

## Calculation Cover Sheet

MOL.19990702.0030

Complete only applicable items.

1. QA: L

Page: 1

Of: 51

2. Calculation Title EQ6 Calculations for Chemical Degradation of Enrico Fermi Spent Nuclear Fuel Waste Packages			
3. Document Identifier (including Revision Number) BBA000000-01717-0210-00029 REV 00			4. Total Pages 51
5. Total Attachments 3	6. Attachment Numbers - Number of pages in each I-1, II-1, III-6		
	Print Name	Signature	Date
7. Originator	Kaveh Zarrabi	<i>K. Zarrabi</i>	5-28-1999
8. Checker	Harlan W. Stockman	<i>H. W. Stockman</i>	5-28-1999
9. Lead	Peter Gottlieb	<i>P. Gottlieb</i>	6-1-1999
10. Remarks			
Revision History			
11. Revision No.	12. Description of Revision		
00	Initial Issue		

**CONTENTS**

	Page
1. PURPOSE.....	5
2. METHOD .....	6
3. ASSUMPTIONS.....	7
4. USE OF COMPUTER SOFTWARE AND MODELS.....	12
4.1 EQ3/6 SOFTWARE PACKAGE .....	12
4.2 SOLID-CENTERED FLOW-THROUGH MODE .....	12
4.3 SOFTWARE ROUTINES.....	13
4.4 SOFTWARE APPROVED FOR QA WORK.....	13
5. CALCULATION.....	15
5.1 CALCULATION INPUTS.....	15
5.1.1 WP Materials and Performance Parameters.....	15
5.1.1.1 Physical and Chemical Form of Fermi Fuel WPs .....	15
5.1.1.2 Chemical Composition of J-13 Well Water .....	20
5.1.1.3 Drip Rate of J-13 Well Water into a WP .....	20
5.1.1.4 Densities and Molecular Weights of Solids .....	21
5.1.1.5 Atomic Weights .....	22
5.2 DATA CONVERSION .....	22
5.3 EQ6 Calculations and Scenarios Modeled .....	22
5.3.1 EQ6 Run Conditions and Nomenclature.....	24
5.3.2 Examination of Cases .....	26
6. RESULTS .....	46
6.1 SUMMARY OF THE RESULTS .....	46
6.2 TBV DISCLAIMER.....	47
7. REFERENCES.....	48
8. ATTACHMENTS .....	51

## FIGURES

## Page

Figure 5-2. Case 2 (N06_1113): Effects of Reactants on pH, Aqueous U, and Soddyite, J-13 Well Water Percolation Rate of 0.15 m <sup>3</sup> /year (molal for aqueous U and moles for solids) .....	29
Figure 5-3. Case 4 (N08_1211): Effects of Reactants (Faster Rates of Glass) on pH and Aqueous U and Gd, and Soddyite with J-13 Well Water Percolation Rate of 0.0015 m <sup>3</sup> /year (molal for aqueous U and Gd, and moles for solids).....	30
Figure 5-4. Case 5 (N09_2211): Effects of Reactants (Faster Rates of Degradation for Both Steel and Glass) on pH on Aqueous U and Pu, and Soddyite and PuO <sub>2</sub> with J-13 Well Water Percolation Rate of 0.0015 m <sup>3</sup> /year (molal for aqueous U and Pu, and moles for solids).....	31
Figure 5-5. Case 5 (N09_2211): Effects of pH on Solubility and Losses of U in Aqueous Phase .....	32
Figure 5-6. Case 6 (N10_2111): Effects of Reactant (Faster Rate of Degradation for Steel) on pH and Aqueous U and Gd, and Soddyite with J-13 Well Water Flow Rate of 0.0015 m <sup>3</sup> /year (molal for aqueous U and Gd and moles for solids).....	33
Figure 5-7. Case 7 (N11_1212/N11_B121): Effects of Reactants (Faster Rate of Degradation for Glass) on pH, Aqueous U and soddyite with J-13 Well Water Flow Rate of 0.015 m <sup>3</sup> /year (molal for aqueous U and moles for solids).....	34
Figure 5-8. Case 8 (N12_1212): Effects of Reactants (Faster Rate of Degradation for Both Steels and Glass) on pH and Aqueous U and Gd and Soddyite with J-13 Well Water Percolation Rate of 0.015 m <sup>3</sup> /year (molal for aqueous U and Gd and moles for solids) .....	35
Figure 5-9. Case 9 (N13_2112): Effects of Reactants (Faster Rate of Degradation for Steel ) on pH and Aqueous U and Gd, and Soddyite with J-13 Well Water Percolation Rate of 0.015 m <sup>3</sup> /year (molal for aqueous U and Gd and moles for solids).....	36
Figure 5-10. Case 10, First Stage (N01A2204): pH and Moles of Package Materials (Outside the DOE SNF Canister), J-13 Well Water Percolation Rate: 0.5 m <sup>3</sup> /year.....	37
Figure 5-11. Case 10, First Stage (N01A2204): Major Minerals and pH as Function of Time, J-13 Well Water Percolation Rate of 0.5 m <sup>3</sup> /year.....	38
Figure 5-12. Case 10, Second Stage (N02B1012): pH and Moles of Package Materials (Inside the DOE SNF Canister and Remaining from First Stage) as a Function of Time, J-13 Well Water Percolation Rate of 0.015 m <sup>3</sup> /year (molal for aqueous U and Gd and moles for solids).....	39
Figure 5-13. Case 14, Second Stage (N16B2011): pH and Moles of Package Materials (Inside the DOE SNF Canister and Remaining from First Stage) as Function of Time with J-13 Well Water Percolation Rate of 0.0015 m <sup>3</sup> /year.....	40
Figure 5-14. Case 15, Second Stage (NH2B2012): pH and Moles of Package Materials (Inside the DOE SNF Canister and Remaining from First Stage) and Aqueous U and Soddyite as a Function of Time (Hematite Suppressed), J-13 Well Water Percolation Rate of 0.015 m <sup>3</sup> /year (molal for aqueous U and moles for solids) .....	41
Figure 5-15. Case 16, First Stage (N17A1203): pH, Aqueous U, Soddyite and Moles Package Materials (Outside the DOE SNF Canister) as a Function of Time, J-13 Well Water Percolation Rate of 0.15 m <sup>3</sup> /year (molal for aqueous U and moles for solids) .....	42
Figure 5-16. Case 16, Second Stage (N17B1011): pH, Aqueous U, Soddyite and Moles Package Materials (Inside the DOE SNF Canister and Remaining from First Stage) as a Function of Time, J-13 Well Water Percolation Rate of 0.015 m <sup>3</sup> /year (molal for aqueous U and moles for solids).....	43
Figure 5-17. Case 18, First Stage (N19A2004): pH, Aqueous U, Soddyite and Moles Package Materials (Outside the DOE SNF Canister) as a Function of Time, J-13 Well Water Percolation Rate of 0.5 m <sup>3</sup> /year (molal for aqueous U and moles for solids) .....	44
Figure 5-18. Case 18, Second stage (N19B1011): pH, Aqueous U, Soddyite and Moles Package Materials (Inside the DOE SNF Canister and Remaining from First Stage) as Function of Time, J-13 Well Water Percolation Rate of 0.015 m <sup>3</sup> /year (molal, moles/kg, for ionic species and moles for solids) .....	45

**TABLES**

	<b>Page</b>
Table 5-1. Steel Compositions and Degradation Rates.....	17
Table 5-2. Aluminum Canisters Composition and Degradation Rates .....	17
Table 5-3. HLW Glass Composition and Degradation Rates .....	18
Table 5-4. Fermi Fuel Compositions and Degradation Rates.....	19
Table 5-5. Composition of J-13 Well Water .....	20
Table 5-6. Densities and Molecular Weights of Precipitated Solids .....	21
Table 5-7. Summary of Single Stage EQ6 Cases for Fermi Fuel.....	23
Table 5-8. Summary of Multiple Stage EQ6 Cases for Fermi Fuel.....	23
Table 5-9. Summary of Run Number, Input File, End Time, and U and Gd Losses for All EQ6 Runs.....	26
Table 5-10. Total Concentration Changes for U and Gd in the Aqueous Phase as Function of Time for Case 1 (N5_{A,B,C,D,E,F,G,H}1114).....	27
Table 5-11. Total Concentration Changes for U and Mo as Function of Time for Case 6 (N10_2111) .....	33
Table 5-12. Total Concentration Changes for U and Gd as Function of Time for Case 9 (N13_{A,B}211).....	36
Table 5-13. Total Concentration Changes for U and Gd as Function of Time for Case 13 (N01A2204/N14B2012) .....	39

## 1. PURPOSE

The Monitored Geologic Repository (MGR) Waste Package Operations (WPO) of the Civilian Radioactive Waste Management System Management & Operating Contractor (CRWMS M&O) performed calculations to provide input for disposal of spent nuclear fuel (SNF) from the Enrico Fermi Atomic Power Plant (Ref. 1). The Fermi fuel has been considered for disposal at the potential Yucca Mountain site. Because of the high content of fissile material in the fuel, the waste package (WP) design requires special consideration of the amount and placement of neutron absorbers, and the possible loss of absorbers and fuel materials over geologic time. For some WPs, the corrosion-allowance barrier and the corrosion-resistant material (CRM) may breach (Refs. 2 and 3), allowing the influx of water. Water in the package may moderate neutrons, increasing likelihood of a criticality within the package; and the water may, in time, gradually leach the fissile components and neutron absorbers from the WP, further affecting the neutronics of the system.

This study presents calculations of the long-term geochemical behavior of WPs containing Fermi fuel assemblies, and high-level waste (HLW) glass canisters arranged according to the codisposal concept (Ref. 4). The specific study objectives were to determine:

- 1) the extent to which criticality control material, suggested for this WP design, will remain in the WP after corrosion/dissolution of the initial package configuration (such that it can be effective in preventing criticality),
- 2) the extent to which fissile plutonium and uranium will be carried out of the degraded WP by infiltrating water (such that internal criticality is no longer possible, but the possibility of external criticality may be enhanced), and
- 3) the nominal chemical composition for the criticality evaluations of the WP design, and to suggest the range of parametric variations for additional evaluations.

For this purpose, the chemical compositions (and consequent criticality evaluations) for some of the simulations are modeled for time periods up to 500,000 years. This longer time frame is closer with the one million years time horizon recently recommended by the National Academy of Sciences to the Environmental Protection Agency for performance assessment related to a nuclear repository (Ref. 5). However, it is important to note that after 100,000 years most of the materials of interest (fissile and absorber materials) will have either been removed from the waste package, reached a steady state, or been transmuted.

The calculation included elements with high neutron-absorption cross-sections, notably Gd, as well as the fissile materials. The results of this analysis will be used to ensure that the type and amount of criticality control material used in the WP design will prevent criticality.

