are provided in Table 34 through Table 36 and also provided in "pH low o2.xls" and "HCO3 abs.xls" (Attachment I), (2) the residual mean square (MS) for each regression, which is provided in "pH low o2.xls" and "HCO3 abs.xls", and (3) a Student t-distribution table.

6.2 BORON ABSTRACTION

Unlike U, B does not form any minerals within the WP, no matter the pH of the system. Boron is known to sorb onto aluminum and iron oxides (Hatcher et al. 1967; Goldberg and Glaubig 1985; Goldberg and Glaubig 1988), but for criticality, it is more conservative to not include this sorption. Because of its independence from the pH, at any time, the amount of boron in the system is equal to the boron in the intact neutronit plus the boron in solution from the degraded neutronit. This amount can be calculated at a given time by the following equations:

While neutronit is still degrading ($t < t_f$):

$$N_B(t < t_f) = \frac{V_R D}{v} \left(1 - \exp^{-\frac{tv}{V_R}} \right) + B_i - Dt$$

After neutronit has degraded ($t > t_f$):

$$N_B(t > t_f) = \frac{V_R D}{v} \exp^{-\frac{v(t-t_f)}{V_R}} \left(1 - \exp^{-\frac{t_f v}{V_R}} \right)$$

where:

- N_B = moles B in WP = moles B in liquid + in undegraded neutronit (no B goes into minerals)
- t = time (years)
- t_f = time (years) when the neutronit has fully degraded
- V_R = reactor volume
- D = moles of B added from neutronit/year
- v = volumetric flow rate (liter/t)
- B_i = initial moles of B in neutronit

Table 40 gives the range of values for each of the variables used in the formulas above.

Table 40. Variables Used to Calculate Mass of B Still Left Inside CSNF WPs.

Variable	Description	EQ6 Input (normalized)*
n_i	amount of neutronit initially	4.5 moles
b_i	fraction of boron in the neutronit	0.115 moles
$B_i = n_i * b_i$	initial amount of B in the WP	0.5175 moles
SA	surface area of neutronit	112.9 cm ² /L
S_per_y	sec per year	3.16E+07

Variable	Description	EQ6 Input (normalized)*
VR	volume of WP	1 Liter
Neutronit Degradation Rate (moles/cm².s)		
rk ₁	low	2.5E-14
rk ₂	med	2.5E-13
rk ₃	high	5E-13
Drip rate (liters/sec)		
drip ₁	low	1.01E-11
drip ₂	med	1.01E-10
Time when neutronit has fully degraded = n_i / (rk * SA * S_{per_y}) (years)		
t _{r1}	for rk ₁	50,521
t _{r2}	for rk ₂	5,052
t _{r3}	for rk ₃	2,526
B release from neutronit per year = rk * SA * b_i * S_{per_y} (moles/yr)		
D ₁	for rk ₁	1.02E-05
D ₂	for rk ₂	1.02E-04
D ₃	for rk ₃	2.05E-05
volumetric drip rate = drip rate * S_{per_y} (Liter/year)		
v ₁	for drip rate 1	3.19E-04
v ₂	for drip rate 2	3.19E-03

* To convert "normalized" moles (which are based on a 1-liter system) multiply by the normalization factor (4685 true moles per normalized mole). To convert moles to grams, multiply by 100 g per mole for neutronit, or the molecular weight of Boron is 10.811 g/mole (Parrington 1996).

The above equations were derived from the simple mass balance equation presented below. The derivation of the above formulas is presented in Attachment V.

$$\text{Input} = \text{Output} + \text{Disappearance by reaction} + \text{Accumulation}$$

6.3 STEELS AND IRON MINERALS

The amount of iron in the WP and the density of the "sludge", the degraded material that remains in the WP, are important for criticality concerns. The largest component of the sludge, as predicted by EQ6 is the most common Fe mineral, hematite. As explained in Section 6.3.2, other Fe minerals, which have different densities, are likely to form in addition to hematite. This section discusses those Fe minerals and which conditions would favor their formation.

6.3.1 Total Iron

To calculate the total iron mineral volume in the WP, you need to calculate how much iron has been lost from the WP components. For CSNF, the Fe bearing components include the A516,

316NG, neutronit, and Al-6061. These include 98.3, 65.58, 64.82, and 0.7 wt% Fe respectively. To get the total mass of iron released, the following formula can be implemented:

$$\text{Fe released from component x} = \text{Corrosion rate (g/cm}^2\text{/year)} * \text{Time} * \text{Surface area} * \text{wt\% Fe}$$

The corrosion rate must be expressed in terms of g. This must be converted from the typical rate given in either mils/year or $\mu\text{m/year}$ to $\text{g/cm}^2\text{/year}$. Time is expressed in years, and surface area in cm^2 . This is done using the formula

$$\text{Corrosion rate (g/cm}^2\text{/year)} = \text{Corrosion rate (\mu m/year)} * \text{Conversion factor (for cm)} * \text{Density (g/cm}^3\text{)}$$

The densities for the different WP components can be found in Table 7 and Table 9. In the EQ6 cases simulated, none of the Fe is lost from the waste package, as shown in the “*.elem_tot.txt” files in Attachment I. Therefore, whatever is released from the metal components forms one or several of the iron minerals presented in Table 42. Table 41 presents the major Fe minerals formed in several different studies dealing with steel corrosion. Studies that made Fe oxide determination solely based on color were not included as color/shade of any oxide/hydroxide/oxyhydroxide can change dramatically depending on particle size (Schwertman and Cornell 1991, Plate IV). In the majority of cases, goethite, lepidocrocite, and magnetite were reported as the primary iron minerals. Hematite, maghemite, and Fe(OH)_2 were seen on occasion as were FeS and FeSO_4 in areas containing sulfides or sulfate reducing bacteria. Small amounts of the “minor” Fe minerals presented in Table 42 may also be expected.

Table 41. Sampling of Iron Minerals Reported from Different Corrosive Environments

References	Year	Test	Corrosion products
Smart et al.	2001	Anaerobic corrosion of carbon steel in groundwater	Fe_2O_3
Ahn and Leslie	1998	Lit review (aq corrosion)	$\gamma\text{-FeOOH}$, Fe_3O_4 , and Fe(OH)_2
Raman and Nasrazadani	1990	Analysis of Bridge packing Materials (atm)	Exposed surface = $\alpha + \gamma\text{-FeOOH}$ Unexposed surface = Fe_3O_4 and $\alpha\text{-FeOOH}$
Marsh and Taylor	1988	Submerged granite and bentonite covered steel coupons	Fe_3O_4
Pednekar	1987	Lit review of mild and carbon steels in varied environments	Atmosphere = $\alpha + \gamma\text{-FeOOH}$ and Fe_3O_4
			Fresh water = $\alpha + \gamma\text{-FeOOH}$, Fe_3O_4 , and $\alpha + \gamma\text{-Fe}_2\text{O}_3$
			Saltwater = $\alpha + \gamma\text{-FeOOH}$, Fe_3O_4 , and $\gamma\text{-Fe}_2\text{O}_3$
			Bacteria influenced = α, γ , and $\delta\text{-FeOOH}$, Fe_3O_4 , $\alpha + \gamma\text{-Fe}_2\text{O}_3$, FeS, and FeSO_4
Brush and Pearl	1972	Submerged steel coupons	Fe_3O_4 and $\alpha\text{-FeOOH}$ with some $\alpha\text{-Fe}_2\text{O}_3$ at the water-oxide interface

6.3.2 Iron Minerals

The database from which the EQ6 cases are run contains only hematite, goethite, magnetite, $\text{Fe}(\text{OH})_2$, and $\text{Fe}(\text{OH})_3$ for the major iron minerals (DTN: MO0009THERMODYN.001). Since the database is a thermodynamic database, unless suppressed in the EQ6 files, the most thermodynamically stable mineral (in this case, hematite) will always form as the primary Fe mineral. That primary Fe mineral, acting as an Fe sink, will not allow any other Fe minerals to form. In a natural, more realistic setting, a combination of Fe minerals (such as goethite, lepidocrocite, magnetite, and green rusts) would exist together in the WP. However, EQ6 is not able to model this.

To better understand the Fe mineral assemblages that may form in the WPs, a short synopsis of iron minerals that may form in a water filled WP is presented below, as is a discussion of cation replacement (Cr^{3+} and Mo^{3+}) in the structure of the Fe oxides/hydroxides. Most of the information on the major iron minerals in this section comes from Schwertmann and Cornell, 1991 and Schwertmann and Taylor, 1995. Any material not from these two sources will have an accompanying reference as to its source.

Goethite ($\alpha\text{-FeOOH}$) and hematite ($\alpha\text{-Fe}_2\text{O}_3$) are the two most thermodynamically stable Fe minerals under aerobic conditions. This makes them the most widespread Fe minerals. Goethite is found in almost all soils and in other areas such as lakes and streams. Hematite, on the other hand, is usually found in tropical and subtropical regions where higher temperatures and lower water activities aid in its formation. It is generally accepted that goethite forms through precipitation directly from solution. Hematite needs a precursor such as ferrihydrite from whence it forms through dehydration and rearrangement. Under surface conditions, simple transformation of goethite to hematite has not yet been observed, though it may occur after sediment burial. Besides hematite and goethite, other Fe minerals are found in the natural environment. Even though less thermodynamically stable, they may be kinetically more favorable for formation depending on the environment. Over time, these minerals would be expected to change/transform into the more thermodynamically stable hematite and/or goethite. The exact process depends on time, temperature, chemical environment, etc., and so far there is no exact model. A simplified diagram showing some of these transformations and the required conditions is presented in Figure 37. The "rust flow chart" comes from a compilation of information primarily from Schwertmann and Cornell 1991, Schwertmann and Taylor 1995, and Misawa et al. 1974. Minor contributions were made by Jobe et al. 1997 and Pednekar 1987. This diagram does not present all of the processes possible, but the ones that are well understood and occur frequently.

Figure 37. Simplified Diagram of Interactions Between Fe Oxides, Hydroxides, and Oxyhydroxides

Lepidocrocite (γ -FeOOH) forms from the oxidation of Fe^{2+} . The formation of lepidocrocite is usually kinetically favored over that of goethite and its transformation to goethite is extremely slow so that it may exist on the time scale of several thousand years. However, in carbonate rich solutions and those containing Al, goethite is more favored to form than lepidocrocite from Fe^{2+} . On the other hand, Cl and Si favor lepidocrocite formation and Si also helps to stabilize the structure of the mineral so that its transformation to goethite is stunted.

When iron corrodes in aerated solutions of neutral pH, the overall reaction can be written:

However, in oxygen rich environments, this Fe hydroxide is unstable and is oxidized to lepidocrocite, which in time changes to magnetite, maghemite, or hematite (Pednekar 1987).

Maghemite (γ - Fe_2O_3) occurs primarily in the soils of tropical and subtropical regions, but has been found in temperate regions. Besides oxidation of magnetite and dehydration of lepidocrocite, maghemite can be formed from other Fe oxides such as goethite. However, an essential prerequisite for this is the presence of organic matter and heat. In temperate zones the heat is usually provided by bush or forest fires.

Magnetite (Fe_3O_4) is usually found on the protected side of any "rust deposit". That is, directly against the metal and below any other oxide/hydroxide that may have formed. It is common in low oxygen and higher temperature conditions.

Only a few occurrences of feroxyhyte (δ' -FeOOH) have been reported. Rapid oxidation is presumed to be required for its formation.

Green rusts are not oxides or hydroxides in a strict sense but contain anions as an essential structural component. Forms with chloride, sulfate, and carbonate are known. The name is derived from the bluish-green color of the compounds and their occurrence as anoxic products of steel corrosion. They usually occur as an intermediate form between Fe^{2+} solutions and FeOOH. Green rusts are very sensitive to oxidation from which they quickly transform to other more stable iron oxide/hydroxides.

Ferrihydrite ($\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$) is limited to situations where fast hydrolysis occurs and where organic matter, phosphates, and silicates inhibit crystallization of more stable minerals. These inhibitors also retard its formation to stable minerals such as hematite. Because of its high solubility and unstable crystalline structure, it may only last on the order of days to a few years.

Akaganeite (β -FeOOH) requires the presence of high chloride concentrations and elevated temperatures ($\approx 60^\circ\text{C}$).

Wüstite (FeO) forms from the dehydration of $\text{Fe}(\text{OH})_2$ at higher temperatures in non-oxygenated atmospheres. At lower temperatures wüstite decomposes into Fe_3O_4 and Fe.

$\text{Fe}(\text{OH})_3$ in the EQ6 database is actually representative of amorphous or poorly crystalized Fe hydroxides such as ferrihydrite, with a general chemical formula of $\text{Fe}(\text{OH})_3$ (am). True

crystalline $\text{Fe}(\text{OH})_3$ is called bernalite. It was accepted as a mineral name only in 1992 (Birch et al. 1992; Birch et al. 1993). This crystalline form of $\text{Fe}(\text{OH})_3$ is very rare and occurs in very limited quantities so is not expected to form in the WP.

Other "minor" Fe minerals can also form under the temperature, solution, and pH conditions possible in a flooded corroding WP. These, along with the major Fe oxides / hydroxides / oxyhydroxides, and characteristics of each can be found in Table 42.