## 2. METHOD

The method used for this analysis involves the following steps:

- Use of basic EQ3/6 (software package, Section 4.1) capability for tracing the progress of reactions with evolution of the chemistry, which includes the estimation of the concentrations remaining in solution and the composition of the precipitated solids. (EQ3 is used to determine a starting fluid composition for EQ6 calculations; it does not simulate reaction progress.)
- Evaluation of available data on the range of dissolution rates for the materials involved, to be used as material/species input for each time step.
- Use of "solid-centered flow-through" mode (SCFT) in EQ6; in this mode, an increment of aqueous "feed" solution is added continuously to the WP system, and a like volume of the existing solution is removed, simulating a continuously-stirred tank reactor. This mode is discussed in Section 4.2.
- Determination of fissile material concentrations in solution as a function of time (from the output of EQ6 simulated reaction times up to  $5 \times 10^5$  years).
- Calculation of the amount of fissile material released from the WP as a function of time (fissile loss reduces the chance of criticality within the WP).
- Determination of concentrations of neutron absorbers, such as Gd and B, in solution as a function of time (from the output of EQ6 over times up to or somewhat greater than  $5.0 \times 10^5$  years).
- Calculation of the amount of neutron absorbers retained within the WP as a function of time.
- Composition and amounts of solids (precipitated minerals or corrosion products, and unreacted package materials).

Further detail on the specific methods employed for each step is available in Section 5 of this set of calculations.

### 3. ASSUMPTIONS

All assumptions are for preliminary design; these assumptions will require verification before this analysis can be used to support procurement, fabrication, or construction activities. All assumptions are used throughout Section 5.

- 3.1 It is assumed that an aqueous solution fills all voids within WPs, and that the solutions that drip into the package will have the composition of J-13 well water (as given in Ref. 6; this composition is given in Table 5-5) for  $\sim 5 \times 10^5$  years. The basis for the first part of this assumption is that it provides the maximum degradation rate with the potential for the fastest flushing of the neutron absorber from the WP, and is thereby conservative. The basis for the second part of the assumption is that the groundwater composition is controlled largely by transport through the host rock, over pathways of hundreds of meters, and the host rock composition is not expected to change substantially over  $10^6$  years. For a few thousand years after waste emplacement the composition may differ because of perturbations resulting from reactions with engineered materials and from the thermal pulse. These are not taken into account in this calculation because the corrosion allowance barrier and CRM are not expected to breach until after that perturbed period. Therefore, the early perturbation is not relevant to the calculations reported in this document. See Assumption 3.3.
- 3.2 It is assumed that the density of J-13 well water is  $1.0 \text{ g/cm}^3$ . The basis is that for dilute solutions, the density differs extremely little from that for pure water and that any differences are insignificant in 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 parts per million to molalities.
- 3.3 The assumption that the water entering the waste package can be approximated by the J-13 well water implicitly assumes: (1) that the infiltrating water will have only a minimal contact, if any at all, with undegraded metal in the corrosion allowance barrier, and (2) that any effects of contact with the drift liner will be minimal after a few thousand years. The basis for the first part of this assumption is that the water should move rapidly enough through openings in the waste package barriers that its residence time in the corroded barrier will be too small for significant reaction to occur. Furthermore, the water flowing through the barriers will be in contact with the corrosion products left from the barrier corrosion that created the holes in the first place, but these corrosion products will closely resemble iron oxides and hydroxides in the overlying rock. Consequently, the water should already be close to equilibrium with these compounds and would be unaffected by further contact with them, even if it flowed slowly enough to permit significant reaction. The basis for the second part of this assumption is justified by the following: (1) the drift liner at the top of the drift is expected to collapse with the roof support well before 1000 years, and (2) the water flowing through the concrete liner, dominantly along fractures, will be in contact with the degradation products of the liner which will have come close to equilibrium with the water moving through the rock above

the repository. Interaction of water in the fractures with any undegraded concrete between fractures would be minimal owing to the slow rate of diffusion through the matrix compared to rate of flow through fractures.

- 3.4 It is assumed that water may circulate freely enough in the partially degraded WP that all degraded solid products may react with each other through the aqueous solution medium. The basis for this assumption is that this provides one bound for the extent of chemical interactions within the WP.
- 3.5 It is assumed that the existing database supplied with the EQ3/6 computer package is sufficiently accurate for the purposes of this calculation. The basis for this assumption is that the data have been carefully scrutinized by many experts over the course of several decades and carefully selected by Lawrence Livermore National Laboratory (LLNL) for incorporation into the data base (Refs. 7, 8, 9, and 10). These databases are periodically updated and/or new databases added, such as one including extensive data on the lanthanides (Ref. 11). Every run of either EQ3 or EQ6 documents automatically which database is used. The databases include references internally for the sources of the data. The reader is referred to this documentation, included in the electronic files labeled data0 that accompany this calculation, for details (Ref. 12). Nevertheless, the quality of data needs to be verified in the future.
- 3.6 It is assumed that the calculations can be modeled with the 25 °C thermodynamic database. The basis for this assumption is that the initial breach may occur when the package contents are at temperatures  $\geq 50$  °C (Ref. 13, Figures 3-20 through 3-22), though at times  $> 25,000$  years, the package temperatures are likely to be closer to 25 °C. Since the solubility of  $\text{GdPO}_4$  is retrograde (Ref. 14) (i.e., decreases with increasing temperature), use of the lower-temperature database is likely to be conservative.
- 3.7 In general it is assumed that chromium and molybdenum will oxidize fully to chromate (or dichromate) and molybdate, respectively. This assumption is based on the available thermodynamic data, which indicate that in the presence of air the chromium and molybdenum would both oxidize to the VI valence state. Laboratory observation of the corrosion of Cr and Mo containing steels and alloys, however, indicates that any such oxidation would be extremely slow. In fact, oxidation to the VI state may not occur at a significant rate in respect to the time frame of interest, or there may exist stable  $\text{Cr}^{(\text{III})}$  solids (not present in the EQ3/6 thermodynamic database) that substantially lower aqueous Cr concentration. For the present analyses, the assumption is made that over the times of concern the oxidation will occur. This is conservative for times of several thousand years after WP breach, when the high pH solution from any drift liner effects, has been flushed out of the WP. Extreme acidification of the water will enhance solubility (Ref. 2) and transport of neutron absorber out of the WP thereby separating it preferentially from fissile material.



- 3.8 It is assumed that the CRM (the inner barrier) of the WP will react so slowly with the infiltrating water (and water already in the WP) as to have negligible effect on the chemistry. The basis for this assumption is that the CRM is fabricated from Alloy 22 (see nomenclature in Section 5.1.1), which corrodes very slowly compared (1) to other reactants in the WP and (2) to the rate at which soluble corrosion products will likely be flushed from the package.
- 3.9 It is assumed that gases in the solution in the WP will remain in equilibrium with the ambient atmosphere outside the WP. In other words, it is assumed that there is sufficient contact with the gas phase in the repository to maintain equilibrium with the  $\text{CO}_2$  and  $\text{O}_2$  present, whether or not this be the normal atmosphere in open air or rock gas that seeps out of the adjacent tuff. Under these conditions the partial pressure of  $\text{CO}_2$  exerts important controls on the pH and carbonate concentration in the solution and hence on the solubility of uranium, gadolinium, and other elements. The basis for this assumption is that the measured composition of J-13 well water is not in equilibrium with the partial pressure of  $\text{CO}_2$  in the atmosphere (Ref. 15). By adjusting the average measured composition of the water slightly, well within the standard deviation of the measurements, it is possible to determine a partial pressure of  $\text{CO}_2$  nearly ten times atmospheric (Ref. 15, Table 8; and Ref. 16, p. F-210), with which this water was apparently in equilibrium at depth in the well. This high partial pressure is close to the maximum found by measurement of the rock gas composition (Ref. 15, Table 8). Therefore this high partial pressure was chosen for all of the computer runs used in this analysis. In another EQ6 calculation (Ref. 2) two runs with normal atmospheric  $\text{CO}_2$  levels were used to determine the sensitivity of the calculations to this parameter. The high  $\text{CO}_2$  tends to increase the concentration of free carbonate ion and its complexation with the dissolved  $\text{U}^{(\text{VI})}$ , thereby tending to increase the solubility of U, but this is moderated by the reduction of the pH. There is little overall net effect on actinide solubility for otherwise comparable conditions. The effect on Gd solubility is somewhat more complex; higher  $\text{CO}_2$  pressures decrease pH, thereby increasing the chance that solid  $\text{GdOHCO}_3$  will be dissolved; however, higher  $\text{CO}_2$  pressures also increase the capacity of the system to buffer toward intermediate pH (~7.7).
- 3.10 It is assumed that precipitated solids that are deposited remain in place, and are not mechanically eroded or entrained as colloids in the advected water. The basis for this assumption is that it conservatively maximizes the size of potential deposits of fissile material inside the WP.
- 3.11 It is assumed that the corrosion rates will not be significantly enhanced by microbial induced corrosion. The basis for this assumption is that due to lack of organic nutrients available to them. It is assumed that bacteria act as catalysts, and are not expected to significantly change the types of solid formed in the package.

- 3.12 It is assumed that sufficient decay heat is retained within the WP over times of interest to cause convective circulation and mixing of the water inside the package. The analysis that serves as the basis for this assumption is discussed in Ref. 17.
- 3.13 It is assumed that the reported alkalinity in analyses of J-13 well water corresponds to bicarbonate ( $\text{HCO}_3^-$ ) alkalinity. Contributors to alkalinity in J-13 well water, in addition to bicarbonate, potentially include borate, phosphate, and silicate. However, at pH less than 9 the contribution of silicate will be small, and in any case the concentrations of all three of these components in J-13 well water are small. Fluoride ion will not contribute to a typical measured alkalinity because the titration will not be carried out to a sufficiently low pH for its influence to be detectable. Nitrate will likewise not contribute. The basis for this assumption is the observation that the calculated electrical neutrality, using the assumption, is zero within the analytical uncertainty, as it should be. The same assumption is implicitly made in (Ref. 6, Table 4.1, p. 4.2).
- 3.14 It is assumed that the rate of entry of water into, as well as the rate of egress from, a WP is equal to the rate at which water drips onto the package. The basis for this assumption is that for most of the time frame of interest, i.e., long after the corrosion barriers become largely degraded, it is more reasonable to assume that all or most of the drip will enter the degraded package than to assume that a significant portion will instead be diverted around the remains. Diversion of the water with a consequent lower entry rate has not been modeled by the lower drip rates incorporated into the present calculations.
- 3.15 It is assumed that the most insoluble solids for a fissile radionuclide will form, i.e., equilibrium will be reached. The basis for this assumption is to have a conservative approach for internal criticality because the assumption will lead to simulation for maximal retention of fissile material within the WP.
- 3.16 A number of minor assumptions have been made about the geometry of the Fermi codisposal package. These assumptions are outlined and referenced in the spreadsheet *Fermi\_Fuel\_kz.xls* (Ref. 12), and are also discussed in Section 5.1. The bases for these assumptions are to obtain the greatest accuracy in the representation of the package geometry, and where inadequate information is available to choose among competing geometry models, the choice that appears to lead to greatest conservatism is always chosen.
- 3.17 For any package components that were described as "316" stainless steel, without indication of the carbon grade, the alloy was assumed to be the low-carbon equivalent (see Section 5.1.1 for nomenclature). The basis for this assumption is that, in general, the carbon in the steel is totally insignificant compared to the carbon supplied by the fixed  $\text{CO}_2$  fugacity of the EQ3/6 calculation, and to the constant influx of carbonate via J-13 well water. An underestimation of carbon in steel leads to a slight overestimation of metals in the steel, which increases acid production very slightly and is therefore conservative.

- 3.18 It was assumed that the aluminum alloys would last for about 200 years and an approximate degradation rate was calculated from this assumption. The basis for this assumption is that the corrosion rate under conditions applicable to Yucca Mountain appears not to be well known. However, common experience derived from observations of the durability of aluminum window frames and other widely used aluminum items indicate that aluminum alloys will persist for several decades. On the other hand, corrosion of the aluminum does occur, as evidenced by the buildup of white solid products over such time frames. This suggests that the alloy will corrode entirely in a few centuries. The exact lifetime of the alloy is of only minor importance to the chemical simulation so long as it is modeled as corroding much faster than the stainless steels.
- 3.19 Zr and Zircaloy corrosion kinetics studies (Ref. 18) revealed these materials to be resistant against chemical and biological corrosion. Recent studies on corrosion of Zircaloy clad fuel indicates growth of oxide films for a time span of a million year to be about  $7.6\text{E-}03$  millimeter (0.3 mil). It was assumed that Zr cladding would breach soon after it comes in contact with water. The basis for this assumption is that it is conservative and accounts for any cladding that is damaged during storage, shipping, or packing.

#### 4. USE OF COMPUTER SOFTWARE AND MODELS

This section describes the computer software used to carry out the analysis.

##### 4.1 EQ3/6 SOFTWARE PACKAGE

The EQ3/6 software package originated in the mid-1970s at Northwestern University (Ref. 7). Since 1978 Lawrence Livermore National Laboratory has been responsible for maintenance of EQ3/6. The software has most recently been maintained under the sponsorship of the Civilian Radioactive Waste Management Program of the United States Department of Energy (DOE). The major components of the EQ3/6 package include: EQ3NR, a speciation-solubility code; EQ6, a reaction path code which models water/rock interaction or fluid mixing in either a pure reaction progress mode or a time mode; EQPT, a data file preprocessor; EQLIB, a supporting software library; and several (>5) supporting thermodynamic data files. The software deals with the concepts of the thermodynamic equilibrium, thermodynamic disequilibrium and reaction kinetics. The supporting data files contain both standard state and activity coefficient-related data. Most of the data files support the use of the Davies or B-dot equations for the activity coefficients; two others support the use of Pitzer's equations. The temperature range of the thermodynamic data on the data files varies from 25 °C only for some species to a full range of 0-300 °C for others. EQPT takes a formatted data file (a "data0" file) and writes an unformatted near-equivalent called a data1 file, which is actually the form read by EQ3NR and EQ6. EQ3NR is useful for analyzing groundwater chemistry data, calculating solubility limits and determining whether certain reactions are in states of partial equilibrium or disequilibrium. EQ3NR is also required to initialize an EQ6 calculation.

EQ6 models the consequences of reacting an aqueous solution with a set of reactants, which react irreversibly. It can also model fluid mixing and the consequences of changes in temperature. This code operates both in a pure reaction progress frame and in a time frame. In a time frame calculation, the user specifies rate laws for the progress of the irreversible reactions. Otherwise, only relative rates are specified. EQ3NR and EQ6 use a hybrid Newton-Raphson technique to make thermodynamic calculations. This is supported by a set of algorithms, which create and optimize starting values. EQ6 uses an ordinary differential equation (ODE) integration algorithm to solve rate equations in time mode. The codes in the EQ3/6 package are written in FORTRAN 77 and have been developed to run under the UNIX operating system on computers ranging from workstations to supercomputers. Further information on the codes of the EQ3/6 package is provided (Refs. 7, 8, 9, and 10).

##### 4.2 SOLID-CENTERED FLOW-THROUGH MODE

EQ6 version 7.2b, as distributed by LLNL, does not contain an SCFT mode. To add this mode, it is necessary to change the eq6.for source code, and recompile the source. However, by using a variant of the "special reactant" type built into EQ6, it is possible to add the functionality of

SCFT mode in a very simple and straightforward manner. This mode was added to EQ6 per Software Change Request (SCR) LSCR198, and the Software Qualification Report (SQR) for Media Number 30084-M04-001.

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

This new EQ6 mode acts as a substitute for the allpost/nxtinput method described in Ref. 19 and Ref. 21.

#### 4.3 SOFTWARE ROUTINES

Spreadsheet analyses were performed with Microsoft Excel version 97, installed on a PC. The specific spreadsheets used for calculations reported in this document, are included in the electronic media (Ref. 12). These spreadsheets involve simple formulas for area and volume calculations that allow an independent repetition of the computations using hand calculations.

#### 4.4 SOFTWARE APPROVED FOR QA WORK

The software package, EQ3/6, Version 7.2b, was approved for QA (quality affecting) work by LLNL and is identified as Computer Software Configuration Item (CSCI): UCRL-MA-110662. An installation and test report (Ref. 20) was written and submitted to Software Configuration Management (SCM), and the proper installation was verified, before the runs described in this calculation were made. The implementation of the SCFT mode is covered by Software Change Request (SCR) LSCR198, and the Software Qualification Report (SQR) for Media Number 30084-M04-001. The SCFT addendum was installed on three of the Central Processing Units (CPUs) identified in block 16 of the SCR, and the installation and test reports were filed and returned to SCM before the calculations were run. All the EQ6 runs were performed on a U.S. DOE/YMP system, CPU # 115768, a Dell 200 MHz Pentium and on a Sandia National Laboratory system, CPU # S803293, a Dell 300 MHz Pentium II. In this study EQ3/6 was used to provide the followings:

- 1) a general overview, of the expected, chemical reactions,
- 2) the degradation products from corrosion of the waste forms and canisters, and
- 3) an indication of the minerals, and their amounts, likely to precipitate within the WP.

The programs have not been used outside the range of parameters for which they have been verified. The EQ3/6 calculations reported in this document used version 7.2b of the code, which is appropriate for the application, and were executed on Pentium series (including "Pentium II") personal computers (PCs).

The EQ3/6 package has been verified by its present custodian, Lawrence Livermore National Laboratory. The source codes were obtained from SCM in accordance with the Management & Operating contractor (M&O) QAP-SI.1Q procedure. The code was installed on the Pentium PCs according to an M&O-approved Installation and Test procedure (Ref. 20).

## 5. CALCULATION

The calculations begin with selection of data for compositions, amounts, surface areas, and reaction rates of the various components of Fermi fuel WPs. These quantities are recalculated to the form required for entry into EQ6. For example, weight percentages of elements or component oxides are converted to mole fractions of elements; degradation rates in micrometers/year are converted into moles per square centimeter per second, etc. Spreadsheets (Ref. 12) provide details of these calculations, and the general procedure is also described in detail in Ref. 21. The final part of the input to EQ6 consists of the composition of J-13 well water together with a rate of influx to the WP that corresponds to suitably chosen percolation rates into a drift and drip rate into a WP (Section 5.1.1.3). The EQ6 output provides the results of modeling of the chemical degradation of the WP, or components thereof. Sometimes the degradation of the WP is divided into phases, e.g., degradation of HLW glass before breach and exposure of the fuel assemblies and basket materials to the water. The results include the compositions and amounts of solid products and of substances in solution. Details of the results are presented below.

Existing data were used in the development of the results presented in this section. Therefore, the use of any data from this calculation for input into documents supporting procurement, fabrication, or construction is required to be identified and tracked as TBV (to be verified) in accordance with appropriate procedures.

### 5.1 CALCULATION INPUTS

#### 5.1.1 WP Materials and Performance Parameters

This section provides a brief overview of the physical and chemical characteristics of Fermi fuel WPs, and describes how the package is represented in the EQ6 inputs. The conversion of the package physical description, into parameters suitable for the EQ6 input files, is performed by the spreadsheet `Fermi_Fuel_kz.xls`. Additional details of the description may be found in References 1 and 2 and the references cited therein.

Material nomenclature used throughout this document includes: SB-575 N06022 (hereafter referred to as Alloy 22), SA-240 S31603 (hereafter referred to as 316L), UNS N06625 and SA-240 S30403 (hereafter referred to as 304L), SA-516 (hereafter referred to as A516), and SB-209A96061 (hereafter referred to as Aluminum Alloy).

##### 5.1.1.1 Physical and Chemical Form of Fermi Fuel WPs

It is convenient to consider the Fermi fuel waste package as several structural components, specifically :

- (1) The outer shell, consisting of the corrosion-allowance barrier and the CRM.

- (2) The "outerweb," a carbon steel (A516) structure designed to hold the high-level waste (HLW) glass-pour canisters (GPCs) in place.
- (3) The GPCs (the 304L containers of the solidified HLW glass).
- (4) The DOE standardized SNF canister (sometimes called the "DOE 18-inch canister").
- (5) The fuel assemblies, including the shipping canisters and assemblies exclusive of the fuel pins.
- (6) The individual fuel pins.

The details of each of the above numbered components are in the spreadsheet *Fermi\_Fuel\_kz.xls* (Ref. 12). Table 5-1 provides a summary of the compositions of the principal alloys used in the calculations, along with reasonable maxima and averages for the degradation rates. For a comparable specific surface area, the carbon steel is expected to degrade much more rapidly than the stainless steels (316L and 304L). In addition, the stainless steels contain significant amounts of Cr and Mo, and under the assumption of complete oxidation (Assumption 3.7), should produce more acid, per volume, than the carbon steel. In Table 5-1 and all tables from this document, the number of digits reported does not necessarily reflect the accuracy or precision of the calculation. In most tables, three to four digits after the decimal place have been retained, to prevent round-off errors in subsequent calculations.



Table 5-1. Steel Compositions and Degradation Rates

A516 Carbon Steel			304L Stainless Steel		316L Stainless Steel		A516 with 1 wt% GdPO4	
Element	wt%	Atom Frac.	wt%	Atom Frac.	wt%	Atom Frac.	wt%	Atom Frac.
C	0.30	0.0137513	0.03	0.0013654	0.03	0.00138281	0.279	0.013572
Mn	1.025	0.0102719	2.00	0.0199003	2.0	0.02015474	1.01475	0.010138
P	0.035	0.0006221	0.045	0.0007942	0.045	0.00080434	0.15745	0.002790
S	0.035	0.0006001	0.03	0.0005114	0.03	0.00051796	0.03465	0.000593
Si	0.275	0.0053907	0.75	0.0145978	0.75	0.01478426	0.27225	0.00532
Cr			19.0	0.1997495	17.0	0.18100834		
Ni			10.0	0.0931406	12.0	0.11319770		
Mo					2.5	0.01442649		
N			0.1	0.0039027	0.1	0.00395261		
Fe	98.33	0.9693630	68.045	0.6660384	65.545	0.64977076	97.3467	0.956707
Gd							0.62346	0.002176
O							0.25374	0.008704
Total	100.00	1.0000000	100.00	1.0000000	100.00	1.0000000	100.00	1.00
Molecular Weight (g/mole)	55.055			54.664		55.363		54.886
Density (g/cm <sup>3</sup> )	7.85			7.94		7.98		7.85
Average Rate (μm/year)	35			0.1		0.1		35
Average Rate (moles/cm <sup>2</sup> /s)	1.584E-11			4.611E-14		4.576E-14		1.584E-11
High Rate (μm/year)	1.0E+02			1.0		1.0		1.0E+02
High Rate (moles/cm <sup>2</sup> /s)	4.526E-11			4.611E-13		4.576E-13		4.526E-11
Reference 12, spreadsheet: Fermi_Fuel_kz.xls, sheets "MoleFr,MolWt&Den", and "Rates".								