Table 42. Iron Minerals

Iron Mineral	Chemical Formula	Density (meas.)	Density (calc.)	Di/tri/poly-morphous with?	Group or series	Reference
Major Iron oxides/hydroxides/oxyhydroxides						
Hematite*	$\alpha\text{-Fe}_2\text{O}_3$	5.26	5.256	Maghemite	Hematite	Roberts et al. 1990, page 356
Goethite*	$\alpha\text{-FeO}(\text{OH})$	3.3-4.3	4.264	Akaganeite Feroxyhyte Lepidocrocite	Diaspore	Roberts et al. 1990, Page 324
Lepidocrocite	$\gamma\text{-FeO}(\text{OH})$	3.854	3.97	Akaganeite Goethite	-----	Roberts et al. 1990, Page 483
Maghemite	$\gamma\text{-Fe}_2\text{O}_3$	4.90	-----	Hematite	-----	Roberts et al. 1990, Page 509
Magnetite*	Fe_3O_4	5.175	5.197	-----	Spinel	Roberts et al. 1990, Page 515
Akaganeite	$\beta\text{-FeO}(\text{OH}, \text{Cl})$	-----	3.555	Feroxyhyte Goethite Lepidocrocite	-----	Roberts et al. 1990, Page 9
Feroxyhyte	$\delta'\text{-FeO}(\text{OH})$	-----	4.20	Akaganeite Goethite Lepidocrocite	-----	Roberts et al. 1990, Page 272
Ferrihydrite	$5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$	3.80	3.80	$\text{Fe}(\text{OH})_3$ in EQ6 database ymp.R0	-----	Roberts et al. 1990, Page 273
	$\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$ $\text{Fe}_5(\text{O}_4\text{H}_3)_3$ $\text{Fe}_2\text{O}_3 \pm 2\text{FeOOH} \cdot 2.6\text{H}_2\text{O}$	3.96	-----			Schwertmann and Taylor 1995, Table 8-1
	$\text{Fe}(\text{OH})_3 \cdot n\text{H}_2\text{O}$	-----	-----			Langmuir 1997, Table 12.3
Wüstite	FeO	5.88		-----	Periclase	Roberts et al. 1990, Page 954
$\text{Fe}(\text{OH})_2^*$	$\text{Fe}(\text{OH})_2$	3.4		-----	-----	Lide 1994, p. 4-65
Green Rusts	Varied (Example: $\text{Fe}_2^{3+}\text{Fe}_2^{2+}\text{O}_5 \cdot \text{H}_2\text{O}$)	varied	varied	-----	-----	Lide 1994; Donnay and Ondik 1973, p.O-102
Bernalite	Crystalline $\text{Fe}(\text{OH})_3$	Not available due to rarity of mineral				Jobe et al. 1997
Fe	Fe	7.86		-----	-----	Lide 1994, p. 4-64

Iron Mineral	Chemical Formula	Density (meas.)	Density (calc.)	Di/tri/poly-morphous with?	Group or series	Reference
Minor Fe Minerals						
Pyrite*	FeS	5.00-5.028	5.013	marcasite	Pyrite	Roberts et al. 1990, Page 702
Bornite*	Cu ₅ FeS ₄	5.079	5.09		-----	Roberts et al. 1990, Page 106
Chacopyrite*	CuFeS ₄	4.35	4.40		Chalco-pyrite	Roberts et al. 1990, Page 157
Trevorite*	NiFe ₂ O ₄	5.165	5.24		Spinel	Roberts et al. 1990, Page 880
Fe ₂ (MoO ₄) ₃ *	Fe ₂ (MoO ₄) ₃	3.804			-----	Donnay and Ondik 1973, p. O-120
Siderite	FeCO ₃	3.96			Calcite	Roberts et al. 1990, Page 785
Marcasite	FeS ₂	4.92	4.875	Pyrite	Marcasite	Roberts et al. 1990, Page 528
FeSO ₄	FeSO ₄	3.653			-----	Donnay and Ondik 1973, p. O-176

NOTE: * signifies minerals that are in the Data0.ymf.R0 database

For the mineral ferrihydrite, The accepted density of 3.80 from Roberts et al., 1990 should be used.

The "minor" minerals presented in Table 42 are those found in EQ6 cases (*) as well as those that may possibly form in the WP. In the presence of sulfides or sulfate reducing bacteria, FeS and FeSO₄ are also recorded as corrosion products of steels. This is shown in Booth et al. 1967a and Booth et al. 1967b and in the literature review by Pedneker 1987. Siderite, an Fe carbonate is also a common mineral in carbonate rich waters.

The Fe³⁺ in the octahedral position may be partially replaced by other trivalent metal cations of similar size such as Al³⁺, Mn³⁺, and Cr³⁺ without modifying the structure. In the base case for the abstraction, the O₂ fugacity is high enough to cause the complete oxidation of Fe(0) to Fe(III), Cr(0) to Cr(VI), and Mo(0) to Mo(VI). This oxidation of the Cr and Mo causes the pH of the system to drop significantly. This Cr and Mo may, however, replace some of the Fe in the structure of the Fe minerals due to the very similar ionic radii of the ions (Fe³⁺ = 0.064 and Cr³⁺ = 0.061, Table 1-2, Schwertman and Cornell 1991). Chromium replacement of iron is known to occur in goethite and lepidocrocite (Fe(OH)₃ in the database) (Schwertman and Cornell 1991; Eary and Rai 1989; Deng et al. 1996). Molybdenum replacement of Fe in Fe oxides is highly dependent on pH of the system. Molybdenum adsorption reaches a maximum between pH 4 and 5 and then decreases as pH increases until, at pH of 8, very little sorption occurs (Goldberg et al. 1996).

Currently, Mo and Cr replaced Fe oxides do not exist in the Data0.ymf.R0 database. This abstraction is based on cases run with the "ymf" database (Section 4.1.1.4), an adapted version of "ymp", in which these minerals were added. Calculations in which minerals such as Cr-ferrihydrite (Fe₄(CrO₄)(OH)₁₀) and Fe₂(MoO₄)₃ were added to the database do not see as marked early decrease in the pH as is seen in cases where those minerals are missing from the database

(BSC 2001k, Figure 14). This more realistically represents the pH of the system since Mo and Cr species are responsible for extreme drops in pH early in the cases.

6.4 ALUMINUM ALLOY AND ALUMINUM MINERALS

6.4.1 Total Aluminum

To calculate the total Al mineral volume in the WP, you need to calculate how much Al has been lost from the WP components. For CSNF, the only Al bearing component is the Al-6061. This alloy contains 96.68 Wt% Al. To get the total mass of Al released, the following formula can be implemented:

$$\begin{array}{ccccccc} \text{Corrosion} & & & & & & \\ \text{rate} & * & \text{Time} & * & \text{Surface} & * & \text{Wt\% Al} = \text{Al released from} \\ (\text{g/cm}^2/\text{year}) & & & & \text{area} & & \text{component x} \end{array}$$

The corrosion rate must be expressed in terms of g. This must be converted from the typical rate given in either mils/year or $\mu\text{m}/\text{year}$ to $\text{g}/\text{cm}^2/\text{year}$. Time is expressed in years, and surface area in cm^2 . This is done using the formula

$$\begin{array}{ccccccc} \text{Corrosion} & & \text{Corrosion} & & \text{Conversion} & & 2.70 \\ \text{rate} & = & \text{rate} & * & \text{factor} & * & \text{g/cm}^3 \\ (\text{g/cm}^2/\text{year}) & & (\mu\text{m}/\text{year}) & & (\text{for cm}) & & (\text{Density}) \end{array}$$

In the EQ6 cases simulated, none of the Al is lost from the waste package. Therefore, whatever is released from the Al-6061 forms one or several of the Al minerals presented in Table 43 through Table 46.

6.4.2 Aluminum Minerals

Like iron, aluminum forms a number of different minerals and a mixture of these are expected to form in the CSNF WPs. However, unlike the iron minerals where usually only one forms in the simulation of WP degradation, a primary mineral (an oxide, hydroxide, or oxyhydroxide) will form (gibbsite in the EQ6 cases) along with a host of clay minerals including smectites, kaolins, and zeolites. A sampling of these minerals can be found in Table 43. A more in-depth discussion follows.

Crystalline $\text{Al}(\text{OH})_3$ exists as four polymorphs; gibbsite, nordstrandite, doyleite, and bayerite, of which gibbsite is the most common. Most naturally occurring $\text{Al}(\text{OH})_3$ polymorphs are very finely crystalline and usually admixed with each other and other other Al minerals. Gibbsite is the most abundant of these polymorphs (Hsu 1995). Bayerite can be most readily synthesized, but it is rarely seen in nature while norstrandite is the most frequently occurring, after gibbsite, in the natural environment (Apps et al. 1989).

Aluminum oxyhydroxides ($\text{AlO}(\text{OH})$ – boemite and diaspore) are rarer than the hydroxides and are known to exist in many bauxite deposits. They are thus regarded as the ultimate product of intensive weathering of primary Al silicates in soils (Allen and Hajek 1995).

Table 43. Aluminum Minerals

Aluminum Mineral	Chemical Formula	Density (meas.)	Density (calc.)	Di/tri/poly-morphous with?	Group	Reference
Aluminum oxides/hydroxides/oxyhydroxides						
Bayerite	Al(OH) ₃	2.53	2.51	doyleite gibbsite norstrandite		Roberts et al. 1990, page 75
Gibbsite*	Al(OH) ₃	2.40	2.435	doyleite bayerite norstrandite		Roberts et al. 1990, Page 316
Nordstrandite	Al(OH) ₃	2.42	2.510	doyleite gibbsite bayerite		Roberts et al. 1990, Page 615
Doyleite	Al(OH) ₃	2.48	2.482	bayerite gibbsite norstrandite		Roberts et al. 1990, Page 233
Boehmite*	AlO(OH)	-----	3.070	diaspore		Roberts et al. 1990, Page 100
Diaspore*	AlO(OH)	3.3-3.5	3.380	boehmite	diaspore	Roberts et al. 1990, Page 226
Corundum*	Al ₂ O ₃	4.0-4.1	3.987	-----	hematite	Roberts et al. 1990, Page 194
Kaolins, Smectites, and Zeolites						
Kaolinite*	Al ₂ Si ₂ O ₅ (OH) ₄	2.6 -2.63	2.594	Dickite Halloysite nacrte	kaolinite- serpentine	Roberts et al. 1990, Page 429
Nontronite*	Na _{0.33} Fe ₂ (Si,Al) ₄ O ₁₀ (OH) ₂ ·nH ₂ O	Variable, 2-3			smectite	Roberts et al. 1990, Page 613
Montmorillinite ⁿ	(Na,Ca) _{0.3} (Al,Mg) ₂ Si ₄ O ₁₀ (OH) ₂ ·nH ₂ O	Variable, 2-3			smectite	Roberts et al. 1990, Page 575
Beidellite*	(Na,Ca _{0.05}) _{0.33} Al ₂ (Al,Si) ₄ O ₁₀ (OH) ₂ ·nH ₂ O	Variable, 2-3			smectite	Roberts et al. 1990, Page 79
Mesolite*	Na ₂ Ca ₂ Al ₆ Si ₉ O ₃₀ ·8H ₂ O	2.259	2.250		zeolite	Roberts et al. 1990, Page 547

NOTES: * signifies minerals that are in the Data0.ymp.R0 database

ⁿ signifies minerals that were added for the new database, Data0.ymp.R2

6.4.2.1 Smectites

Smectites are any monoclinic layer silicates of the general formula $X_{0.33}Y_{2.67}Z_4O_{10}(OH,F)_2 \cdot nH_2O$, where X = Ca, Li, or Na; Y = Al, Cr⁺³, Fe⁺², Fe⁺³, Li, Mg, Ni, or Zn; and Z = Al, Si (Roberts et al. 1990). The three most common forms of smectite are found in Table 43 above. Less common Al containing smectites are presented in Table 44. Smectites are common soil minerals in temperate and cold climates. They do not form where leaching is intense due to loss of bases and/or silica. They form through alteration of other phyllosilicates and synthesis. Where weathering and leaching are extensive, smectites usually alter to kaolinite.

Table 44. Minor Smectite Clays Containing Aluminum

Mineral	Density (g/cm ³)	Mineral	Density (g/cm ³)
Saponite*	2.10 (calc)	Sauconite	N/D
Sobotkite	2.31 (meas)	Swinefordite	N/D

Source: Roberts et al., 1990

NOTES: * signifies minerals that are in the Data0.ymp.R0 database

6.4.2.2 Kaolins

Minerals in the Kaolinite-Serpentine Group are silicates of the general formula $M_{2-3}Z_2O_5(OH)_4 \cdot nH_2O$, where $M = Al, Fe^{+2}, Fe^{+3}, Mg, Mn^{+2}, Ni$, or Zn and $Z = Al, Fe^{+3}$, or Si (Roberts et al. 1990). The most common are kaolinite and halloysite (Dixon 1995). Other less common Al containing kaolins presented in Table 45.

Table 45. Minor Kaolins Containing Aluminum

Mineral	Density (g/cm ³)	Mineral	Density (g/cm ³)	Mineral	Density (g/cm ³)	Mineral	Density (g/cm ³)
Amesite*	2.77 ^m	Baumite	2.92	Berthierine	3.04	Brindleyite	3.17 ^m
Dickite	2.599	Endellite	2.11-2.17 ^m	Fraipontite	N/D	Halloysite	2-2.2 ^m
Kellyite	3.11	Nacrite	2.582				

Source: Roberts et al., 1990

NOTES: * signifies minerals that are in the Data0.ymp.R0 database

^m measured density (otherwise it is the calculated density)

6.4.2.3 Zeolites

Zeolites are hydrous aluminosilicates of alkali and alkali earth elements characterized by the ratio $(Al+Si):O = 1:2$, and the reversible loss of water (Roberts et al. 1990). The most commonly reported zeolites in sedimentary environments are analcime, chabazite, clinoptilolite, erionite, heulandite, laumontite, mordenite, and phillipsite with clinoptilolite being the most abundant. In the EQ6 cases, mesolite is the most abundant zeolite formed in the WP ("*.elem_min.txt" files on Attachment I). Occurrences of zeolites have been lumped into the following categories on the basis of their hydrologic mode of formation (Ming and Mumpton 1995):

- (1) volcanic sediments in closed hydrologic systems (saline and alkaline lake deposits)
- (2) alkaline soils
- (3) volcanic sediments in metamorphic deposits
 - (a) burial
 - (b) contact
- (4) volcanic sediments in open hydrologic systems (fresh water lakes or groundwater environments)
- (5) volcanic material in hydrothermal or hot spring deposits

(6) marine deposits (deep sea and near shore environments)

(a) sediments

(b) volcanic rock

(7) nonvolcanic material transformed in other types of aqueous environments.