Table 5-2 provides molar composition and rates of degradation for two types of aluminum alloy canisters used for Fermi SNF.

Table 5-2. Aluminum Canisters Composition and Degradation Rates

Aluminum, Type 3003			Aluminum, Type 6061			Atom Frac.
Element	wt%	Atom Frac.	Element	At. Wt. (g/mole)	wt%	
Si	0.6	0.005831	Si	28.0855	0.6	0.005812
Fe	0.7	0.003421	Fe	55.847	0.7	0.00341
Cu	0.12	0.000515	Cu	63.546	0.275	0.001177
Mn	1.25	0.00621	Mn	54.93805	0.15	0.000743
Zn	0.1	0.000417	Mg	24.305	1	0.011193
Al	97.23	0.983604	Cr	51.9961	0.195	0.00102
Total	100	1	Zn	65.39	0.25	0.00104

## Waste Package Operations

## Calculation

Title: EQ6 Calculations for Chemical Degradation of Enrico Fermi Spent Nuclear Fuel Waste Packages

Document Identifier: BBA000000-01717-0210-00029 REV 00

Page 18 of 51

Mol. Wt. (g/mole)	27.29523		Ti	47.88	0.15	0.000852
Density (g/cm <sup>3</sup> )	2.71		Al	26.98154	96.68	0.974754
Average Rate (moles/cm <sup>2</sup> /s)*	1.1886E-10		Total		100	1
			Mol. Wt. (g/mole)	27.20351		
			Density (g/cm <sup>3</sup> )	2.71		
			Average Rate (moles/cm <sup>2</sup> /s)*	1.1886E-10		
Reference 12 spreadsheets: Fermi_Fuel_kz.xls, sheets "MoleFr,MolWt&Den" and "Rates"						
*Table 5.2.3-2 Ref. 21						

Table 5-3 gives the molar composition of the glass used in the calculations (Ref. 22). The actual glass composition used in the GPCs may vary significantly from these values, since the sources of the glass and melting processes are not currently fixed. For example, compositions proposed for Savannah River glass vary by a factor of ~6 in U<sub>3</sub>O<sub>8</sub> content, from 0.53 to 3.16 wt% (Ref. 23). The silica and alkali contents (Na, Li, and K) of the glass have perhaps the most significant bearing on EQ6 calculations. The amount of silica in the glass strongly controls the amount of clay that forms in the WP, and the silica activity controls the presence of insoluble uranium phases such as soddyite ((UO<sub>2</sub>)<sub>2</sub>SiO<sub>4</sub>·2H<sub>2</sub>O). The alkali content can induce pH to rise in the early stages of the EQ6 run, as glass degrades. The Si and alkali contents in Table 5-3 are typical for proposed DOE glasses (Ref. 22). Rates for glass degradation were taken from Ref. 24 (Figure 6.2-5), and normalized in spreadsheet Fermi\_Fuel\_kz.xls, sheets "A&V glass", "Rates", and "Norm" (Ref. 12). The high rate corresponds approximately to pH 9 at 70 °C, and the low rate to pH 8 at 25 °C.

Table 5-3. HLW Glass Composition and Degradation Rates

Element	Normalized wt%	G-Atoms	Atom Frac.	Element	Normalized wt%	G-Atoms	Atom Frac.
O	44.76964	2.798E+0	5.726E-1	Ni	0.734904	1.252E-2	2.562E-3
U-234	0.000328	1.401E-6	2.867E-7	Pb	0.060961	2.942E-4	6.021E-5
U-235	0.004351	1.851E-5	3.789E-6	Si	21.88782	7.793E-1	1.595E-1
U-236	0.001042	4.412E-6	9.029E-7	Th-232	0.185591	7.997E-4	1.636E-4
U-238	1.866591	7.841E-3	1.605E-3	Ti	0.596761	1.246E-2	2.551E-3
U*		7.864E-3	1.609E-3	Zn	0.064636	9.885E-4	2.023E-4
Pu-238	0.005182	2.177E-5	4.455E-6	B-10	0.591758	5.910E-2	1.209E-2
Pu-239	0.012412	5.192E-5	1.063E-5	B-11	2.61892	2.379E-1	4.868E-2
Pu-240	0.002277	9.487E-6	1.941E-6	B*		2.970E-1	6.077E-2
Pu-241	0.000969	4.018E-6	8.223E-7	Li-6	0.095955	1.595E-2	3.264E-3
PU-242	0.000192	7.919E-7	1.621E-7	Li-7	1.380358	1.967E-1	4.026E-2
Pu*		5.271E-5	1.079E-5	Li*		2.127E-1	4.353E-2
Cs-133	0.040948	3.081E-4	6.305E-5	F	0.031852	1.677E-3	3.431E-4
Cs-135	0.005162	3.826E-5	7.830E-6	Cu	0.15264	2.402E-3	4.916E-4

## Waste Package Operations

## Calculation

Title: EQ6 Calculations for Chemical Degradation of Enrico Fermi Spent Nuclear Fuel Waste Packages

Document Identifier: BBA000000-01717-0210-00029 REV 00

Page 19 of 51

Cs*		3.464E-4	7.088E-5	Fe	7.390665	1.323E-1	2.708E-2
Ba-137	0.112669	8.230E-4	1.684E-4	K	2.988689	7.644E-2	1.564E-2
Al	2.331821	8.642E-2	1.769E-2	Mg	0.824754	3.393E-2	6.944E-3
S	0.129454	4.037E-3	8.262E-4	Mn	1.55765	2.835E-2	5.802E-3
Ca	0.661884	1.651E-2	3.380E-3	Na	8.628352	3.753E-1	7.680E-2
P	0.014059	4.539E-4	9.289E-5	Cl	0.115909	3.269E-3	6.691E-4
Cr	0.082567	1.588E-3	3.250E-4	Ag	0.050282	4.661E-4	9.539E-5
TOTAL					100	4.887E+0	1.000E+0
*Mol. Wt., weight of 1 "mole" of glass      100/4.887=20.4641 g/mol"							
Average and high rates of HLW glass degradation : 5.656E-15 and 1.697E-12 mol/(cm <sup>2</sup> *s)							
*HLW glass elements with more than one isotope were combined							
Reference spreadsheet: Fermi_Fuel_kz.xls, sheets "MoleFr,MolWt&Den" and "Rates".							

Table 5-4 summarizes the assumed characteristics of the Fermi fuel. No fission product inventory was available, so the calculations used the composition of fresh fuel. Use of fresh fuel is conservative, since most fission products have significant neutron absorption cross sections, and the unirradiated fuel has a higher fissile content than partially spent fuel.

Table 5-4. Fermi Fuel Compositions and Degradation Rates

Element	Wt. Fraction	g-Atoms	Atom Fraction	
U	0.8973929	0.003770101	0.77901198	
Mo	0.1026071	0.001069492	0.22098802	
Total	1	0.004839593	1	
Average Molecular Weight (g/mol)				206.6290
Density of Fuel Pellets (g/cm <sup>3</sup> )				17.242
Average Fuel Degradation Rate (mg/m <sup>2</sup> /day)				3.000E-01
Average Fuel Degradation Rate (moles/cm <sup>2</sup> /s)				7.947E-14
Reference 12: spreadsheet: Fermi_Fuel_kz.xls, sheets "MoleFr,MolWt&Den" and "Rates"				

The outer web (Attachment I) is composed of A516 carbon steel, and serves two purposes: it centers and holds in place the DOE SNF canister; and it separates the GPCs and prevents them from transmitting undue stress to the SNF canister in the event of a fall (tip-over) of the entire WP. At the center of the outer web is a thick (3.175 cm) cylindrical support tube, also fabricated of A516. In a breach scenario, the outer web will be exposed to water and corrosion before the rest of the package, and is expected to degrade within a few hundred to a few thousand years. The transformation of steel's iron, the web's most abundant element, into hematite (Fe<sub>2</sub>O<sub>3</sub>) can decrease the void space in the package by ~13%, and the transformation to goethite (FeOOH) can decrease the void space by ~22% (Ref. 2). The differences are due to larger molar volume of goethite compared to hematite (Table 5-6). Thus the void space can be significantly reduced, soon after breach of the package, by the alteration of the outer web.

The DOE SNF canister fits inside the central support tube of the outer web. The canister is composed primarily of 316L, with two internal, thick impact plates of carbon steel (approximated as A516 in the calculations). In order to improve mechanical strength of DOE SNF canister and reduce the probability of fuel exposure to water, iron pellets are included in the DOE SNF canister for preferential corrosion by incoming water after the canister is breached. The primary corrosion products will be either hematite and/or goethite, which possess molar volumes greater than the original pellets. The larger volume of these products could seal and decrease the void volume within DOE SNF canister that is accessible to water. In addition,  $\text{GdPO}_4$  (1%, volume/volume) will be added to the iron shot to decrease chances of internal criticality. The iron shot will be distributed among and inside the 4-inch pipes containing the fuel assemblies.

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

It was assumed that the water composition entering the WP would be the same as for water from well J-13 (Assumptions 3.1 and 3.3). This water has been analyzed repeatedly over a span of at least two decades (Ref. 6). This composition is reproduced in Table 5-5.

Table 5-5. Composition of J-13 Well Water

Component	Units <sup>1</sup>
Na <sup>+</sup>	45.8
K <sup>+</sup>	5.04
Ca <sup>++</sup>	13.0
Mg <sup>++</sup>	2.01
NO <sub>3</sub> <sup>-</sup>	8.78
Cl <sup>-</sup>	7.14
F	2.18
SO <sub>4</sub> <sup>2-</sup>	18.4
Si	28.5
PO <sub>4</sub> <sup>3-</sup>	0.12
Alkalinity <sup>2</sup>	128.9
pH	7.41
1. mg/l, except for pH.	
2. mg/HCO <sub>3</sub> <sup>-</sup> .	

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

It is assumed (Assumption 3.14) that the drip rate onto a WP is the same as the rate at which water flows through the WP. The drip rate is taken from a correlation between percolation rate and drip rate (Ref. 25, Tables 2.3-49 and 2.3-50). Specifically, percolation rates of 40 mm/year and 8 mm/year correlate with drip rates onto the WP of 0.15 m<sup>3</sup>/year and 0.015 m<sup>3</sup>/year, respectively. The choice of these particular percolation and drip rates is discussed in detail in Ref. 21, p. 19.

For the present study, the range of allowed drip rates was extended to include an upper value of  $0.5 \text{ m}^3/\text{yr}$  and a lower value of  $0.0015 \text{ m}^3/\text{yr}$ . The upper value corresponds to the 95 percentile upper limit for a percolation rate of 40 mm/year, and the lower value is simply  $1/10^{\text{th}}$  the mean value for the percolation rate of 8 mm/year (Ref. 25, Figure 2.3-108). These extreme values were used, because prior studies (Ref. 26, p. 28 and Ref. 27, p. 5-19) suggested that when waste forms are codisposed with glass, the greatest chance of Gd removal occurs when: (1) initial high drip rates cause glass leaching and removal of alkali, and (2) subsequent low drip rates allow acid to build from steel degradation.

#### 5.1.1.4 Densities and Molecular Weights of Solids

For input to criticality calculations, one must convert moles of solids to solid volumes. A few solid phases contribute to the overwhelming bulk of the total volume; Table 5-6 provides some of the densities and molar volumes for these phases. The current version of EQ6 (Section 4.2) performs the volume calculations for each element automatically and generates four different types of text output files. Ref. 12 contains tab delimited text files with the names like N?????.elem?????.txt. The text files list total moles of elements in aqueous phase (\*.elem\_aqu.txt), total moles of each element in aqueous and mineral phases (\*.elem\_m\_a.txt), total moles of each element produced by minerals (\*.elem\_min.txt), and total concentration of each element which is the sum of aqueous, mineral and unreacted reactants (\*.elem\_tot.txt). The electronic media (Ref. 12) includes Excel files listing total molar inventory, including total volume of each elements for all simulations as functions of time.

Table 5-6. Densities and Molecular Weights of Precipitated Solids

Solid	Density (kg/m <sup>3</sup> )	Molecular Weight <sup>c</sup> (g/mol)	Mol. Vol. (cm <sup>3</sup> /mol) <sup>c</sup>	Calc. Density (g/cm <sup>3</sup> )
Diaspore (AlOOH)	3400 <sup>a</sup>	59.988	17.760	3.378
Hematite (Fe <sub>2</sub> O <sub>3</sub> )	5240 <sup>a</sup>	159.692	30.274	5.275
Pyrolusite (MnO <sub>2</sub> )	5060 <sup>a</sup>	86.937	17.181	5.060 <sup>a</sup>
Goethite (FeOOH)		88.854	20.820	4.268
Ni <sub>2</sub> SiO <sub>4</sub>		209.463	42.610	4.916
Trevorite (NiFe <sub>2</sub> O <sub>4</sub> )		234.382	44.524	
Nontronite-Ca		424.293	131.100	3.236
Nontronite-K		430.583	135.270	3.183
Nontronite-Mg		421.691	129.760	3.250
Nontronite-Na		425.267	132.110	3.219
References:				
<sup>a</sup> Ref. 28, p. 172				
<sup>b</sup> Ref. 16, p. B-121				
<sup>c</sup> Ref. 12 (EQ3/6 Data base, data0.nuc.R8a), g/mole, except for pyrolusite, which is calculated from the density and molecular weight. Trevorite given same molar volume as magnetite in EQ3/6 database.				

### 5.1.1.5 Atomic Weights

Atomic weights were taken from Ref. 29 and Ref. 30, and are listed in Ref. 12 (spreadsheet Fermi\_Fuel\_kz.xls, sheet "Atomic Weights").

## 5.2 DATA CONVERSION

The data presented in Section 5.1 are largely not in a form suitable for entry into EQ3/6. The transformation to EQ3/6 format consists largely of converting mass fractions to mole fractions; normalizing surface areas, volumes, and moles to 1 liter reactive water in the system; and converting rates to moles/(cm<sup>2</sup>s). Most of these conversions are straightforward and are performed in the spreadsheets, which are included in the electronic media for this document (Ref. 12). Ref. 21 describes the conversion process in detail.

## 5.3 EQ6 Calculations and Scenarios Modeled

The rationale for selection of scenarios in EQ6 simulations is to provide conservative assessments of solubility and transport of fissile materials (i.e., U compounds) and neutron absorbers species (i.e., GdPO<sub>4</sub>) in the WP. Gd PO<sub>4</sub> exhibits solubility minimum at pH ranges of 6 to 7, and has enhanced solubility at very low and high pH (Ref. 2, p. 26). In addition, at high pH, uranium carbonate species could produce complexes and cause an increase in solubility of uranium. The "Disposal Criticality Analysis Methodology Topical Report" document defined the internal and external degradation scenarios for disposal criticality analysis (Ref. 31, pp. 3-9 to 3-12). The internal degradation configurations are based on the assumption that groundwater drips on the upper surface of the WP and penetrates it. Groundwater accumulates inside the WP, which could dissolve and flush either neutron absorber or the SNF from the WP. Following is a summary of three groups of degradation configurations from Ref. 31.

1. WP internals degrade faster than waste forms
2. WP internals degrade at the same rate as the waste form
3. WP internals degrade slower than waste forms

The WP internals include all components within the waste package including neutron absorber materials (GdPO<sub>4</sub>-doped iron shot) except SNF. The waste forms refer to SNF. The above configurations set the framework in which EQ6 scenarios could be developed. The scenarios are based on sequence of chemical reactions as function of time and could be divided into two general categories:

Single stage cases: In these calculations all WP internals, including SNF, come in contact with groundwater simultaneously. These cases correspond to an extreme in which the zirconium cladding is fully breached immediately, thereby exposing all the spent fuel as soon as the waste package corrosion barriers are breached. These cases simulate the highest concentrations of the radionuclides in solution, and could provide the most conservative loss estimate of fissile and

neutron absorber materials. These cases were designed to maximize exposure of the Gd-doped iron shot to high pH, and to stress the enhanced solubility of  $\text{GdPO}_4$  under alkaline conditions.

**Multiple stage cases:** These EQ6 calculations start with the breach of DHLW waste package allowing groundwater to come in contact with WP internals outside the DOE SNF canister ("stage A"); during this stage the DOE SNF canister remains intact. The second-stage ("stage B") starts with the breach of DOE SNF canister and interaction of groundwater with material inside DOE SNF canister, including waste forms and undegraded reactants left from stage A. These cases were designed to produce the lowest possible pH, by first exposing the HLW glass to J-13 well water to remove alkalinity, prior to exposure of the fuel and Gd-doped iron shot in the second stage. Thus, these cases were intended to test the enhanced Gd solubility at low pH.

In total, 18 cases of single and multiple stage EQ6 simulations, with different degradation rates of steel and HLW glass, and different water fluxes through the waste package were run. Tables 5-7 and 5-8 present a summary of EQ6 runs and their corresponding degradation configurations.

Table 5-7. Summary of Single Stage EQ6 Cases for Fermi Fuel

Case Number	Rates of Degradation for			J13 Drip Rates ( $\text{m}^3/\text{year}$ )	Case Identification (ID)	Degradation Configuration
	Steel	Glass	Fuel			
1	Average	Average	Average	0.5	N5_{A,B,C,D,E,F,G,H}1114	2
2	Average	Average	Average	0.15	N06_1113	2
3	Average	Average	Average	0.0015	N07_1111	2
4	Average	High	Average	0.0015	N08_1211	1
5	High	High	Average	0.0015	N09_2211	1
6	High	Average	Average	0.0015	N10_2111	1
7	Average	High	Average	0.015	N11_1212/N11_B121	1
8	High	High	Average	0.015	N12_2212	1
9	High	Average	Average	0.015	N13_2112/N13_B211	1

Table 5-8. Summary of Multiple Stage EQ6 Cases for Fermi Fuel

Case Number	Rates of Degradation for			J13 Drip Rates ( $\text{m}^3/\text{year}$ )	Case ID	Degradation Configuration
	Steel	Glass	Fuel			
10(a)	High	High	No fuel present	0.5	N01A2204	
10(b)	Average	No glass present	Average	0.015	N02B1012	2
11(a)	High	High	No fuel present	0.5	N01A2204	

## Waste Package Operations

## Calculation

Title: EQ6 Calculations for Chemical Degradation of Enrico Fermi Spent Nuclear Fuel Waste Packages

Document Identifier: BBA000000-01717-0210-00029 REV 00

Page 24 of 51

11(b)	Average	No glass present	Average	0.015	N03B1012	2
12(a)	High	High	No fuel present	0.5	N01A2204	
12(b)	Average	No glass present	Average	0.015	N04{B,^}1012	2
13(a)	High	High	No fuel present	0.5	N01A2204	
13(b)	High	No glass present	Average	0.015	N14B2012	1
14(a)	High	High	No fuel present	0.5	NH1A2204	
14(b)	High	No glass present	Average	0.015	NH2B2012	1
15(a)	High	High	No fuel present	0.5	N01A2204	
15(b)	High	No glass present	Average	0.0015	N16B2011	1
16(a)	Average	High	No fuel present	0.15	N17A1203	
16(b)	Average	No glass present	Average	0.0015	N17{B,C} 1011	2
17(a)	Average	Average	No fuel present	0.15	N18A1103	
17(b)	Average	Average	Average	0.015	N18{B,C,D} 1012	2
18(a)	High	No glass present	No fuel present	0.5	N01A2004	
18(b)	Average	Average	Average	0.015	N19{B,C,D} 1112	2

### 5.3.1 EQ6 Run Conditions and Nomenclature

The EQ6 code was used to run the 18 cases summarized in Tables 5-7 and 5-8. In general, each case could be classified as single or multiple stage. Cases 1 through 9 in Table 5-7 are all single stage runs and Cases 10 through 18 of Table 5-8 were all multiple stage runs.

Tables 5-7 and 5-8 under "Case ID" column give the file names used to describe the runs. The EQ6 input files corresponding to these runs end with the extension ".6i" (e.g., N07\_1111.6i is the EQ6 input file name for Case 3); these input files are included in the electronic media accompanying this calculation (Ref. 12). Each EQ6 run has associated tab-delimited text files, also included in the electronic media (e.g., N07\_1111.elem\_aqu.txt for Case 3). Several input files, corresponding to separate EQ6 runs, may be grouped into a "Case". Most of the important run conditions could be inferred from the "Case ID." Evaluation of a Case ID for most cases from left to right is as follows:

The first letter "N" corresponds to Fermi Fuel (eNrico Fermi).

The second and third characters (first and second digits after "N") correspond to revision of input file; for each case the numbers range from 00 to 99.

The fourth character corresponds to stage number in multiple stage run (e.g., "A," "B") or single stage run ("\_"). Single stage runs that do not converge usually require ("stage A") removal of the



exhausted reactants and restart of the run. Each step is identified as A, B, C, etc. (i.e., N5\_{A,B,C,D,E,F,G,H}1114) which appears after the “\_” character. For run numbers greater than 10 the letters representing steps replaced the steel rate on the fifth character (e.g., N11\_1212/N11\_B121).

The fifth digit in the “Case ID” is 1 or 2, corresponding to the average or high rate of steel corrosion in Table 5-1.

The sixth digit in the “Case ID” is 1, 2, or 0, with 1 and 2 corresponding, respectively, to the low and high glass corrosion rates listed in Table 5-3, and 0 corresponding to no HLW glass present in the EQ6 run.

The seventh digit in the “Case ID” is 1 or 0, with 1 corresponding to the average rate of fuel dissolution in Table 5-3, and 0 corresponding to no fuel present in the EQ6 run.

The last digit in the “Case ID” encodes the choice of J-13 well water flush rate, with 1, 2, 3, and 4 corresponding to 0.0015 m<sup>3</sup>/year, 0.015 m<sup>3</sup>/year, 0.15 m<sup>3</sup>/year and 0.5 m<sup>3</sup>/year, respectively.

Hematite and goethite are major iron oxide minerals observed to form in rust, though the EQ6 thermodynamic database indicates that hematite is thermodynamically more stable, and hematite’s stability increases with temperature. In an EQ6 simulation where the second letter (from left) of the “Case ID” is “H,” it indicates that formation of hematite in that run was suppressed (i.e., NH1A2204/NH2B2012). All the other characters in the “Case ID” are the same as those runs in which hematite was not suppressed.