The naturally occurring zeolites, along with their possible environments of formation, are listed in Table 46.

It should be noted that the environments listed below are very general. The type of zeolite formed depends highly on aqueous composition, temperature, pressure, and activity of several aqueous components including Ca^{2+} , Na^+ , K^+ , and the activity ratio of Si to Al. Discussing this in any detail is not in the scope of this report. Information on this can be found in the references listed in Table 46 as well as Mariner and Surdam, 1970; Iijima and Utada, 1966; Smyth, 1982; and Hay, 1966. These are only a few of the many references dealing with zeolite formation vs environment but they provide a good starting point for understanding this complex chemical system.

Table 46. Naturally Occurring Zeolite Minerals

Mineral	Density (g/cm ³)	Hydrologic Mode of Formation	Mode of Formation Reference
Amicite	2.146		
*Analcime	2.22-2.29 ^m	1. closed hydrologic systems 2. soils and land surfaces 3a. burial metamorphic deposits 3b. contact metamorphic deposits 4. open hydrologic systems 5. hydrothermal or hot spring deposits 6a. marine sediment deposits 6b. volcanic rock marine deposits	Surdam 1977 Hay, 1978 Hay, 1978 Iijima, 1980 (p. 2118) Hay and Sheppard 1977 Iijima, 1980 (p. 2119) Hay, 1978 Hay, 1978
Barrerite	2.11		
Bikitaite	2.28		
Brewsterite	2.453	5. hydrothermal or hot spring deposits	Roberts et al., 1990
ⁿ Chabazite	2.05-2.16 ^m	1. closed hydrologic systems 2. soils and land surfaces 4. open hydrologic systems 5. hydrothermal or hot spring deposits 6b. volcanic rock marine deposits	Surdam 1977 Hay, 1978 Hay, 1978 Iijima, 1980 (p. 2119) Boles, 1977b
*Clinoptilolite	2.1-2.2 ^m	1. closed hydrologic systems 3a. burial metamorphic deposits 3b. contact metamorphic deposits 4. open hydrologic systems 5. hydrothermal or hot spring deposits 6a. marine sediment deposits 6b. volcanic rock marine deposits	Surdam 1977 Hay, 1978 Iijima, 1980 (p. 2118) Hay and Sheppard, 1977 Iijima, 1980 (p. 2119) Hay, 1978 Hay, 1978
Cowlesite	2.14 ^m		
Dachiardite	2.138		
Edingtonite	2.821		
Epistilbite	2.266	3b. contact metamorphic deposits	Iijima, 1980 (p. 2118)
ⁿ Erionite	2.04	1. closed hydrologic systems 6a. marine sediment deposits	Surdam 1977 Hay, 1978
Faujasite	1.92 ^m		

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Mineral	Density (g/cm ³)	Hydrologic Mode of Formation	Mode of Formation Reference
Ferrierite	2.11	5. hydrothermal or hot spring deposits	Iijima, 1980 (p. 2119)
Garronite	2.201		
ⁿ Gismondine	2.28		
Gmelinite	2.098	6b. volcanic rock marine deposits	Boles, 1977b
Gobbinsite	2.147		
Gonnardite	2.252	4. open hydrologic systems	Hay and Sheppard, 1977
Goosecreekite	2.16		
Harmotome	2.41-2.50 ^m	6a. marine sediment deposits	Boles, 1977b
Herschelite	2.050		
*Heulandite	2.1-2.2 ^m	3a. burial metamorphic deposits 3b. contact metamorphic deposits 5. hydrothermal or hot spring deposits	Hay, 1978 Iijima, 1980 (p. 2118) Iijima, 1980 (p. 2119)
Laumonite	2.405	3a. burial metamorphic deposits 3b. contact metamorphic deposits 5. hydrothermal or hot spring deposits 6a. marine sediment deposits	Hay, 1978 Iijima, 1980 (p. 2118) Iijima, 1980 (p. 2119) Boles, 1977b
Levyne	2.121		
Mazzite	2.108		
Merlinoite	2.18		
*Mesolite	2.250	3b. contact metamorphic deposits 5. hydrothermal or hot spring deposits	Iijima, 1980 (p. 2118) Iijima, 1980 (p. 2119)
*Mordenite	2.12-2.15 ^m	1. closed hydrologic systems 3a. burial metamorphic deposits 3b. contact metamorphic deposits 4. open hydrologic systems 5. hydrothermal or hot spring deposits 6a. marine sediment deposits	Surdam 1977 Hay, 1978 Iijima, 1980 (p. 2118) Hay and Sheppard 1977 Iijima, 1980 (p. 2119) Hay, 1978
*Natrolite	2.215	2. soils and land surfaces 4. open hydrologic systems 5. hydrothermal or hot spring deposits 6b. volcanic rock marine deposits	Hay, 1978 Hay and Sheppard, 1977 Iijima, 1980 (p. 2119) Boles, 1977b
Offretite	2.13 ^m		
Paranatrolite	2.20		
Paulingite	N/D		
Perliaite	2.15		
ⁿ Phillipsite	2.20 ^m	1. closed hydrologic systems 2. soils and land surfaces 3a. burial metamorphic deposits 4. open hydrologic systems 6a. marine sediment deposits 6b. volcanic rock marine deposits	Surdam 1977 Hay, 1978 Boles, 1977a Hay and Sheppard 1977 Hay, 1978 Hay, 1978
Pollucite	2.94		
*Scolecite	2.274	5. hydrothermal or hot spring deposits	Iijima, 1980 (p. 2119)
Sodium Dachiardite	2.16 ^m		
Stellerite	2.12		
*Stilbite	2.186	3b. contact metamorphic deposits 5. hydrothermal or hot spring deposits	Iijima, 1980 (p. 2118) Iijima, 1980 (p. 2119)
Tetranatrolite	2.22		

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MODEL REVISION RECORD

1. QA: QA

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2. Model Title:

Geochemistry Model Abstraction and Sensitivity Studies for the 21 PWR CSNF Waste Packages

3. DI (Including Rev. No. and Change No., If applicable):

MDL-DSU-MD-000001 REV 00

4. Revision/Change No.

5. Description of Revision/Change

Rev 00

Initial Issue

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1. PURPOSE

The purpose of this model, as directed by the Technical Work Plan (TWP) (BSC 2002b) is to abstract results from the Material Degradation and Release Model (BSC 2001a) applied to the Pressurized Water Reactor (PWR) Commercial Spent Nuclear Fuel (CSNF) waste package. The abstraction model focuses on developing correlations among parameters important to criticality, such as water influx rates as well as quantities of neutron absorbers and fissile material in the waste package and their form. The abstraction model will be used by the configuration generator model for calculating the probability of in-package criticality. The output of this abstraction will be the regression curves of pH (as a function of water flux, metals corrosion, and waste form exposure) for the CSNF waste packages. From pH, all other parameters such as fuel degradation rate and the total carbon of the system can be calculated. Another abstraction was performed for a special case of a limited oxygen environment, in which the bicarbonate (HCO_3^-) concentration was abstracted, in addition to pH. The output of this abstraction is not intended for Total System Performance Assessment (TSPA) calculations.

Limitations of this model include using degradation and drip rates within the range used in this report, given in Table 5. For the base case model abstraction (Section 6.1.1), the drip rates were expanded, and the limits for these rates are given in Table 29. This model should only be used in cases where the ionic strength is less than 4.0 (see discussion in Section 3). Additionally, as the components of the WP degrade, they form minerals of lower density, so the volume of material increases. This model is only valid while the volume of solids is less than two thirds of the total volume of the WP (see Assumption 5.2f).

This report combines the calculation and the model listed in Addendum B of the TWP (BSC 2002b): Geochemistry Sensitivity Studies for Waste Package Degradation (calculation), and Geochemistry Abstraction Model for CSNF Waste Package Degradation (model) into this single model report.

2. QUALITY ASSURANCE

An activity evaluation (BSC 2002b, Addendum A), determined that the quality assurance (QA) program (DOE 2002) applies to the activity under which this model was developed according to AP-SIII.10Q.

The quality level of the CSNF WP was classified as Level 1 in CRWMS M&O 1999a and discussed in BSC 2001m.

With regard to the development of this document, the control of the electronic management of data was evaluated in accordance with AP-SI.1Q *Control of Electronic Management of Information*. The evaluation determined that current work processes and procedures are in accordance with the controls specified in the TWP (BSC 2002b).

3. USE OF SOFTWARE

This section describes the computer software used to carry out the calculations in Section 4 and the regression analysis in Section 6.

Table 1. Computer Software Used in this Model Abstraction

Software Name	Version	Software Tracking Number (Qualification Status)	Description and Components Used	Input and Output Files ^a (Included in Attachment I)
ASPRIN	1.0	10487-1.0-00 (Qualified on Windows 95, BSC 2001b)	ASPRIN: performs post-processing of numerical information (from an output data file created by EQ6), to calculate isotopic inventories for elements of interest	input: *.bin (from EQ6) output: *.txt
EQ3/6	7.2b	LLNL:UCRL-MA-110662 (Qualified on Windows 95, CRWMS M&O 1998a)	EQ3NR: a speciation-solubility code	input: *.3i pickup: *.3p output: *.3o
			EQPT: a data file preprocessor	input: data0.* output: data1.*
EQ6	7.2bLV	10075-7.2bLV-00 (Qualified on Windows 95, CRWMS M&O 1999b) 10075-7.2bLV-02 (Qualified on Windows 2000 and NT, BSC 2002c)	EQ6: a reaction path code which models water/rock interaction or fluid mixing in either a pure reaction progress mode or a time mode	input: *.6i pickup: *.6p output: *.6o *.elem_aqu.txt *.elem_min.txt *.elem_tot.txt *.min_info.txt *.bin
MS EXCEL	Version 97 SR-2	Commercial off-the-shelf software: Exempt in accordance with AP-SI.1Q, Section 2.1.	Used in this document for graphical representation and arithmetical manipulations	input: *.elem_*.txt output: *.xls
PP	NA	Stockman, H.W. 1994. Used solely for visual display or graphical representation: Exempt in accordance with AP-SI.1Q, Section 2.1.2.	A plotting tool used for graphical representation	input: *.bin (from EQ6) output: *.wmf

NOTE: ^a Files are explained in more detail in Attachment II.

All applicable products were obtained from Software Configuration Management (SCM) and been verified appropriate for the application. The software products were run on standard personal computers listed in Table 2.

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Table 2: Computers Used

Computer Make	CPU #	Operating System	Software Used
Dell Optiplex Gxa	117728	Windows 95	ASPRIN 1.0, EQ3/6 V7.2b, EQ6 V7.2bLV, MS Excel, PP
Dell Optiplex GXa	115815	Windows 95	ASPRIN 1.0, EQ3/6 V7.2b, EQ6 V7.2bLV, MS Excel, PP
Dell Optiplex GX400	151295	Windows NT	EQ6 V7.2bLV, MS Excel, PP

The ASPRIN 1.0 and EQ3/6 V7.2b software were used within their range of validation.

The EQ6 V7.2bLV software was used within its range of validation. However, some runs simulated periods of high ionic strength (1 to ~4) listed in Table 3. While EQ6 is capable of handling high ionic strengths, there is no Yucca Mountain Project (YMP)-qualified thermodynamic database with corrections for high ionic strength (see Assumption 5.3 a).

Table 3. Occurrences of Ionic Strength > 1.0

Case Name	Duration of EQ6 Run	Peak Ionic Strength if > 1.0	Time period of ionic strength > 1.0 (in years after breach)
C30_211a	50749	2.53	907-50749
C30_231a	50821	2.72	785-50821
C30_311a	50774	3.45	534-27308
C30_331a	50753	4.13	402-27308
cn_a_111	203,020	1.07	8,742-51070
C211_g7a	202960	2.52	951-54616
C221_g7a	203290	2.68	2263-54616
C231_g7a	203050	2.70	1055-54616
C311_g7a	203110	3.41	460-27308
C321_g7a	203140	3.58	956-27308
C331_g7a	124700	4.10	446-27308
C331_g4a	221940	4.24	457-27308
C331_g3b	221960	4.18	402-28062
C331_g2a	222270	4.53	256-27308
C331_g1c	2455	4.10	473-2455
C331_g1a	82456	4.13	471-27308

4. INPUTS

4.1 DATA AND PARAMETERS

This report uses the software code EQ6 to model different geochemical scenarios, and the results of these runs are used as input to the model abstraction.

4.1.1 EQ6 Inputs

This section contains all of the values used as input to the EQ6 runs. The EQ6 runs were performed using the Material Degradation and Release Model, following Section 6.2, Model Implementation (BSC 2001a). The input files used for this model are contained in DTN: MO0208MWDINF01.006.

The material nomenclature and shorthand for the metals used throughout this document are listed in Table 4.

Table 4. Materials Nomenclature

Material Nomenclature	Shorthand
HASTELLOY® Alloy C-22, UNS N06022	Alloy 22
SA-240 S31600 Nuclear Grade Stainless Steel	316NG
SA-516 Grade 70 Carbon Steel	A516
SB-209 6061	Al-6061
Neutronit A976	Neutronit

It is convenient to consider the CSNF WP as several structural components, specifically:

- The Outer Shell, constructed of Alloy 22 (not modeled in EQ6 runs - see Assumption 5.2 c)
- The Inner Shell, constructed of 316NG
- The Fuel Basket Assembly, which is made up of the following components:
 - Four Fuel Plate Assemblies, constructed of Neutronit and Al-6061
 - Four Side/Corner-Guide/Stiffeners, constructed of A516
 - 21 Fuel Basket Tubes, constructed of A516
 - 21 PWR Fuel Assemblies, constructed of zircaloy cladding and PWR fuel

The details of these components come from sketch SK-0219 Rev 02, (Attachment III of BSC 2002a), as simplified in "CSNF WP Model Abstraction.xls", worksheet "Volumes and Surface Areas" (Attachment I of this document). The details of the fuel assemblies are discussed later in this Section.