An example is Case 13 (a, b) in Table 5-8 that lists “Case ID” names N01A2204/N14B2012 for the two input files. The first file name, N01A2204, covers the time period before the breach of the DOE SNF canister, and represents run number 01 (second and third characters). The fourth character, A, indicates this is a stage one of a multi stage runs. The fifth character is 2, and corresponds to the selection of the faster degradation rates for the A516, 304L, and 316L steels in the package (Table 5-1). The sixth character is 2, corresponding to the faster glass degradation rate in Table 5-3. The seventh character is 0, corresponding to absence of fuel in the EQ6 system (since the run is pre-breach, the fuel is not yet exposed to chemical corrosion). The last character is 4, corresponding to the highest J-13 well water flush rate of 0.5 m<sup>3</sup>/year.

The second file name, N14B2012, covers the time after breach of the DOE SNF canister, and is Case 13 (second and third characters). As always, the last block of characters, 2012, indicates the rates. The fifth character again corresponds to the faster steel corrosion rate. The time of breach for the DOE canister was chosen to correspond to a low pH plateau that followed the complete degradation of all glass in the system (e.g., see Figure 5-2). Thus the sixth character is 0, since no glass remains in the EQ6 system (though the glass corrosion products are carried through the calculation). The seventh character corresponds to the average fuel corrosion rate in Table 5-4, and the last corresponds to a J-13 well water drip rate of 0.015 m<sup>3</sup>/year. In general, the first-stage of a multi-stage run is comparatively short (~10<sup>3</sup> to ~10<sup>4</sup> years), and the second-

stage of the run is carried out to at least  $1 \times 10^5$  and up to  $5 \times 10^5$  years. While the first-stage is important in setting up the chemical conditions, the second-stage is generally of greater interest for neutronics calculations, since the corrosion product compositions can vary greatly in the first stage, but achieve a quasi-steady state composition at long times.

### 5.3.2 Examination of Cases

Table 5-9 summarizes the total percentage Gd and U remaining at the end of the EQ6 runs. The complete output tables (aqueous, mineral, and total moles) for all the cases are included in the electronic media, (Ref. 12) as tab-delimited text files. A summary of the files included in the electronic media is given in Attachment III.

Table 5-9. Summary of Run Number, Input File, End Time, and U and Gd Losses for All EQ6 Runs

Case	Case ID	Years	%U Loss	%Gd Loss
1	N5_{A,B,C,D,E,F,G,H}1114	70563	0.28	0.06
2	N06_1113	250010	13.97	0.47
3	N07_1111	250040	92.57	0.50
4	N08_1211	250440	91.92	0.00
5	N09_2211	250320	100.00	0.00
6	N10_2111	250270	92.60	2.30
7	N11_1212/N11_B121	250030	100.00	0.01
8	N12_2212	250020	61.00	0.03
9	N13_2112/N13_B211	250030	16.87	1.51
10	N01A2204/N02B1012	250020	0.04	0.03
11	N01A2204/N03B1012	250020	0.43	0.03
12	N01A2204/N04B1012	250030	4.15	0.03
13	N01A2204/N14B2012	250020	0.00	0.00
14	N01A2204/N16B2011	250190	0.00	0.00
15	NH1A2204/NH2B2012	250010	0.07	0.04
16	N17A1203/N17{B,C}1011	500050	0.09	0.07
17	N18A1103/N18{B,C,D}1012	105920	0.26	0.35
18	N19A2004/N19{B,C,D}1112	106340	0.47	0.65

Two basic types of degradation scenarios were simulated:

Cases 1-8 are "single stage," and involve simultaneous exposure of the fuel and the package materials to groundwater. Considering the fuel rods that are contained within zirconium cladding, for a conservative approach, it was assumed (Assumption 3.19, Section 3) that cladding is fully breached immediately after contact with water.

Cases 10-18 are called "multiple stage." In these cases groundwater first interacts with everything inside the WP, but outside the DOE SNF canister including the outside surface of the

DOE SNF canister. It is also assumed that zirconium cladding would breach just after the breach of the DOE SNF canister.

Plots of reactant concentration changes, pH, and mineral formation/dissolution changes will be used to examine each case. In all these figures, when units of moles are used on the left axis, the quantity is scaled relative to 1 liter of coexisting J-13 well water (which is equivalent to 1 liter of initial void space in the package). To obtain the total moles of product minerals or package materials in the WP, the mole quantities in the figures, must be multiplied by the package void volume

Case 1 resulted in practically no loss of U or Gd from the WP (Tables 5-9 and 5-10). The combination of high pH and high dissolved carbonate could increase U solubility. The dissolution of HLW glass could make the solution alkaline, however, fast percolation rate of groundwater ( $0.5 \text{ m}^3/\text{year}$ ) and capacities of stainless steel components to lower the pH resulted in pH regimes that each U and Gd exhibit low solubility (Ref. 2). Even upon exhaustion of all steel components, pH of the WP did not get higher than 7.68; at this pH, soddyite, the major mineral form of uranium, is not soluble.  $\text{GdPO}_4$  is soluble only in extreme acidic and alkaline conditions (Ref. 2, p. 26) that were not achieved in this case. In Cases 2 and 3, due to slower percolation rate of water, soddyite starts to dissolve as pH arrives above 8.3. Figures 5-1 and 5-2 indicate that % loss of U is a function of pH and, after exhaustion of all stainless steel reactants, is controlled by dissolution of the HLW glass. The decrease of 100 fold in water flow through the WP in Case 3 compared to Case 2, resulted in about 7 fold higher losses of uranium due to higher pH.

Table 5-10. Total Concentration Changes for U and Gd in the Aqueous Phase as Function of Time for Case 1 (N5\_{A,B,C,D,E,F,G,H}1114)

Time (years)	U (moles/l)	Gd (moles/l)	pH
0.00E+00	6.17E-01	4.34E-02	7.59E+00
1.41E+00	6.17E-01	4.34E-02	3.50E+00
3.34E+02	6.17E-01	4.34E-02	7.22E+00
3.44E+03	6.17E-01	4.34E-02	7.46E+00
3.26E+04	6.16E-01	4.34E-02	7.54E+00
5.47E+04	6.16E-01	4.34E-02	7.68E+00
7.06E+04	6.15E-01	4.34E-02	7.68E+00

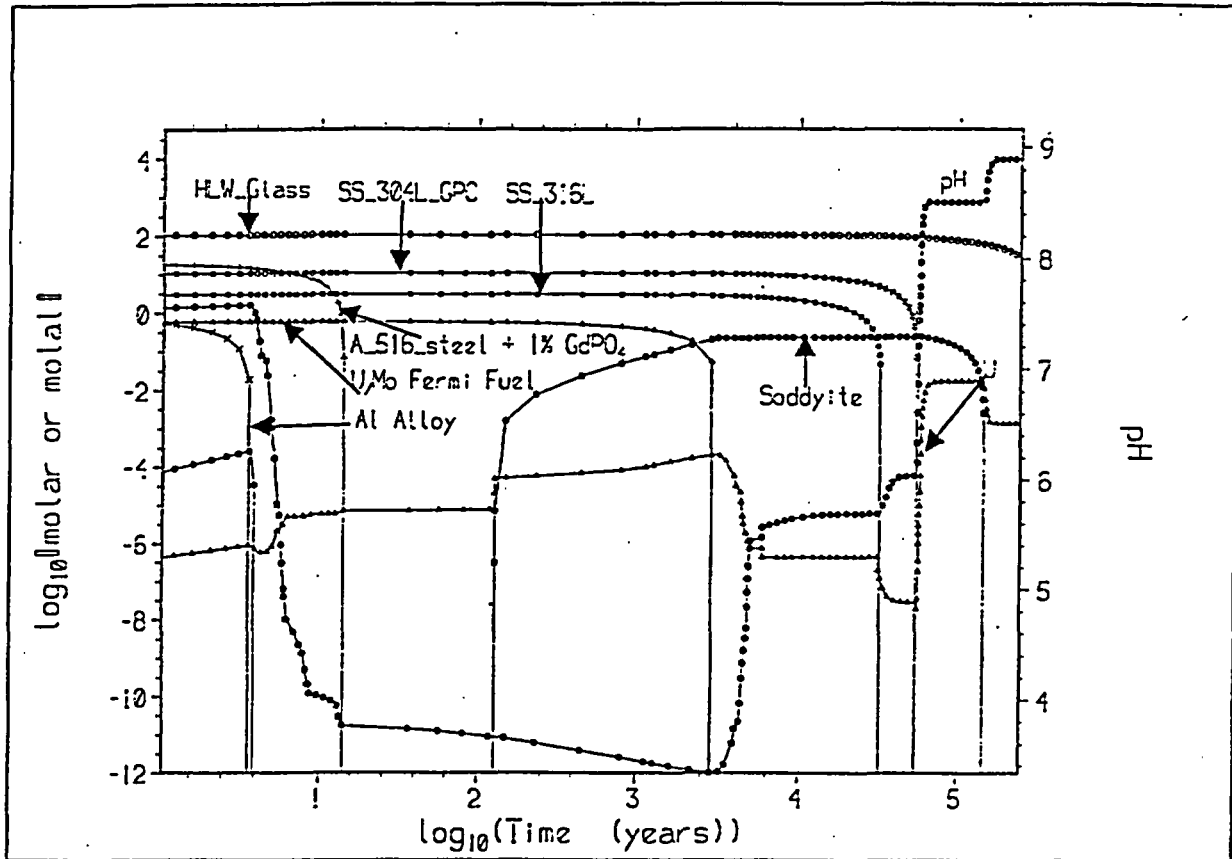


Figure 5-1. Case 3 (N07\_1111): Effects of Reactants on pH, Aqueous U, and Sodyite. J-13 Well Water Percolation Rate of 0.0015 m<sup>3</sup>/year (molal for aqueous U and moles for solids)