4.1.1.1 Moles, Surface Areas, and Reaction Rates of Reactants

The EQ6 model is a scaled down model of the waste package with water filling all of the voids in the waste package. Instead of using the actual volume of water that would fill the voids, EQ6 uses one liter of water in the calculations. The actual void volume of the CSNF waste package is 4,685 liters (calculated as the variable "Normalization_Factor" in "CSNF WP Model Abstraction.xls", sheet: "Volumes and Surface Areas"). Therefore, the other materials in the waste package must be scaled to EQ6's one liter by dividing by the "normalization factor". These "normalized" values are presented in Table 5.

The initial moles of materials given in Table 5 use a convenient "pseudo mole" convention, which means that one mole of material equals 100 grams. The reason for this convention is that it does not require the molecular weight of the WP components. The reaction rates for the WP components are also listed in Table 5. These values are converted to units used by EQ6. The original units and references for the rates for the steels and alloys are presented in Table 6.

Table 5. Properties of Materials in the CSNF Waste Package

Reactant	m_i : Initial Moles ^a	sk : (cm ²) Surface Area ^a	rk : Reaction Rate (mol/cm ² ·s)		
			1	2	3
A516_FBT ^f (Fuel Basket Tube)	7.44	379	1.80E-11 ^b	2.74E-12 ^{a,i}	N/A
A516_Guides ^f	5.18	131	1.80E-11 ^b	N/A	N/A
Neutronit ^f	4.48	113	2.5E-14 ^a	2.5E-13 ^a	5E-13 ^a
Al-6061 ^f	0.7	55.3	2.54E-13 ^b	2.54E-12 ^b	2.54E-11 ^b
316NG_Inner Shell ^g	22.5	51.6	2.53E-14 ^b	2.53E-13 ^b	5.06E-13 ^b
CSNF Fuel ^{a,c}	23.1	4860	25°C	2.14E-11× [H ⁺] ^{0.41} + 7.78E-14 × [HCO ₃] ^{-0.12}	
			27.1°C	2.27E-11× [H ⁺] ^{0.41} + 8.24E-14 × [HCO ₃] ^{-0.12}	
			27.3°C	2.29E-11× [H ⁺] ^{0.41} + 8.31E-14 × [HCO ₃] ^{-0.12}	
			54°C	4.50E-11× [H ⁺] ^{0.41} + 1.63E-13 × [HCO ₃] ^{-0.12}	
			73°C	6.90E-11× [H ⁺] ^{0.41} + 2.51E-13 × [HCO ₃] ^{-0.12}	
			96°C	1.07E-10× [H ⁺] ^{0.41} + 3.90E-13 × [HCO ₃] ^{-0.12}	
HNO ₃ (aq)	1.00 (1x)	1.00	5.01E-14 ^{a,d} (1x)		
	5.00 ^h (5x)	1.00	2.51E-13 ^{a,d} (5x)		
	100.00 ^h (100x)	1.00	5.01E-12 ^{a,d} (100x)		
J-13 Water	N/A	N/A	1.01E-11 ^{a,e}	1.01E-10 ^{a,e}	1.01E-09 ^{a,e}

Sources: ^aCalculated in sheets "Volumes and Surface Areas" and "Rates" of "CSNF WP Model Abstraction.xls" and "CSNF Fuel Model Abstraction.xls" (Attachment I).

^bTaken from CRWMS M&O 2001 (Table 4); for Al-6061, the medium and high rates are 10 and 100 times the low rate; for 316NG, the medium rate is 10 times the low rate.

^cCRWMS M&O 2000a (p. 82 for rate, p. 22 for the surface area)

^dBSC 2001e (Table 6.1)

^eBased on CRWMS M&O 2000c, (Assumption 5.1 f, conversion of 0.0015, 0.015 and 0.15 m³/year).

NOTES: ^fSeveral Assumptions were made about the geometry of these components (see Assumption 5.4 e).

^gOnly the inside surface area of the inner shell was considered (see Assumption 5.2 b).

^hThe moles of HNO₃ are simply a reservoir, the rate of release is the significant parameter. This reservoir was increased for the higher rates of release to insure that it did not run out.

ⁱThis lower degradation rate was used only in the concentrated pore water sensitivity cases

Table 6. Reaction Rates for the Steels and Alloys in the CSNF Waste Package

Reactant	Reaction Rate ($\mu\text{m}/\text{year}$)		
	1	2	3
A516	72 ^a	11 ^a	N/A
Neutronit	0.1 ^b	1 ^e	2 ^c
Al-6061	2.953 ^d	29.53 ^e	295.3 ^f
316NG	0.1 ^b	1 ^e	2 ^c

Sources:^a McCright 1998 (pp. 2.2-96 - 2.2-98), lowest rate (2) is for concentrated solutions

^b CRWMS M&O 1997a (pp. 11-13)

^c BSC 2001d (50% value from Fig. 12 and Eq. 17)

^d from ASM International 1987 (Table 12, p. 603), calculated in "NReactor.xls" (Attachment III of CRWMS M&O 2001.

^e Ten times the low rate

^f One hundred times the low rate

The values in Table 5 differ from the latest CSNF calculation (BSC 2002a). The calculation did not include all of the A516 that made up the "A516_Guides", so the additional A516 was included in this model. This change affects the moles and surface area for all of the components because the additional volume of A516 changed the calculated "void volume" which is used to normalize all these components.

The degradation rates and surface areas for each reactant are given in Table 5, and the true rate at which EQ6 degrades the reactants is a function of both (the reaction rate, r_k and the surface area, sk). The corrosion rates for the metals include microbially assisted degradation, but these rates are not principally controlled by bacteria (see Assumption 5.2 a).

The drip rate is taken from a correlation between percolation flux and drip rate, also called mean seep flow rate (CRWMS M&O 2000c, Figure 3.2-15). The drip rates correspond to percolation fluxes ranging from about 10 mm/year (high infiltration rate for the present-day climate) to 80 mm/year (twice the high infiltration rate for the glacial-transition climate) CRWMS M&O 2000c, Table 3.2-2. The net infiltration rate and percolation flux are equal at the potential repository level (CRWMS M&O 2000c, Section 3.2.3.4, p. 3-33).

4.1.1.2 Elemental Compositions of Reactants

The compositions of the steels and alloys are given in Table 7.

Table 7. Steels and Alloys: Composition, Density, and Molar Volume

Element	A516		Neutronit		Al-6061		316NG	
	wt% ^a	moles ^b	wt% ^c	moles ^d	wt% ^e	moles ^d	wt% ^f	Moles ^d
C	0.28	2.33E-02	0.04	3.33E-03			0.02	1.67E-03
Mn	1.045	1.90E-02			0.15	2.73E-03	2	3.64E-02
P	0.035	1.13E-03					0.045	1.45E-03
S	0.035	1.09E-03					0.03	9.36E-04
Si	0.29	1.03E-02			0.6	2.14E-02	0.75	2.67E-02
Cr			18.5	3.56E-01	0.195	3.75E-03	17	3.27E-01
Ni			13	2.21E-01			12	2.04E-01
Co			0.2	3.39E-03				
Mo			2.2	2.29E-02			2.5	2.61E-02
N							0.08	5.71E-03
Fe	98.3	1.76E+00	64.82	1.16E+00	0.7	1.25E-02	65.58	1.17E+00
B			1.245	1.15E-01				
Zn					0.25	3.82E-03		
Cu					0.275	4.33E-03		
Mg					1.0	4.11E-02		
Ti					0.15	3.13E-03		
Al					96.68	3.58E+00		
Total	100.0	1.82	100.0	1.88	100.0	3.68	100.0	1.81
Density (g/cm³)	7.85^g		7.76^h		2.70ⁱ		8.00^j	
Molar Volume (cm³/mol)^k	12.74		12.88		37.04		12.50^k	

- Sources: ^a ASME 1998 (Section II, SA-516/SA-516M, Table 1, p. 925)
^b Moles / 100 g of material calculated by dividing the weight percent of each element by the molecular weight.
^c DTN: MO0109RIB00049.001 (under section titled "Material Properties of Neutronit A976/A978"); for B content: ASTM A 887-89 2000 (Table 1, S30463, S30464, and S30466)
^d Moles / 100 g of material, normalized in "CSNF WP Model Abstraction.xls" worksheet "Materials" (Attachment I of BSC2002a)
^e ASME 1998 (Section II, SB-209, Table 1, p. 236)
^f ASME 1998 (Section II, SA-240, p. 366, Table 1) for composition of 316, ASM International 1987 (p. 931) for C and N content for 316NG
^g ASME 1998 (Section II, SA-20/SA-20M, Section 14.1, p. 67)
^h DTN: MO0109RIB00049.001 (under section titled "Material Properties of Neutronit A976/A978")
ⁱ ASTM G 1-90 (Table X1.1)
^j DTN: MO0003RIB0076.000 (under section "Properties of Type 316N Grade Stainless Steel")
^k Molar volume = molecular weight (100 g/mole) divided by density.

NOTE:

The fuel assembly geometry (from Punator 2001, p. 2-5 and BSC 2001c, p. 44) is simplified in "CSNF WP Model Abstraction.xls," worksheet "Volumes and Surface Areas" (Attachment I of BSC 2002a), and given in Table 8.

Table 8. CSNF Simplified Geometry

Parameter	Value
Pellet Radius	0.468 cm ^a
Active Fuel Height	360 cm ^a
Fuel Pins / Assembly	208 ^a
Node Height	20.01 cm ^b
Mass of Fuel	10,843,178 g ^c
Volume of 1 PWR Assembly	81,000.00 cm ^{3d}

Source: ^a Punator 2001, p. 2-5 (see Assumption 5.4 a)

^b BSC 2001c, p. 44 (see Assumption 5.4 a)

^c Calculated in "CSNF WP Model Abstraction.xls".

^d CRWMS M&O 1997a, Table 4.1-1, (see Assumption 5.4 c)

The fuel composition comes from an ASCII file from BSC 2001c, (Disk 1 of 9, "ATT III/ LPM1/ uniform_profile/ 3.5/ ft71-case10.N04").

- **/3.5/** means 3.5% U-235 enrichment
- **case10** means the fuel at 11,000 years
- **N04** means 40 GWd/mtU fuel burnup
(BSC 2001c, Attachment III, p. III-1).

The "ft71-case10.N04" file was simplified in "case10.txt", and is included in Attachment I of BSC 2002a.

The fuel composition is simplified in "CSNF Fuel Model Abstraction.xls", worksheet "Simplified Fuel Composition" in Attachment I of BSC 2002a. The light elements (structural components of the fuel assembly) were not included in this calculation (see Assumption 5.4 b). This composition was added to the database "data0.ymf" to allow the CSNF fuel to be modeled as a mineral.

Table 9 summarizes the reported characteristics of the CSNF fuel.

Table 9. CSNF Fuel: Composition, Density, and Molar Volume

Element ^a	(Moles/100g)	Isotope Percent ^a	
U	0.3617	U-234	0.04%
		U-235	1.11%
		U-236	0.69%
		U-238	98.16%
Np	0.0009	Np-237	100.00%
Pu	0.0027	Pu-239	76.66%
		Pu-240	13.78%
		Pu-242	9.56%
Zr	0.0005	Zr-93	100.00%
Mo	0.0009	Mo-95	100.00%
Tc	0.0008	Tc-99	100.00%
Ru	0.0020	Ru-101	100.00%
Cs	0.0013	Cs-133	79.57%
		Cs-135	20.43%
Ba	0.0010	Ba-138	100.00%
REE ^b	0.0035	Y-89	15.51%
		Pr-141	24.63%
		Nd-143	17.79%
		Nd-145	14.06%
		Nd-148	7.81%
		Sm-147	4.78%
		Sm-149	0.11%
		Sm-150	6.83%
		Sm-152	2.58%
		Eu-151	0.39%
		Eu-153	2.54%
		Gd-154	0.62%
		Gd-155	0.13%
		Gd-156	1.72%
		Gd-158	0.47%
O	0.7385	O-16	100.00%
Density ^c (g/cm ³)		10.02	
Molar Volume ^d (cm ³ /mol)		9.980	

Source: ^aIsotopic Composition from BSC 2001c, as simplified in "CSNF Fuel Model Abstraction.xls", worksheet "Complete Fuel Composition" (Attachment I).

^bThe Rare Earth Elements (REE) were combined and modeled as Gd. See Assumption 5.3 d.

^cDensity calculated in "CSNF WP Model Abstraction.xls", worksheet "Volumes and Surface Areas" (Attachment I)

NOTE: ^dMolar volume = molecular weight (100 g/mole) divided by density

It was assumed that the water composition entering the WP can be approximated as J-13 well water (Assumptions 5.1 a, b, c, e, and f) with a few adjustments, given in Table 10.