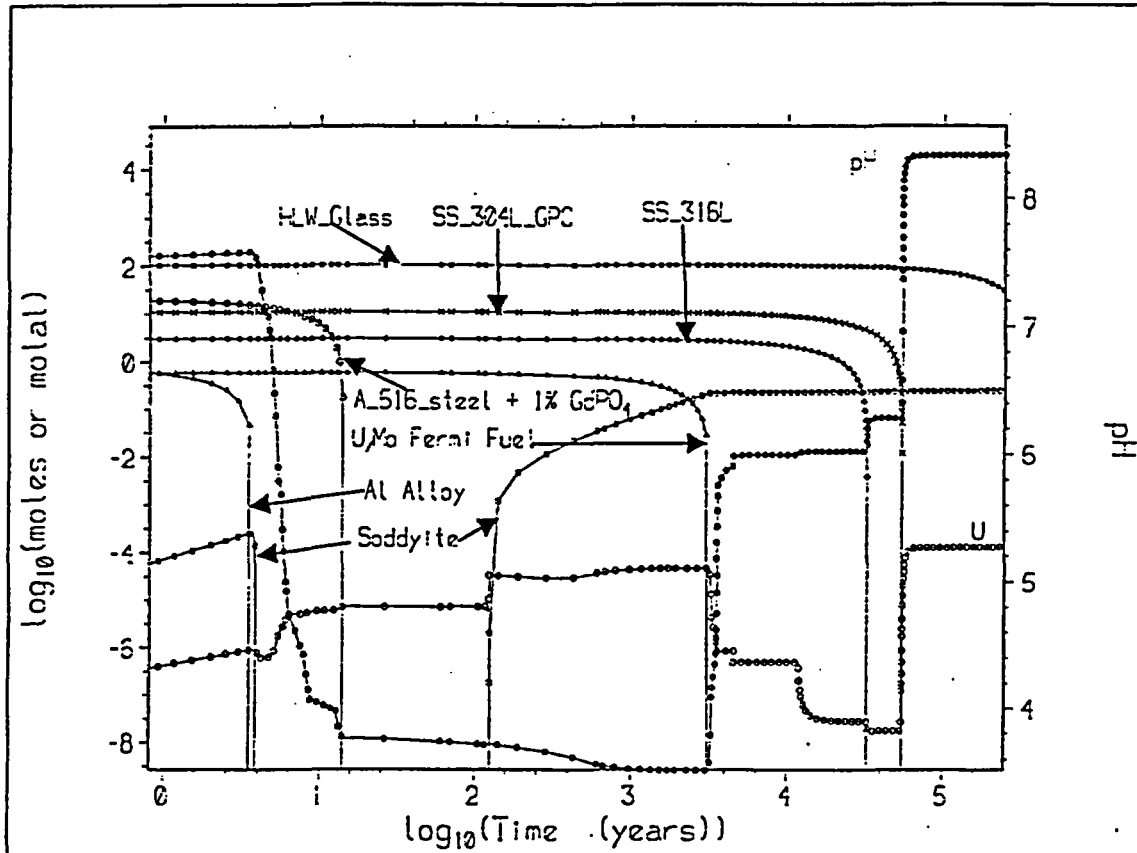


Figure 5-2. Case 2 (N06\_1113): Effects of Reactants on pH, Aqueous U, and Soddyite, J-13 Well Water Percolation Rate of  $0.15 \text{ m}^3/\text{year}$  (molal for aqueous U and moles for solids)

Cases 4, 5, and 6 (N08\_1211, N09\_2211, and N10\_2111) were single stage runs that differed in the degradation rates of glass and stainless steel, but maintained a constant drip rate of  $0.0015 \text{ m}^3/\text{year}$ . The EQ6 calculation results are presented in Figures 5-3, 5-4, and 5-5. The results were similar to those of Case 3 (N07\_1111) with similar percolation rate of groundwater. In Case 3 faster degradation rates of HLW glass combined with slow rate of water percolation contributes to high pH, up to pH of 9.8, at times of  $\sim 300$ - $10,000$  years. During this period about 90% of uranium is dissolved and flushed out of the waste package.

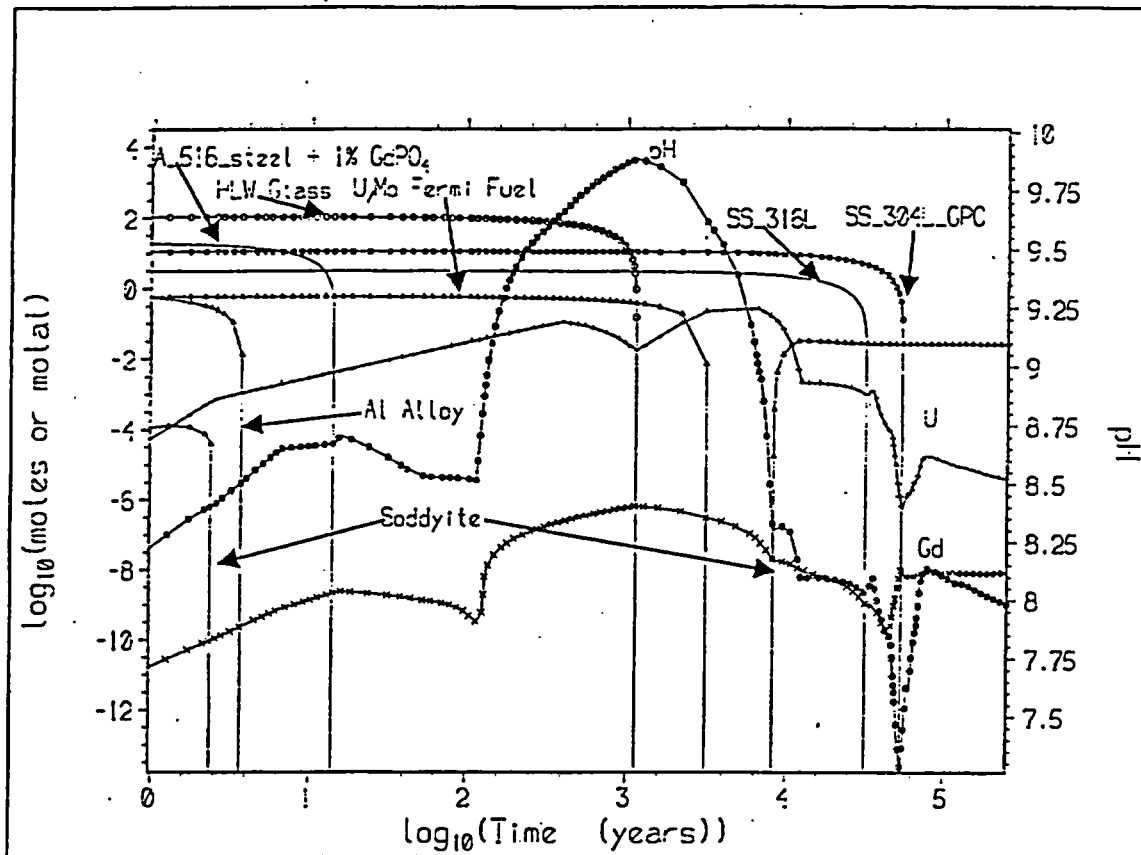


Figure 5-3. Case 4 (N08\_1211): Effects of Reactants (Faster Rates of Glass) on pH and Aqueous U and Gd, and Soddyite with J-13 Well Water Percolation Rate of 0.0015 m<sup>3</sup>/year (molal for aqueous U and Gd, and moles for solids)

In Case 5 (Figures 5-4 and 5-5, N09\_2211), high rates of glass degradation eventually caused high pH values, after exhaustion of most steel components. At this high pH, most soddyite dissolved. More than 90% of uranium inventory was lost during these periods of high pH. Most of this loss was in the U "plateau" between approximately 20,000 and 68,000 years (Figure 5-5). The U losses can be estimated for any specific time line from the figure via:

Concentration of U = 0.026 moles/kg water

Examined time = 68,000 – 20,000 = 48,000 years

Water percolation rate = 0.0015 m<sup>3</sup>/year

$(0.026 \text{ moles/liter})(1000 \text{ liter/m}^3)(0.0015 \text{ m}^3/\text{year})(48,000 \text{ year}) = 1,872 \text{ moles U lost.}$  The system contained 2,616 moles of U, therefore 71.6% (1,872 moles lost U/ 2,616 moles total U\*100) of the U was lost in the period from ~20,000 to 68,000 years.

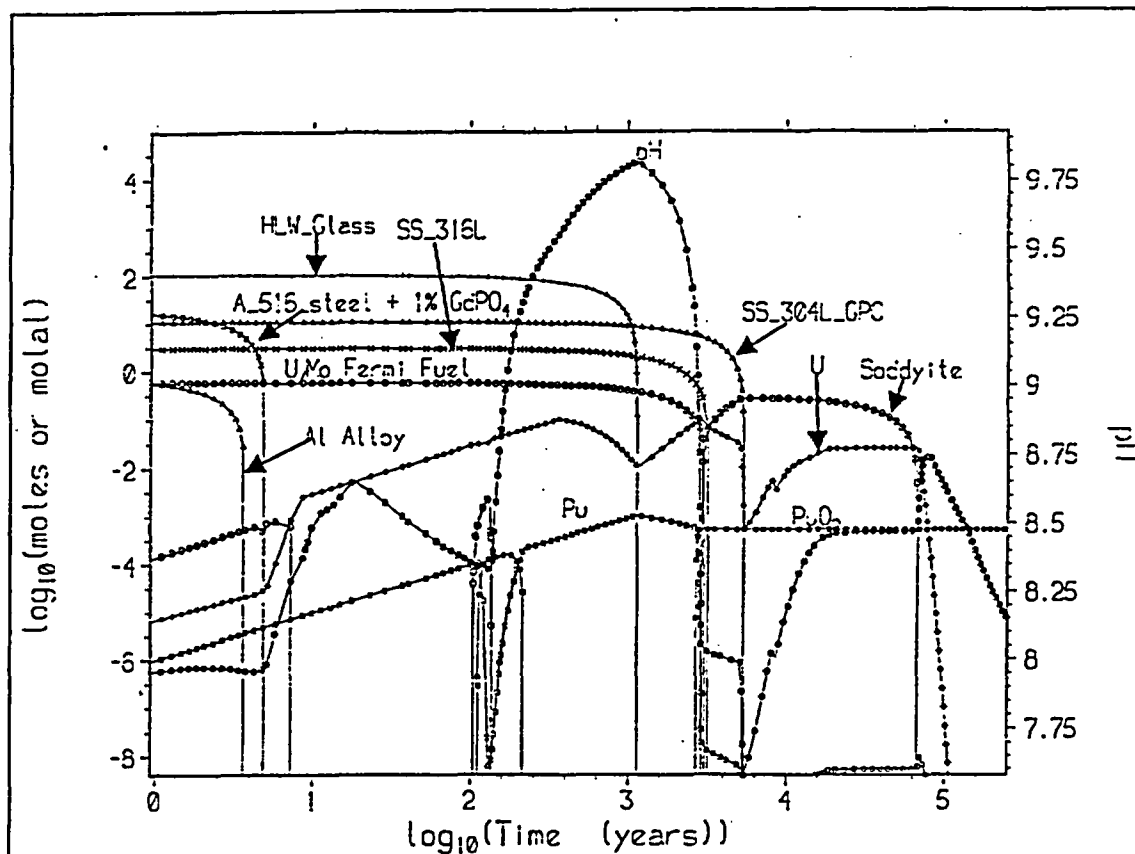


Figure 5-4. Case 5 (N09\_2211): Effects of Reactants (Faster Rates of Degradation for Both Steel and Glass) on pH on Aqueous U and Pu, and Soddyite and PuO<sub>2</sub> with J-13 Well Water Percolation Rate of 0.0015 m<sup>3</sup>/year (molal for aqueous U and Pu, and moles for solids)