Table 10. EQ3NR and EQ6 Input Values for J-13 Well Water Composition

EQ3NR Input File				EQ6 Input File	
Basis Species	Basis Switch ^f	Concentration	Units	Element	Mole/kg
Redox		-0.7 ^a	log fO ₂	O	5.55E+01
Na ⁺		45.8 ^a	mg/L	Na	1.99E-03
SiO ₂ (aq)		60.97 ^b	mg/L	Si	1.02E-03
Ca ⁺⁺		13.0 ^a	mg/L	Ca	3.24E-04
K ⁺		5.04 ^a	mg/L	K	1.29E-04
Mg ⁺⁺		2.01 ^a	mg/L	Mg	8.27E-05
H ⁺		8.1 ^d	pH	H	1.11E+02
HCO ₃ ⁻	CO ₂ (g)	-3 ^e	log fCO ₂	C	2.07E-03
F ⁻		2.18 ^a	mg/L	F	1.15E-04
Cl ⁻		7.14 ^a	mg/L	Cl	2.01E-04
NO ₃ ⁻	NH ₃ (aq)	8.78 ^a	mg/L	N	1.42E-04
SO ₄ ⁻⁻		18.4 ^a	mg/L	S	1.92E-04
HPO ₄ ⁻⁻	Trace	1.000E-16 ^c	Molality	P	1.00E-16
Al ⁺⁺⁺	Trace	1.000E-16 ^c	Molality	Al	1.00E-16
B(OH) ₃ (aq)	Trace	1.000E-16 ^c	Molality	B	1.00E-16
Ba ⁺⁺	Trace	1.000E-16 ^c	Molality	Ba	1.00E-16
CrO ₄ ⁻⁻	Trace	1.000E-16 ^c	Molality	Cr	1.00E-16
Cu ⁺⁺	Trace	1.000E-16 ^c	Molality	Cu	1.00E-16
Fe ⁺⁺	Trace	1.000E-16 ^c	Molality	Fe	1.00E-16
Gd ⁺⁺⁺	Trace	1.000E-16 ^c	Molality	Gd	1.00E-16
Mn ⁺⁺	Trace	1.000E-16 ^c	Molality	Mn	1.00E-16
MoO ₄ ⁻⁻	Trace	1.000E-16 ^c	Molality	Mo	1.00E-16
Ni ⁺⁺	Trace	1.000E-16 ^c	Molality	Ni	1.00E-16
Np ⁺⁺⁺	Trace	1.000E-16 ^c	Molality	Np	1.00E-16
Pu ⁺⁺⁺	Trace	1.000E-16 ^c	Molality	Pu	1.00E-16
TcO ₄ ⁻	Trace	1.000E-16 ^c	Molality	Tc	1.00E-16
Ti(OH) ₄ (aq)	Trace	1.000E-16 ^c	Molality	Ti	1.00E-16
UO ₂ ⁺⁺	Trace	1.000E-16 ^c	Molality	U	1.00E-16
Zn ⁺⁺	Trace	1.000E-16 ^c	Molality	Zn	1.00E-16
ZrO ⁺⁺	Trace	1.000E-16 ^c	Molality	Zr	1.00E-16

Sources: ^aDTN: MO0006J13WTRCM.000.

^bBSC 2001f (Section 5.1.3) based on DTN: MO0006J13WTRCM.000.

NOTES: ^cA trace concentration (1.00E-16 molal) is added for numerical stability in EQ3/6 runs.

^dIf log(fCO₂) = -3, then EQ3NR calculates pH = 8.1.

^eSee Assumption 5.1 b and e.

^f"Switched" some chemical species to those recognized by EQ3NR and EQ6.

Several pore water compositions were used as input from two Engineered Barrier System (EBS) calculations (BSC 2001g and BSC 2001h) and are listed in Table 11.

Table 11. Selections of Pore Waters

Pore Water	Temperature	Source	Description*
g_1	25.89	BSC 2001g, Table 11	Low Temperature, High P_{CO_2} in the Tptpl Lithology for Seepage at the Crown of the Drift: Transition to Ambient (30,001-100,000 years)
g_2	27.10	BSC 2001h, Table 6.1-6	Evaporated Tptpmn Lithology Crown Seepage Waters (Alcove 5 Pore Water): Transition to Ambient
g_3	96.00	BSC 2001h, Table 6.1-8	Evaporated Drift Test Scale Water: Case 1
g_4	54.02	BSC 2001h, Table 6.2-10	Tptpl Lithology Crown Seepage (Alcove 5 Pore Water)/ Grout Leachate, High Temperature, High P_{CO_2} : Extended Cooldown, Leachate + $CO_2(g)$
g_5	27.37	BSC 2001h, Table 6.2-10	Tptpl Lithology Crown Seepage (Alcove 5 Pore Water)/ Grout Leachate, High Temperature, High P_{CO_2} : Transition to Ambient, Leachate + $CO_2(g)$
g_6	73.40	BSC 2001h, Table 6.2-11	Tptpl Lithology Crown Seepage (Alcove 5 Pore Water)/ Grout Leachate, Low Temperature, High P_{CO_2} : Post Closure Hot, Leachate + $CO_2(g)$
g_7	24	BSC 2001h, Table 6.2-16	Evaporated Perched Water Seepage/Grout Leachate: Ambient

* The pore water description is the column heading from the original table listed as the source for the pore water. The "High Temperature" vs "Low Temperature" comments are relative to the original tables, not this table.

The compositions of these seven pore waters were added to EQ3NR input files. The EQ3NR input values are given in Table 12. The output of EQ3NR is used in the EQ6 input files as the equilibrium pore water composition, and these values are given in Table 13. The composition of all the pore waters and J-13 are plotted in Figure 1.

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Table 12. EQ3NR Input Values for Pore Water Composition

Basis Species	Pore Water Composition							Units
	g_1	g_2	g_3	g_4	g_5	g_6	g_7	
redox	-0.7	-0.7	-0.7	-0.7	-0.7	-0.7	-0.7	logfO ₂
Na ⁺	4.79E-03	3.24E-01	3.56E-01	4.53E-03	4.79E-03	4.57E-03	3.89E-01	Molality
SiO ₂ (aq)	1.55E-03	1.88E-04	6.12E-03	1.99E-05	1.36E-05	2.44E-05	8.89E-04	Molality
Ca ⁺⁺	2.14E-03	1.61E-02	1.72E-06	1.32E-03	1.22E-03	1.61E-03	7.89E-06	Molality
K ⁺	1.06E-04	7.56E-03	4.49E-02	2.09E-04	1.12E-04	2.66E-04	2.52E-02	Molality
Mg ⁺⁺	1.97E-04	1.39E-02	3.52E-08	4.45E-08	2.97E-08	5.90E-08	1.09E-09	Molality
H ⁺	8.35	7.56	9.55	7.5	7.86	7.59	11.22	pH
HCO ₃ ⁻	3.31E-03 ^b	-2.87	-3.00	-2.46	-2.97	-2.83	-6	logfCO ₂
F ⁻	3.06E-04	3.49E-04	2.86E-02	3.91E-04	3.14E-04	4.69E-04	1.00E-16	Molality
Cl ⁻	3.31E-03	2.14E-01	1.21E-01	3.28E-03	3.31E-03	3.40E-03	5.24E-02	Molality
NO ₃ ^{-a} NH ₃ (aq)	1.00E-16	2.14E-02	1.77E-02	1.00E-16	1.00E-16	1.00E-16	6.10E-02	Molality
SO ₄ ⁻⁻	1.20E-03	7.75E-02	6.02E-02	1.25E-03	1.20E-03	1.85E-03	3.80E-02	Molality
Al ⁺⁺⁺	6.64E-10	3.22E-09	1.00E-16	3.32E-07	6.27E-08	1.90E-06	5.34E-06	Molality
B(OH) ₃ (aq)	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	Molality
Ba ⁺⁺	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	Molality
CrO ₄ ⁻⁻	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	Molality
Cs ⁺	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	Molality
Cu ⁺⁺	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	Molality
Fe ⁺⁺	2.00E-12	6.85E-14	1.00E-16	1.27E-11	1.44E-12	4.49E-11	1.00E-16	Molality
Gd ⁺⁺⁺	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	Molality
HPO ₄ ⁻⁻	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	Molality
Mn ⁺⁺	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	Molality
MoO ₄ ⁻⁻	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	Molality
Ni ⁺⁺	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	Molality
Co ⁺⁺	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	Molality
Np ⁺⁺⁺⁺	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	Molality
Pu ⁺⁺⁺⁺	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	Molality
RuO ₄ ⁻⁻	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	Molality
TcO ₄ ⁻	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	Molality
Ti(OH) ₄ (aq)	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	Molality
UO ₂ ⁺⁺	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	Molality
Zn ⁺⁺	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	Molality
ZrO ⁺⁺	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	Molality

Sources: See Table 11.

NOTES: A trace amount (1.00E-16 molal) is added for all elements in the WP, for numerical stability in EQ3/6 runs.

The carbon from

^a"Switched" chemical species to that recognized by EQ3NR and EQ6

^bUnits are Molality

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Table 13. EQ6 Input Values for Pore Water Composition

Element	Pore Water Composition (Mole/kg)						
	g_1	g_2	g_3	g_4	g_5	g_6	g_7
O	5.55E+01	5.59E+01	5.60E+01	5.55E+01	5.55E+01	5.55E+01	5.62E+01
Na	4.79E-03	3.24E-01	3.56E-01	4.53E-03	4.79E-03	4.57E-03	3.89E-01
Si	1.55E-03	1.88E-04	6.12E-03	1.99E-05	1.36E-05	2.44E-05	8.89E-04
Ca	2.14E-03	1.61E-02	1.72E-06	1.32E-03	1.22E-03	1.61E-03	7.89E-06
K	1.06E-04	7.56E-03	4.49E-02	2.09E-04	1.12E-04	2.66E-04	2.52E-02
Mg	1.97E-04	1.39E-02	3.52E-08	4.45E-08	2.97E-08	5.90E-08	1.09E-09
H	1.11E+02	1.11E+02	1.11E+02	1.11E+02	1.11E+02	1.11E+02	1.11E+02
C	3.31E-03	8.28E-04	6.68E-02	1.26E-03	1.34E-03	4.87E-04	1.13E-01
F	3.06E-04	3.49E-04	2.86E-02	3.91E-04	3.14E-04	4.69E-04	1.00E-16
Cl	3.31E-03	2.14E-01	1.21E-01	3.28E-03	3.31E-03	3.40E-03	5.24E-02
N	1.00E-16	2.14E-02	1.77E-02	1.00E-16	1.00E-16	1.00E-16	6.10E-02
S	1.20E-03	7.75E-02	6.02E-02	1.25E-03	1.20E-03	1.85E-03	3.80E-02
Al	6.64E-10	3.22E-09	1.00E-16	3.32E-07	6.27E-08	1.90E-06	5.34E-06
B	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16
Ba	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16
Cr	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16
Cs	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16
Cu	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16
Fe	2.00E-12	6.85E-14	1.00E-16	1.27E-11	1.44E-12	4.49E-11	1.00E-16
Gd	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16
P	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16
Mn	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16
Mo	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16
Ni	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16
Co	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16
Np	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16
Pu	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16
Ru	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16
Tc	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16
Ti	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16
U	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16
Zn	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16
Zr	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16	1.00E-16

Sources: From EQ3NR pickup files (*.3p) in Attachment I.

NOTES: A trace amount (1.00E-16 molal) is added for all elements in the WP, for numerical stability in EQ3/6 runs.
 "Switched" chemical species to that recognized by EQ3NR and EQ6

Figure 1: Incoming Water Compositions

4.1.1.3 Suppressed Minerals

The following minerals were suppressed (not allowed to form) in all EQ6 runs:

Quartz	Tridymite	CaZrO ₃	Muscovite	Celadonite
Dolomite	Dolomite-dis	Dolomite-ord	Annite	Phlogopite

The micas (muscovite, annite, celadonite and phlogopite) quartz and tridymite are high temperature (>500°C) minerals (Roberts et al.) so not expected to form in the WP. Celadonite can form at low temperatures, but this is due to either diagenesis of pre-existing material, very low grade metamorphic processes, or concentration of the liquid environment through evaporation (Li et al., 1997a and Li et al., 1997b), so it is not expected to form in a flooded WP.

Dolomite is usually derived by secondary mineralization; since it rarely occurs as a primary mineral, it was also suppressed. (Klein and Hurlbut, 1999).

For the second stage of the cases with limited O₂ and CO₂, the following minerals were suppressed because they are not expected to form under repository conditions of low temperature and pressure: Laurite, Chalcocite, Polydymite, Heazlewoodite, Magnesiochromite, Chromite, Linnaeite, Bornite, Chalcopyrite, Troilite, Ilmenite, Nickel, and Pyrrhotite (Roberts et al. 1990). Technetium and molybdenum were suppressed because they do not occur in native form (Weast and Astle 1979, p. B-22, B-14). Copper was suppressed because it occurs mainly with lava, where deposition results from reaction of hydrothermal solutions with iron oxide (Klein and Hurlbut 1985, p. 260). U₃S₅ was suppressed and uraninite was allowed to form in its place since uraninite has been observed in low-temperature uranium deposits that form in reducing zones (Langmuir 1997, Section 13.3.1).

4.1.1.4 Thermodynamic Database

The thermodynamic database used for the EQ6 calculations was the "data0.ymf" file used at 25°C, which is the qualified database ("data0.ymf.R0" DTN: MO0009THERMODYN.001, see Assumption 5.3 b) with the following changes:

- Several Cr- and Fe-bearing minerals and an aqueous species [Cr-ettringite (Ca₆Al₂(CrO₄)₃(OH)₁₂·26H₂O), Cr-ferrihydrite (Fe₄(CrO₄)(OH)₁₀), CaCrO₄^{aq}, and Fe₂(MoO₄)₃] were added for a more complete database. The logK values were calculated in BSC 2001i (p. 15) and Perkins and Palmer 1999 (pp. 1203-1218). Although unqualified, the data for the minerals 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.
- GdOHCO₃ solubility was added to the database. The logK was assumed to be the same as the logK for NdOHCO₃ in the data0.ymf.R0 since Gd and Nd are both lanthanides and chemically similar. See Assumption 5.3 d.

- The logK of GdHPO_4^+ was found to be incorrect in the database and changed from the value of 185 to -5.7 to match the value given in Spahiu and Bruno 1995 (p. 39), which is the source listed in the database for that reaction.
- Molar volumes of the minerals in Table 14 were added to the database in order to calculate the density of the degradation products that are formed during the calculations.
- The CSNF fuel (composition given in Table 9) was added to the database in order to take advantage of EQ3/6's ability to use a pH-dependent and carbonate-dependent rate law, using the EQ6 transition state theory (TST) formalism to describe the degradation. Only reactants entered as "minerals" (solids contained in the database) can specify a range of degradation rates based on pH; "special reactants" (reactants not contained in the database) must have a fixed degradation rate.

The R2 database (DTN: MO0204SPATHDYN.000) was used for special sensitivity runs to see the impact of using this new database. This database is not yet qualified, and the output of these sensitivities was not carried forth and used in the model. This data0 file was named "data0.yms", and was modified to include the CSNF fuel.

The database used for the EQ6 calculations with limited O_2 and CO_2 ("data0.ymg") was adapted from "data0.ymf" with the following changes:

- Added fictitious minerals Buffer_O2, Buffer_CO2, Buffer_N2, Buffer_H2, and Buffer_CH4. These additions prevent an unnatural build up of gases in the waste package. EQ6 does not allow gases to be released from the WP, which would happen under repository conditions. The gases would diffuse away from the WP as they accumulated.
- Removed molar volumes for the following solids: CaUO_4 , Cr-ettringite, $\text{Cu}_3(\text{PO}_4)_2$, GdOHCO_3 , KNpO_2CO_3 , $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$, $\text{Ni}_3(\text{PO}_4)_2$, $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$. The values of molar volume were originally added to "data0.ymf" to more accurately estimate the volume of the solids produced in the WP (Assumption 5.3 c). However, a qualified source is not available in the Technical Information Center to corroborate the values.

4.1.1.5 Densities and Molecular Weights of Solids

EQ6 calculates the total volume of minerals using the molar volume values (VOPrTr) from the EQ3/6 data0 file (included in the electronic media, Attachment I). The mineral volumes are used to calculate the density of the sludge (degraded WP components) for Section 6 of this report. For many solids in the EQ6 database, the molar volumes are not available and are flagged with fictitious molar volumes of "500." Version 7.2bLV of EQ6 ignores these minerals when calculating volume, so several molar volumes for commonly forming minerals were added to the database and are shown in Table 14.

Table 14. Densities, Molecular Weights and Molar Volumes of Precipitated Solids

Solid	Molecular Weight (g/mole) ^a	Calculated Molar Volume (cm ³ /mole) ^b	Density (g/cm ³)	Reference
Anatase (TiO ₂)	79.866	20.450	3.905	Roberts et al. 1990, pp. 26
Berlinite (AlPO ₄)	121.953	46.2	2.64	Roberts et al. 1990, pp. 83
CaUO ₄	342.105	45.87	7.459	see Assumption 5.3 c
Cr-ettringite (Ca ₆ Al ₂ (CrO ₄) ₃ (OH) ₁₂ ·26H ₂ O)	1314.888	726.900	1.809	Perkins 1999
Cr-ferrihydrite (Fe ₄ (CrO ₄)(OH) ₁₀)	509.444	129.000	3.96	Towe & Bradley 1967 (p. 386)
Cu ₃ (PO ₄) ₂	380.581	84.520	4.503	see Assumption 5.3 c
Fe ₂ (MoO ₄) ₃	508.173	131.850	3.85	Johnson et al. 1992
Fluorapatite [Ca ₅ (PO ₄) ₃ F]	504.302	160	3.2	Roberts et al. 1990, pp. 289
GdOHCO ₃	234.266	737	0.318	see Assumption 5.3 c
Hydroxylapatite [Ca ₅ (PO ₄) ₃ OH]	502.311	163	3.08	Roberts et al. 1990, pp. 389
KNpO ₂ CO ₃	368.106	68.160	5.401	see Assumption 5.3 c
Mesolite Na _{0.676} Ca _{0.657} Al _{1.99} Si _{3.01} O ₁₀ ·2.647H ₂ O	387.783	171.7	2.259	Roberts et al. 1990, pp. 547
Na ₄ UO ₂ (CO ₃) ₃	542.013	149.3	3.63	see Assumption 5.3 c
Ni ₃ (PO ₄) ₂	366.023	83.26	4.396	see Assumption 5.3 c
NpO ₂	268.999	24.220	11.11	Weast and Astle 1979 (p. B101)
PuO ₂	275.999	23.830	11.581	Donnay and Ondik 1973 (p.C-103)
α-Uranophane [Ca(UO ₂ SiO ₃ OH) ₂ ·5H ₂ O]	856.392	224	3.83	Roberts et al. 1990, pp. 903
(UO ₂) ₃ (PO ₄) ₂ ·6H ₂ O	1108.118	320	3.5	see Assumption 5.3 c
Zn ₂ SiO ₄ (Willemite)	222.863	55.200	4.04	Roberts et al. 1990, pp. 946

Source: ^a DTN: MO0009THRMODYN.001.

NOTES: ^b Calculated from the molecular weight and density.

Values for Molecular Weights may differ from those cited in the references for Calculated Density, but the difference is less than 1% and is not expected to affect the results of this calculation.

4.1.1.6 Atomic Weights

Atomic weights were taken from Audi and Wapstra 1995 and Parrington et al. 1996 (Chart of the Nuclides) and are listed in the "Molecular Weights" sheet of the "CSNF WP Model Abstraction.xls" (Attachment I).

4.1.1.7 EQ6 Scenarios Considered

The rationale for selection of scenarios in EQ6 simulations is to provide conservative criticality assessments of solubility and transport of fissile materials (i.e., U and Pu compounds) and neutron absorbers (B and Gd) in the WP. An internal criticality event is possible if fissile material remains behind in the WP while neutron absorbers are flushed out.

The internal degradation configurations are based on the premise that water drips onto the upper surface of the WP and penetrates it. The EQ6 model simulation begins when the outer barrier is breached, and water enters the WP. Water then accumulates inside the WP, dissolving and then flushing the dissolved material from the WP (Assumption 5.2 d). The model is no longer valid when the volume of the total solids, undegraded material plus the precipitated solids, exceeds two thirds of the total volume. At this point, the water only makes up one third of the total

volume, which no longer allows for thorough mixing (Assumption 5.2 f). It is assumed that precipitated solids remain in place and form the most insoluble solids for fissile radionuclides, since this assumption gives the maximum U and Pu retention in the WP (Assumption 5.2 g). The chromium and molybdenum oxidize fully to chromate (or dichromate) and molybdate, respectively because the oxidation lowers the pH, which increases the removal of neutron absorbers (Assumption 5.2 h).

The following parameters were varied in the matrix of runs: degradation rates for the steels and Al-6061, the percent exposure of the fuel, and the drip rate of the incoming water (J-13 or various pore waters). The fuel was exposed at 100%, 10% and 1% (by multiplying the surface area in the input file by 1X, 0.1X and 0.01X).

Pore Water Sensitivity

Seven pore water compositions were selected (Table 11) as the incoming water composition. These waters simulate a variety of environments that the WP could see over geologic time.

Radiolysis Sensitivity

A sensitivity study was performed to observe the results of the release of nitric acid by a sustained criticality. A volume of nitric acid was added to the input file with a release rate that would coincide with the amount of nitric acid produced during a sustained criticality (from BSC 2001e, Table 6.1). To be conservative, the study also looked at cases 5 and 100 times that rate (5 and 100 times the amount of acid produced and released at 5 and 100 times as fast). The rates were converted from moles per year per kW per package to moles per second in the "Rates" worksheet of "CSNF WP Model Abstraction.xls" (Attachment I).

LogK Sensitivity

The logK values for the minerals in the thermodynamic database determine which minerals will form. For that reason, a sensitivity of the logK values for the uranium minerals that have formed in CSNF WP runs, were modified by $\pm 10\%$ to see the results.

Database Sensitivity

A new thermodynamic database, "data0.ymp.R2" (DTN: MO0204SPATHDYN.000), was recently completed, and this sensitivity looks to see the effects of any of the updates to the database. The most significant changes in the R2 database are listed in Table 15.

Table 15: Updates to data0.ymp.R2 Thermodynamic Database

Updates to the data0.ymp.R2 Thermodynamic Database
1. Addition of recent data for Np and Pu species published by the NEA
2. Calculation of equilibrium constants for temperatures above 25°C
3. Addition of several uranium silicate minerals
4. Addition of mineral phases associated with cement
5. Addition of organic species
6. Change in basis for silicate species
7. Addition of additional minerals and aqueous species of interest
8. Correction of errors noted in previous version
9. Folded in the Zeolites DTN: MO0204THDYNZEO.000.
10. Folded in the Clays DTN: MO0205THDYNCLY.000.

Limiting O₂ and CO₂ Sensitivity

In most previous EQ6 calculations, it has been assumed that the liquid inside the WP is well mixed by convection, and the fugacities of O₂ and CO₂ are thus sustained by communication with the atmosphere external to the WP. An oxidizing condition in the WP may not be realistic when considering the large amount of corrosion products from steels and the fuel that will accumulate and limit the mixing of water. The corrosion products would likely collect around degrading materials in the WP and oxygen would be limited by diffusion. To test the effects of limited O₂ and CO₂ on the chemistry of the WP solution, a series of two-stage runs were performed.

In the first stage, the fugacities of O₂ and CO₂ were controlled at 0.2 and 10⁻³ atm, respectively, and the WP degraded under oxidizing conditions. During the first stage the WP was allowed to fill from an initial volume of 1/10th full to completely full of water. To simulate starting with the WP 1/10th full, the moles of each element in the EQ3NR pickup file were divided by 10 and the logarithmic basis variables were reduced by one log unit. To fill the WP, the incoming water was set as a "special" reactant. The drip rate was set to 0.015 m³/year (medium rate) and the ending time for the run was calculated (~300 years) so that the WP would be full at the end of the run. At the end of the first stage, all of the A516 had degraded and the WP was fully flooded.

For the first stage, EQ6 was run twice, with the name ending in "a" and "b", for example, c30x112a and c30x112b. In the "a" run, the EQ6 input file started with 200 moles of O₂. At the end of the run, the moles of O₂ consumed during the run was read from the *.60 output file (about 18 moles for most runs). Next, for the "b" run, the initial moles of O₂ were set equal to the moles of O₂ consumed in the "a" run. This ensured that extra O₂ would not be available to interfere with the diffusion-controlled conditions desired for the second stage.

In the second stage, the rate of O₂ entering the WP was controlled by diffusion, assuming a diffusive layer of corrosion products. Table 16 provides the values used to calculate the depth of corrosion products in the waste package after the first stage. The upper limit of the depth was calculated assuming (1) the corrosion products occur in a single layer at the center of the WP and (2) have a porosity of 40%. The calculated value of 44 cm is an upper limit since the corrosion

products would actually be spread throughout the WP. As a lower estimate of the depth of corrosion products, the volume of sludge was divided by the surface area of the A516 carbon steel in the WP. The surface area of A516 was used because it forms the majority of the corrosion products at the beginning of the second stage. The lower limit was calculated to be 1.2 cm. As a best estimate depth, a value of 10 cm was used in the calculations since it is between the upper and lower limit values, but on the low side such that the diffusion limitation would not be too severe. The diffusion rate of oxygen through the 10 cm layer was calculated using Fick's law of diffusion as shown in Table 17.

Table 16. Calculation of Depth of Corrosion Products

Parameter	Formula	Value
v , Normalized volume of minerals at the end of stage 1 at ~300 years after breach (cm^3)		364 (low volume, case c30x112b) ^a 564 (high volume; case c30x332b) ^a
f , Normalization factor		4685 ^b
V , Total volume minerals (using low volume to minimize depth) (cm^3)	$V = v \times f$	1.705E+06
ϕ , Porosity		40% ^c
W , corrosion product volume (cm^3)	$W = V \div (1 - \phi)$	2.842E+06
D_i , Inner diameter of WP shell (cm)		142.4 ^d
L , length of shell (cm)		458.5 ^e
A , area of WP cross-section (cm^2)	$A = D_i \times L$	65,290
A_s , normalized area of A516 steel in WP (cm^2) (379 + 131 from Table 5)		510
d_L , sludge depth, lower limit (cm)	$d_L = W \div (A_s \times f)$	1.2
d_U , sludge depth, upper limit (cm)	$d_U = W \div A$	44
d_b , sludge depth, best estimate (cm)		10

Source: ^a Files c30x112b.min_info.txt and c30x332b.min_info.txt, Attachment I

^b File CSNF WP Model Abstraction.xls, worksheet "Volumes and Surface Areas", Attachment I

^c Lowest value in range for clay (40-70%) in Freeze and Cherry 1979, Table 2.4, p. 37

^d SK-0219 Rev 02, Sheet 19 of 25, Attachment III, BSC 2002a

^e SK-0219 Rev 02, Sheet 7 of 25, Attachment III, BSC 2002a

Table 17. Calculation of Oxygen Diffusion Rate Through Sludge

Parameter	Formula	Value
D , Diffusion coefficient of oxygen in water (cm^2/s)		$2.5\text{E-}05^a$
ω , an empirical coefficient that takes into account the effect of the solid phase of the porous medium on the diffusion		0.5^b
D^* , apparent diffusion coefficient (cm^2/s)	$D^* = \omega \times D$	$1.25\text{E-}5^c$
ΔC , change of oxygen concentration across the diffusive barrier; assumed to be equal to the oxygen in J-13 water minus zero (mole O_2/cm^3 water)		$1.75\text{E-}7^d$
Δx , depth of diffusive barrier (cm) (same as sludge depth, d_b , from Table 16)		10
F , Fick's law of diffusive flux ($\text{mol}/\text{cm}^2\cdot\text{s}$)	$F = D^* \times \Delta C / \Delta x$	$2.187\text{E-}13^e$
C_n , normalized cross-sectional area (cm^2)	$C_n = A \div f$	13.94
R , rate of oxygen diffusion through diffusive barrier (mol/s)	$R = C_n \times F$	$3.05\text{E-}12$

Source: ^aTable 3-300, "Diffusivities in Liquids (25°C)", Perry and Chilton 1973

^bp. 104, Freeze and Cherry 1979

^cEquation from p. 104, Freeze and Cherry 1979

^dCalculated from $5.6\text{E-}6$ g O_2/g water (p. 4.9, Harrar et al. 1990), Assumption 5.1a; divided by molecular weight of O_2 (31.998), Parrington et al. 1996, p. 63

^eEquation from p. 103, Freeze and Cherry, 1979

The input file for the second stage used the pickup file from the "b" run. The following block of text was added to the second stage input file.

```

|-----|
| REACTANT      | O2_Water_diff      | status | 0 |
| moles remaining | 1000.00             | destroyed | 0.00000 |
| reactant type  | special             | sk      | 1.0 |
| surface type   | 0                   | fk      | 0.0 |
| end-member     |                      | moles   |      |
| volume         |                      |         |      |
| element        | 0                   | moles   | 2.000000 |
| DISSOLUTION LAW | 3                   |         |      |
| rate constant rk1 | 3.05E-12           | csigma1 |      |
| TEMPERATURE (C) | 25.0                |         |      |
| PRECIPITATION LAW | 0                   |         |      |
|-----|
    
```

Adding the block causes oxygen to be supplied to the system at the rate calculated in Table 17 (rate constant $\text{rk1}=3.05\text{E-}12$ mol/sec). In the input file, the fixed fugacity for O_2 was retained (rather than commenting out); with the number of moles equal to 0. This was required to get the second stage to run properly. If the fixed fugacity for O_2 is commented out, then EQ6 will recalculate the totals of all elements at the beginning of the second stage, and the quantities of some elements (such as U) will be reduced from what they should be. In other words, the total mass of material will not be transferred to the second stage. With the fixed fugacity for O_2 still in place, EQ6 will continue with no loss of any elements.

In the second stage, the CO_2 was controlled by the dissolved carbonate in the in-dripping, J-13-like water. This was achieved by removing (commenting out) the fixed fugacity for CO_2 in the

input file and reducing the “fix CO₂ (g)” to an insignificant level (<1 mole). Other changes to the input file are listed in the “NOTES” section at the top of each input file (*.6i).

4.1.1.8 Nomenclature

The EQ6 input filenames are eight characters with the extension “.6i”. Each EQ6 run has associated output tab-delimited text files. The filenames are explained in Table 18. The first character “c” indicates CSNF in all runs. These files are included in Attachment I.

Table 18: File Nomenclature

Base Case	Sample Filename: c30_331a			
	30	" "	331	a = 1 st run b = 2 nd run
	Fugacity = 10 ^{-3.0}	Divider	Rates	Continuation
Pore Water	Sample Filename: c331_g1a			
	331	" "	(g1-g7)	a = 1 st run b = 2 nd run
	Rates	Divider	Grout Pore Water	Continuation
Radiolysis	Sample Filename: cn_a_111			
	n	" "	n = rate from 2001e (Table 6.1)	
			a = 5 times n rate	
			c = 100 times n rate	
	Nitric Acid Sensitivity	Divider	Nitric Acid Release Rate	
Database	Sample Filename: c30d333a			
	30	d	333	a = 1 st run b = 2 nd run
	Fugacity = 10 ^{-3.0}	database sensitivity	Rates	Continuation
LogK	Sample Filename: c30_331_1			
	See Section 4.1.2.4.			
O ₂ and CO ₂ Limiting Case	Sample Filename: c30x331			
	30x = 1 st run, Fugacity = 10 ^{-3.0} 30y = 2 nd run, Fugacity = variable			331
	Continuation			Rates

Rates: The three numerical characters in a row refer to the degradation rates for the neutronit / 316NG, the exposure of the fuel, and the drip rates from Table 5.

Example: c331_g1a.6i

Steel	Fuel	Drip
1. low	1. 1% exposed	<u>1. low</u>
2. medium	2. 10% exposed	2. medium
<u>3. high</u>	<u>3. 100% exposed</u>	3. high

Continuation Character: If the EQ6 run needs to be restarted to converge, the subsequent runs are named with an “b” or “y”.

4.1.2 EQ6 Outputs

Several sensitivity studies were run on the CSNF to see their impact on uranium retention. Three cases: one "base case" and two of the more interesting sensitivity studies, were selected for the abstraction. These three cases were "matrixed", and run many times varying the neutronit / 316NG degradation rate, fuel exposure, and drip rate. The output files for this section are included in Attachment I.

The data in Section 4.1.2 is included in the following DTNs:

MO0210MWDLOG01.006, MO0210MWDRAD01.007, MO0210MWEXCD01.008, MO0210MWDPWS01.010, MO0210MWDBAS01.011, MO0210MWDCO201.012, MO0210MWDDBS01.013, MO0210MWDPWG01.014.

4.1.2.1 Base Case

The base case uses the default J-13 incoming water (see Table 10) and uses the model discussed in the Material Degradation and Release Model (BSC 2001a). The matrix of runs is a combination of different rates for reactants from Table 5. The results of these runs are presented in Table 19.

Table 19: Base Case Matrix: Percent Remaining

EQ6 Run	Years	pH	Vol Solids (cc)	Intact Fuel (moles)	B (%)	Gd (%)	Np (%)	Pu (%)	Ru (%)	Tc (%)	U (%)
c30_111	49,529	5.67	1,024	13.73	6.71	83.00	98.91	99.86	100.00	61.94	99.99
c30_112	50,710	6.22	982	15.63	0.02	89.32	95.80	99.44	100.00	67.82	99.96
c30_121	6,776	5.69	1,114	9.47	91.97	93.62	99.75	99.93	100.00	63.20	100.00
c30_122	6,384	6.02	1,035	12.61	87.79	95.38	98.58	99.54	100.00	56.52	99.98
c30_131	394	5.64	1,003	12.09	99.95	99.35	99.96	99.99	100.00	96.50	100.00
c30_132	409	5.79	1,000	12.21	99.64	96.33	99.65	99.92	100.00	75.43	100.00
c30_211	28,481	5.47	1,015	16.73	0.02	99.98	98.96	99.88	100.00	75.35	100.00
c30_212	35,096	5.84	1,021	17.24	0.00	99.99	95.18	99.61	100.00	74.85	99.99
c30_222	4,973	5.67	1,021	13.88	6.31	83.66	98.97	99.91	100.00	62.58	100.00
c30_231	785	5.53	1,157	7.70	98.19	98.15	99.98	100.00	100.00	92.26	100.00
c30_232	725	5.69	1,109	9.69	91.11	93.36	99.85	99.99	100.00	64.02	100.00
c30_302	50,728	7.22	936	23.10	0.00	100.00	100.00	100.00	100.00	100.00	100.00
c30_311	19,576	5.33	1,018	18.29	0.27	99.96	99.12	99.88	100.00	82.44	100.00
c30_331	537	5.46	1,013	13.08	98.28	98.95	99.99	100.00	100.00	96.80	100.00

Source: These values were calculated in "Base Case elem_tot.xls" included in Attachment I.

NOTES: The values in this table differ slightly from those in Table 11 of BSC 2002a because the input values in Table 5 of this model have changed slightly due to the additional volume of A516.

4.1.2.2 Pore Water Sensitivity

The pore water sensitivity uses various pore waters from Table 13 as input and uses the model discussed in the Material Degradation and Release Model (BSC 2001a). Seven different pore waters were selected, and they were each run with a low rate case, and with a high rate case. The results of these runs are presented in Table 20.

Table 20: Pore Water Percent Remaining

EQ6 Run	Years	pH	Vol Solids(cc)	Intact Fuel (moles)	B (%)	Gd (%)	Np (%)	Pu (%)	Ru (%)	Tc (%)	U (%)
c111_g1a	50,141	5.70	1,025	13.90	7.96	83.70	98.99	99.86	100.00	62.59	99.99
c111_g2a	50,524	5.79	1,027	14.07	7.21	84.56	99.18	99.92	100.00	63.33	100.00
c111_g3a	26,540	5.81	1,163	3.33	54.18	100.00	99.65	99.71	100.00	25.43	100.00
c111_g4a	41,402	5.96	1,121	9.98	25.08	84.17	99.44	99.87	100.00	47.45	100.00
c111_g5a	49,665	5.76	1,028	13.68	8.90	82.81	99.08	99.85	100.00	61.74	99.99
c111_g6a	32,504	5.86	1,118	6.00	42.50	63.85	99.37	99.81	100.00	32.86	100.00
c111_g7a	93,515	7.26	1,028	14.59	0.00	99.53	99.85	99.98	100.00	64.23	99.99
c111_g7c	171,150	10.95	1,044	12.53	0.00	92.08	99.82	97.88	100.00	55.00	99.87
c331_g1a	645	5.46	1,067	11.08	97.59	98.10	99.99	100.00	100.00	95.41	100.00
c331_g1c	759	5.42	1,127	8.65	96.70	96.83	99.98	100.00	100.00	93.58	100.00
c331_g2a	548	5.54	1,018	13.05	98.24	98.80	99.99	100.00	100.00	96.72	100.00
c331_g2c	556	5.54	1,024	12.82	98.19	98.72	99.99	100.00	100.00	96.60	100.00
c331_g3a	237	5.87	1,081	7.14	99.66	99.59	100.00	100.00	100.00	97.60	100.00
c331_g4a	457	6.08	1,069	11.55	98.76	99.93	100.00	100.00	100.00	96.75	100.00
c331_g5a	739	5.47	1,135	8.59	96.87	97.55	99.98	100.00	100.00	93.70	100.00
c331_g6a	353	5.74	1,094	6.29	99.26	99.38	100.00	100.00	100.00	96.37	100.00
c331_g7a	817	5.44	1,117	9.18	96.20	97.07	99.98	100.00	100.00	93.73	100.00

Source: These values were calculated in "PW elem_tot.xls" included in Attachment I.

Table 20 shows that for these cases, the pore water did not affect the uranium loss from the WP. Several of the pore waters (g_3, g_4, and g_6) are at temperatures higher than 25°C. Though much of the data in the thermodynamic database (data0.ymf, Section 4.1.1.4) is for 25°C, the most abundant U minerals formed in the runs at elevated temperatures (schoepite, $\text{UO}_2(\text{OH})_2$ beta, $\text{Na}_2\text{U}_2\text{O}_7$) have data up to 100°C in the database. The "g6" pore water shows the fastest degradation of the fuel, due to its high temperature of 73°C, but the U loss is not affected because the U from the fuel forms minerals and remains in the WP. The grout water "g7" from the sensitivity runs was selected to be matrixed for the model abstraction due to its extreme pH values (incoming pH is 11). The "g7" case uses the "g7" incoming water (see Table 13) and uses the model discussed in the Material Degradation and Release Model (BSC 2001a). The

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matrix of runs is a combination of different rates for reactants from Table 5. The results of these runs are present in Table 21, and some runs show appreciable loss of uranium.

Table 21: "g7" Pore Water Matrix Percent Remaining

EQ6 Run	Years	pH	Vol Solids (cc)	Intact Fuel (moles)	B (%)	Gd (%)	Np (%)	Pu (%)	Ru (%)	Tc (%)	U (%)
c111_g7	93,515	7.26	1,028	14.59	0.00	99.53	99.85	99.98	100.00	64.23	99.99
c112_g7	51,070	9.48	755	18.74	0.61	99.78	98.02	81.25	100.00	81.25	81.25
c121_g7	12,494	6.64	1,067	12.04	81.57	99.97	99.99	100.00	100.00	64.92	99.99
	51,070	6.56	1,429	0.00	6.14	99.45	99.88	99.99	100.00	0.00	99.99
c122_g7	31,590	8.44	1,058	0.00	38.76	99.99	99.95	97.77	100.00	1.00	68.34
	51,070	8.47	899	0.00	0.61	99.98	99.91	93.75	100.00	0.00	22.87
c131_g7	1,647	7.19	1,104	10.08	99.29	100.00	100.00	100.00	100.00	87.70	99.99
	51,070	6.56	1,427	0.00	6.14	99.41	99.88	99.99	100.00	0.00	99.99
c132_g7	1,516	7.38	1,047	11.42	97.64	100.00	99.99	99.97	100.00	59.84	99.95
	51,070	8.47	886	0.00	0.61	99.97	99.88	93.07	100.00	0.00	21.62
c211_g7	28,919	5.57	1,039	17.06	0.02	99.97	99.11	99.91	100.00	76.57	100.00
	54,616	5.57	1,250	11.94	0.00	99.96	98.41	99.85	100.00	54.39	99.99
c212_g7	52,185	9.33	938	18.76	0.00	100.00	99.11	81.31	100.00	81.31	81.31
c221_g7	4,512	5.29	1,036	13.71	58.63	94.60	99.87	99.98	100.00	82.47	100.00
	54,616	5.57	1,535	0.00	0.00	30.29	98.44	99.86	100.00	0.00	100.00
c222_g7	9,351	7.26	1,028	14.59	0.00	99.56	99.85	99.99	100.00	64.22	99.99
	51,142	8.44	1,252	0.00	0.00	99.53	99.76	97.40	100.00	0.00	68.45
c231_g7	1,055	5.63	1,154	8.15	96.91	98.55	99.99	100.00	100.00	91.51	100.00
	54,616	5.57	1,535	0.00	0.00	26.77	98.44	99.86	100.00	0.00	100.00
c232_g7	1,250	6.64	1,066	12.04	81.57	99.97	99.98	99.99	100.00	64.91	99.99
	51,142	8.44	1,245	0.00	0.00	99.39	99.74	97.36	100.00	0.00	67.94
c311_g7	19,657	5.36	1,049	18.39	0.26	99.95	99.17	99.90	100.00	82.81	100.00
	46,893	7.44	1,197	13.47	0.00	99.93	98.56	99.84	100.00	60.03	100.00
c312_g7	51,877	9.53	948	18.78	0.00	99.89	98.36	81.40	100.00	81.40	81.40
c321_g7	3,466	5.20	1,021	14.89	51.19	97.72	99.87	99.99	100.00	87.10	100.00
	46,776	7.44	1,522	0.00	0.00	39.79	98.59	99.85	100.00	0.00	100.00
c322_g7	8,232	7.14	1,080	13.95	0.00	98.02	99.53	99.96	100.00	61.50	99.99
	50,693	8.48	1,233	0.00	0.00	97.94	99.34	96.70	100.00	0.00	63.38
c331_g7	817	5.44	1,117	9.18	96.20	97.07	99.98	100.00	100.00	93.73	100.00
	46,738	7.44	1,523	0.00	0.00	31.93	98.59	99.84	100.00	0.00	99.99
c332_g7	850	5.87	1,081	11.35	78.20	94.02	99.93	100.00	100.00	68.43	100.00
	50,693	8.48	1,208	0.00	0.00	54.45	99.38	96.71	100.00	0.00	63.48

Source: These values were calculated in "PW g7elem_tot.xls" included in Attachment I.

NOTE: The results are shown for the time when the volume of solids first reaches 1,000 cm³, and at 50,000 years when the neutronit has fully degraded in the slowest cases.

4.1.2.3 Radiolysis

Nitric acid was added to two cases (a low rate case and a high rate case) to see the effects of simulated radiolysis. The two cases used were c30_111 and c30_332. For each of the two cases, three different amounts of HNO_3 were added to create a total of six cases; see Table 5 for the amounts. For the low rate case (low steel/alloy degradation, fuel, and drip rates), the addition of the nitric acid had very little effect on the minimum pH of the base case (in the first 50,000 years), as shown in Table 22.

Table 22: pH Minimum for Low Rate Radiolysis Cases

Case Name	Minimum pH
c30_111	3.3530
cn_n_111 (1x)	3.3522
cn_a_111 (5x)	3.3497
cn_c_111 (100x)	3.3014

The low pH is sustained for much longer in the cn_c_111 case due to the addition of the HNO_3 as shown in Figure 2.

Figure 2: Radiolysis Effects on CSNF WP, Low Rates

For the high rate case (high steel/alloy degradation, fuel, and drip rates), the addition of the nitric acid had more of an effect on the minimum pH, but the pH for these cases remains safely above 3.5 because of the high drip rate (with an incoming pH of 8.1). The minimum pH values are given in Table 23.

Table 23: pH Minimum for High Rate Radiolysis Cases

Case Name	Minimum pH
c30_332	5.5541
cn_n_332 (1x)	5.5538
cn_a_332 (5x)	5.5528
cn_c_332 (100x)	3.7320

The low pH is sustained for much longer in the cn_c_332 case due to the addition of the HNO_3 as shown in Figure 3.

Figure 3: Radiolysis Effects on CSNF WP, High Rates

4.1.2.4 LogK Sensitivity Study

Equilibrium-thermodynamic based geochemical codes like EQ6 use logKs to access the position of equilibrium for specific chemical reactions at specific conditions. In most cases, the uncertainty for the logK values (or ΔG values used to calculate the logK values) is not reported in the databases. In order to evaluate the effects of logK's uncertainty on precipitation and solubility of the U minerals, the logK values were altered by $\pm 10\%$ for the principal U minerals that form in these EQ6 runs.

Nguyen et al. 1992 measured thermodynamic properties for some of the U minerals (soddyite, uranophane, Na-boltwoodite, and Na-weeksite) and reported uncertainties of much less than 10%. In addition, uncertainty on molar Gibbs energy of formation for schoepite, $(\text{UO}_2)(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$, and CaUO_4 exhibited uncertainties of less than 0.5% (Grenthe et al. 1992, pp. 32, 45, and 47 respectively). As a result, an augmentation of at least $\pm 10\%$ (log scale) was selected for logK values of the major "U" minerals formed (schoepite and $(\text{UO}_2)(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$) in "c30_111a" and "c30_331a" EQ6 runs.

Table 24 and Table 25 summarize the results of logK augmentations for schoepite and $(\text{UO}_2)(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$ on two selected cases. Table 24 is the description of the EQ6 input files and their differences compared to the two selected cases. Table 25 is a list of percent uranium remaining inside the WP. The results are shown at the time of low pH and when total volume of solids exceeds void volume inside the WP.

The results indicate that even large changes in logKs do not result in any appreciable loss of uranium. Therefore, the results of these runs were not used in the model abstraction.

Table 24: Comparison of selected uranium minerals as function of logK

Eq6 input	Description	Min pH	Years	Schoepite (moles)	$(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$ (moles)
		Vol>1 L (mL)			
C30_111a	Original case	3.35	39	0.00	5.65E-03
		1031	51024	3.49	0.00
C30f1119	12% dec. in logK of Schoepite	3.35	39	0.00	5.65E-03
		1028	49650	3.41	0.00
C30f11_0	12% inc. in logK of Schoepite	3.35	39	0.00	5.65E-03
		1077	78074	5.09 ^a	0.00
C30f11_1	10% inc. in logK of $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$	3.35	39	5.09	5.65E-03 ^b
		1027	49733	3.39	0.00
C30f11_2	10% dec. in logK of $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$	3.35	39	0	5.65E-03
		1027	49752	3.39	0.00
C30_333	Original case	5.91	159	7.92E-01	3.34E-03
		1011	627	3.41	0.00
C30f3319	12% dec. in logK of Schoepite	5.91	159	7.92E-01	3.33E-03
		1011	627	3.41	0.00

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Eq6 input	Description	Min pH	Years	Schoepite (moles)	(UO ₂) ₃ (PO ₄) ₂ :6H ₂ O (moles)
		Vol>1 L (mL)			
C30f330	12% inc. in logK of Schoepite	5.91	159	7.91E-01 ^a	3.35E-03
		1043	875	4.80 ^a	0.00
C30f33_1	10% inc. in logK of (UO ₂) ₃ (PO ₄) ₂ :6H ₂ O	5.91	159	7.92E-01	3.34E-03
		1011	627	3.41	0.00
C30f33_2	10% dec. in logK of (UO ₂) ₃ (PO ₄) ₂ :6H ₂ O	5.91	159	7.92E-01	3.34E-03
		1011	627	3.41	0.00

Note: ^a Major U-mineral formed was UO₂(OH)₂ instead of schoepite.

^b The major uranyl phosphate mineral reported in this case is (UO₂)₃(PO₄)₂:4H₂O instead of (UO₂)₃(PO₄)₂:6H₂O

Table 25: % Uranium Retention Inside the WP After LogK Augmentation:

Eq6 input	% U Rentention at Min pH	Years	% U Retention when Volume>1 L	Years
C30_111a	100.0	39.4	100.0	51024
C30f1119	100.0	39.4	100.0	49650
C30f11_0	100.0	39.4	100.0	78074
C30f11_1	100.0	39.4	100.0	49733
C30f11_2	100.0	39.4	100.0	49752
C30_333	100.0	159.2	100.0	626.6
C30f3319	100.0	159.2	100.0	626.6
C30f33_0	100.0	159.0	100.0	875.4
C30f33_1	100.0	159.2	100.0	626.6
C30f33_2	100.0	159.2	100.0	626.6

Figure 4 is the time line for the original case. Major "U" mineral is schoepite, and the minor mineral is (UO₂)₃(PO₄)₂:6H₂O. The pH fluctuates around 5.5 to 6.0 during the first 100,000 years.

Figure 4: Time line for Case c30_111a

Figure 5: Case C30f11_0 , logK value for schoepite (original case c30_111a) increased by 12%

Figure 5 presents the changes caused by increasing logK values for schoepite by 12%. The following reaction is the chemical equation used in the EQ6 database for formation of schoepite:

An increase of 12% altered major precipitated uranium mineral from schoepite to $\text{UO}_2(\text{OH})_2$ (beta). However, Table 25 indicates that 100% of the uranium remained inside the waste package. No other chemical change was observed within the waste package.

Figure 6: Case C30f11_1, logK value for $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$ (original case c30_111a) increased by 10%

Figure 6 is the time line vs. concentration profile produced by increasing the logK value for $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$ by 10%. The following equation is the chemical reaction used in the EQ6 database:

The time line and Table 24 and Table 25 show very little difference in the chemistry of this run compared to the original case, except that $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ is formed instead of $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$.

Figure 7 exhibited a very similar profile to Figure 4. Decreasing logK values of $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$ by 10% caused no chemical change compared to the original case of c30_111a.

Figure 7: Case C30f11_2, logK value for $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$ (original case c30_111a) decreased by 10%

Figure 8: Case c30_333a

Figure 8 is time line profile on concentration changes of case c30_333. In this case, higher rates of neutronit / 316NG and Al-6061 degradation, 100% exposure of fuel to incoming water, and the high drip rate were employed.

Figure 9: Case C30_3319, logK value for schoepite (original case C30_333) decreased by 10%

In Figure 9, a 10% decrease in the logK values of schoepite did not produce any chemical change on “U” minerals.

Figure 10: Case C30f33_1, logK value for $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$ (case C30_333a) increased by 10%

In Figure 10, a 10% increase in logK of $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$ produced similar mineralization as to Figure 6; again $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ mineral was formed instead of $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$.

In summary, changes in logK values for cases c30_111a and c30_333a did not cause a major change in the evolution or mineralization of the waste package.

4.1.2.5 Database Sensitivity

Two cases, c30_111 and c30_333, that use the current database (data0.ymp.R0, hereafter referred to as "R0") were rerun using the new database (data0.ymp.R2, hereafter referred to as "R2"), with case names c30d111 and c30d333. For all the cases, regardless of the database, the major WP corrosion products are the metal oxides, hematite (Fe_2O_3), gibbsite ($\text{Al}(\text{OH})_3$), pyrolusite (MnO_2) and trevorite (NiFe_2O_4) (Figure 11 through Figure 14). The data from these cases is only shown up to the time at which the corrosion products have filled the entire available WP volume (Figure 11 through Figure 14).

The results from using the different databases differ in the type of phyllosilicate mineral that forms as a corrosion product. Using R0 database in case c30_111, the dominant phyllosilicate mineral is Mg-nontronite during the first 14,000 years after WP breach, and then kaolinite is dominant until 100,000 years (Figure 11). For the same case using the R2 database, case

c30d111a, Mg-nontronite is also the dominant phyllosilicate mineral for 100,000 years after WP breach, but Ca-nontronite also forms at about 58,000 years after WP breach (Figure 12). Using R0 database in case c30_333, the dominant phyllosilicate mineral is Mg-nontronite until ~400 years after WP breach, and then kaolinite is dominant until ~1000 years (Figure 13). For the same case using the R2 database, case c30d333, Mg-nontronite is the dominant phyllosilicate mineral until 1,000 years after WP breach (Figure 14). Although it is possible that either the smectite (nontronite) or kaolinite could form as a result of WP degradation, smectite has been observed as a spent fuel degradation product in laboratory tests (Bruton and Shaw 1988, Figure 1). So, the files run with the revised database (c30d111 and c30d333) predict a more realistic mineral assemblage (Figure 12 and Figure 14). The reason for this may be related to the availability of soluble Si. The ratio of Si to Al in nontronite is 2:1 while the Si:Al in kaolinite is 1:1, so kaolinite will form in environments with less available Si.

Only the cases using the R0 database predict that significant amounts of Co_2SiO_4 may form (Figure 11 and Figure 13). Using the R2 database, a different Co mineral is predicted to form, Co-spinel (Co_3O_4) (Figure 12 and Figure 14). The formation of Co-spinel in these cases is caused by the decrease in solubility of this mineral in the R2 database. Since Co_2SiO_4 does not form in cases c30d111 and c30d333, the available Si is apparently sufficient for precipitation of nontronite rather than kaolinite.

Another minor difference between these cases is that rutile (TiO_2 --a mineral that is not expected to form under conditions of low temperature and pressure) which forms using the R0 database (Figure 11) is replaced by the mineral anatase (also TiO_2) when the R2 database is used (Figure 12). There are other minor minerals that form during these cases that are not shown in Figure 11 through Figure 14. Information about all of the minerals which formed during these cases can be found in the text files (c30_111a.min_info.txt, c30d111a.min_info.txt, c30_333a.min_info.txt, c30d333a.min_info.txt, c30d333b.min_info.txt) in Attachment I.

Figure 11: Major minerals predicted to form during EQ6 case C30_111a.

Figure 12: Major minerals predicted to form during EQ6 case C30d111a.

Figure 13: Major minerals predicted to form during EQ6 case C30_333a.

Figure 14: Major minerals predicted to form during EQ6 case C30d333a.

Figure 15 and Figure 16 show the major radionuclide and Gd minerals that form during case c30_111, which uses the R0 database, and case c30d111, which uses the R2 database. Figure 17 and Figure 18 show the minerals that form during cases c30_333 (R0 database) and c30d333 (R2 database). The major radionuclide minerals formed using both databases are nearly identical with the exception of the mineral $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$ which is stable over a slightly different time frame in cases using the R0 database (Figure 15 and Figure 17), compared to cases using the R2 database (Figure 16 and Figure 18). The Gd mineral, GdOHCO_3 , is only included in the R0 database so it is only present in those cases (Figure 15 and Figure 17).

In summary, during the cases run with the R2 database, similar oxide minerals formed as during cases run with the R0 database, but smectite minerals were more dominant in the cases run with the R2 database. Use of the R2 rather than the R0 database had very little effect on the formation of radionuclide minerals or on the pH of the WP solution during these runs.

Figure 15: Major radionuclide and Gd minerals predicted to form during EQ6 case C30_111a.

Figure 16: Major radionuclide and Gd minerals predicted to form during EQ6 case C30d111a.

Figure 17: Major radionuclide and Gd minerals predicted to form during EQ6 case C30_333a.

Figure 18: Major radionuclide and Gd minerals predicted to form during EQ6 case C30d333a.