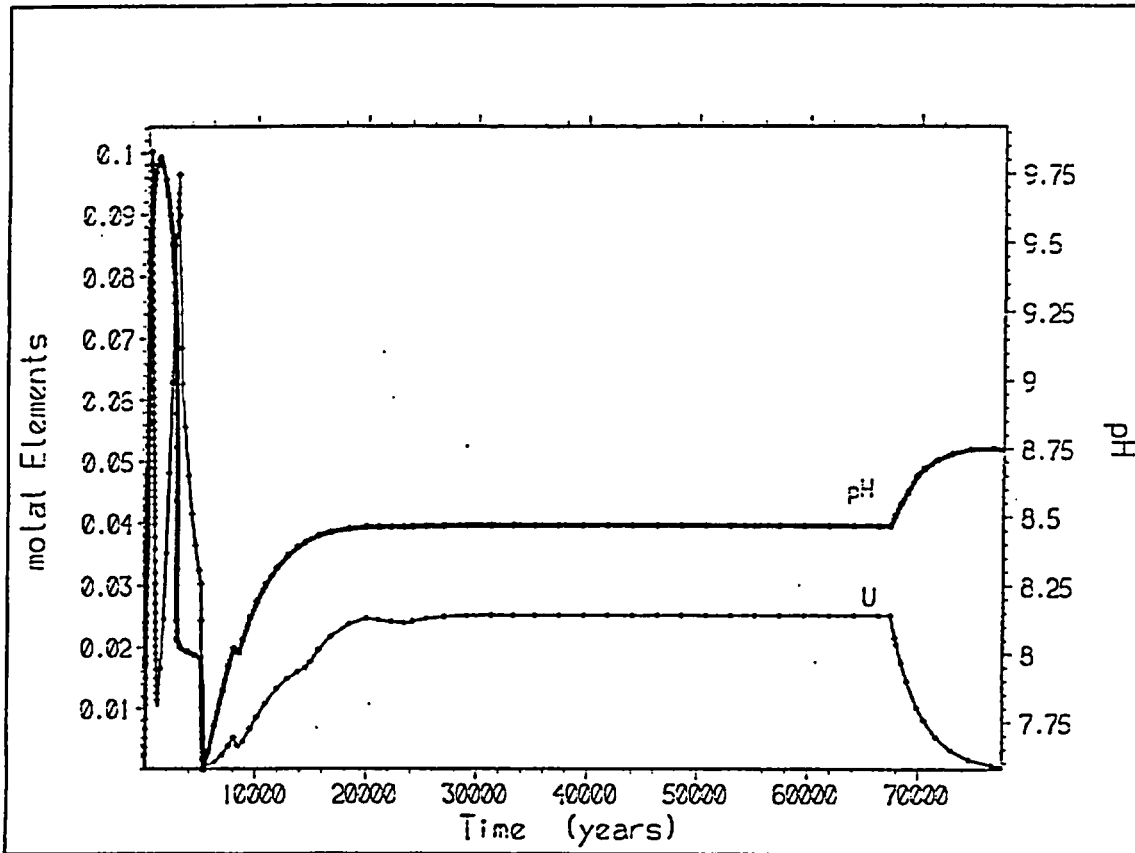


Figure 5-5. Case 5 (N09\_2211): Effects of pH on Solubility and Losses of U in Aqueous Phase

Case 6 (Figure 5-6, N10\_2111), with high rate of degradation for steel and average rate of degradation for HLW glass, reached low pH values during 3,000-10,000 years. The low pH caused about 2.3% of gadolinium loss in the form of  $Gd^{3+}$  (Ref. 2, p. 24). Table 5-11 is a partial listing of U and Gd concentrations for this case.



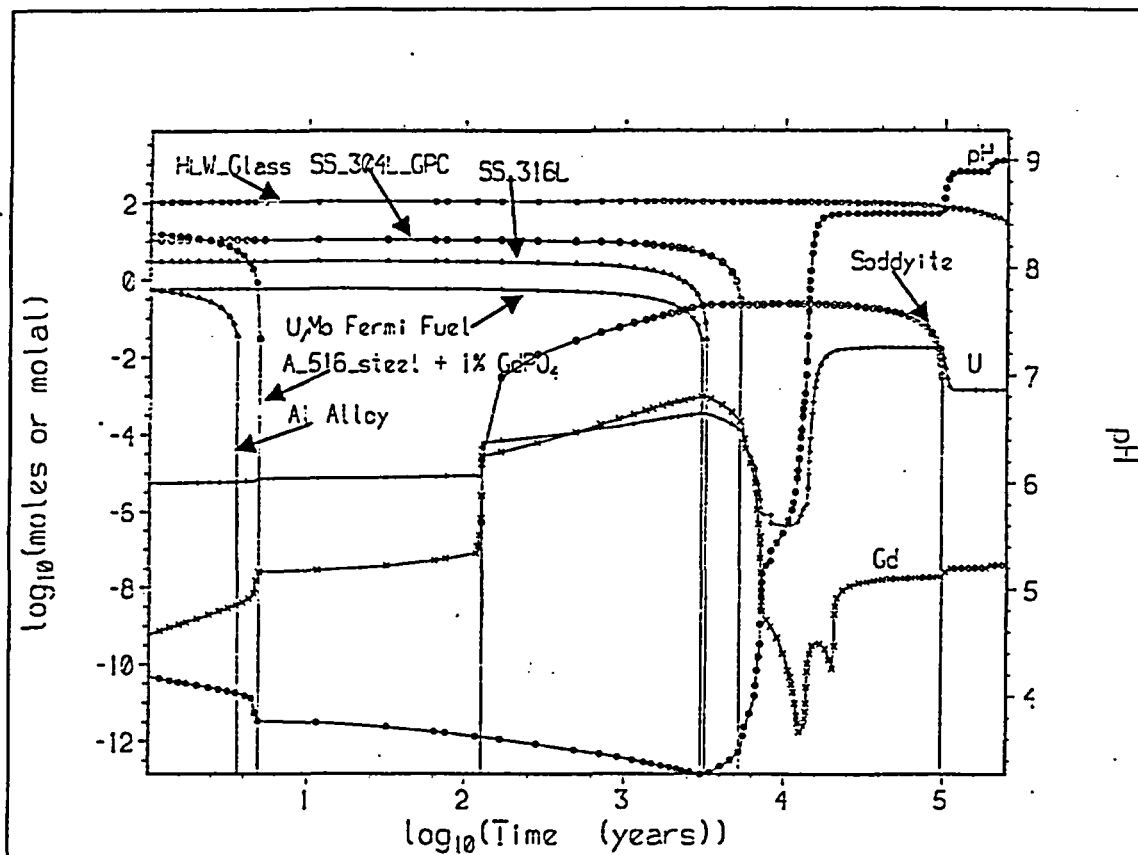


Figure 5-6. Case 6 (N10\_2111): Effects of Reactant (Faster Rate of Degradation for Steel) on pH and Aqueous U and Gd, and Sodyite with J-13 Well Water Flow Rate of 0.0015 m<sup>3</sup>/year (molal for aqueous U and Gd and moles for solids)

Table 5-11. Total Concentration Changes for U and Mo as Function of Time for Case 6 (N10\_2111)

Time (years)	U (moles)	Gd (moles)	PH
0.00E+00	6.19E-01	4.34E-02	7.6
4.82E-01	6.19E-01	4.34E-02	5.0
1.18E+02	6.19E-01	4.34E-02	3.6
2.75E+03	6.18E-01	4.30E-02	3.3
1.09E+04	6.18E-01	4.24E-02	5.7
1.63E+04	6.17E-01	4.24E-02	8.4
3.92E+04	4.92E-01	4.24E-02	8.5
6.18E+04	3.56E-01	4.24E-02	8.5
8.43E+04	2.21E-01	4.24E-02	8.5
1.07E+05	1.17E-01	4.24E-02	8.8
2.50E+05	4.58E-02	4.24E-02	9.0

Cases 7, 8, and 9 (N11\_1212/N11\_B121, N12\_2212 and N13\_2112/N13\_B211) were similar to Cases 4, 5, and 6; the only difference was that the rate of water percolation into the WP was increased from 0.0015 to 0.015 m<sup>3</sup>/year. In Case 7 the faster rate of HLW glass degradation was selected (Figure 5-7). In this calculation pH rapidly (in about 1.5 years) arrived at 8.5 and soddyite was dissolved. The pH continued to increase to a maximum of 9.7 until all the HLW glass was dissolved, after this point pH dropped, however, by this time, all the uranium was flushed out of the system.

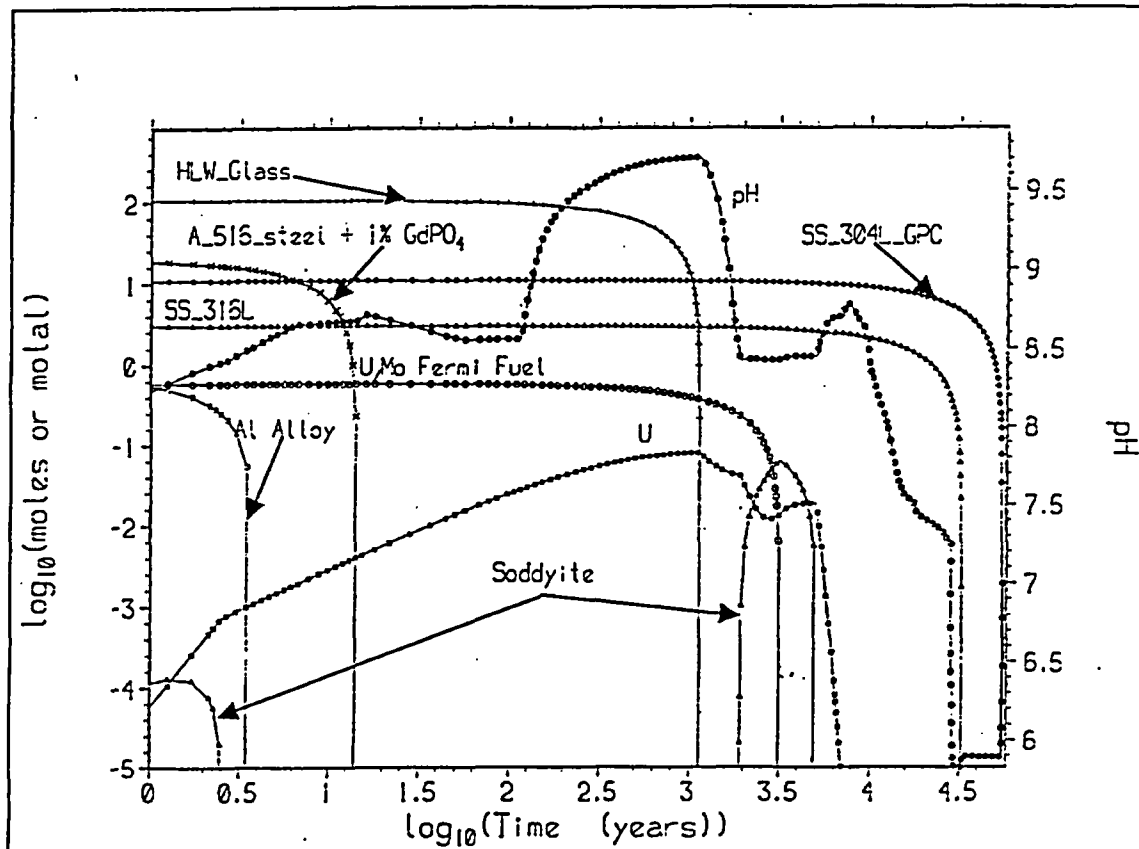


Figure 5-7. Case 7 (N11\_1212/N11\_B121): Effects of Reactants (Raster Rate of Degradation for Glass) on pH, Aqueous U and soddyite with J-13 Well Water Flow Rate of 0.015 m<sup>3</sup>/year (molal for aqueous U and moles for solids)

Case 8 (Figure 5-8, N12\_2212) was simulated with faster rates of steel degradation, which resulted in a more efficient pH buffering, by the steel components. The faster rates resulted in a rapid lowering of pH upon exhaustion of HLW glass. At lower pH soddyite was formed before complete dissolution of the fuel and resulted in a smaller loss of U compared to Case 7.

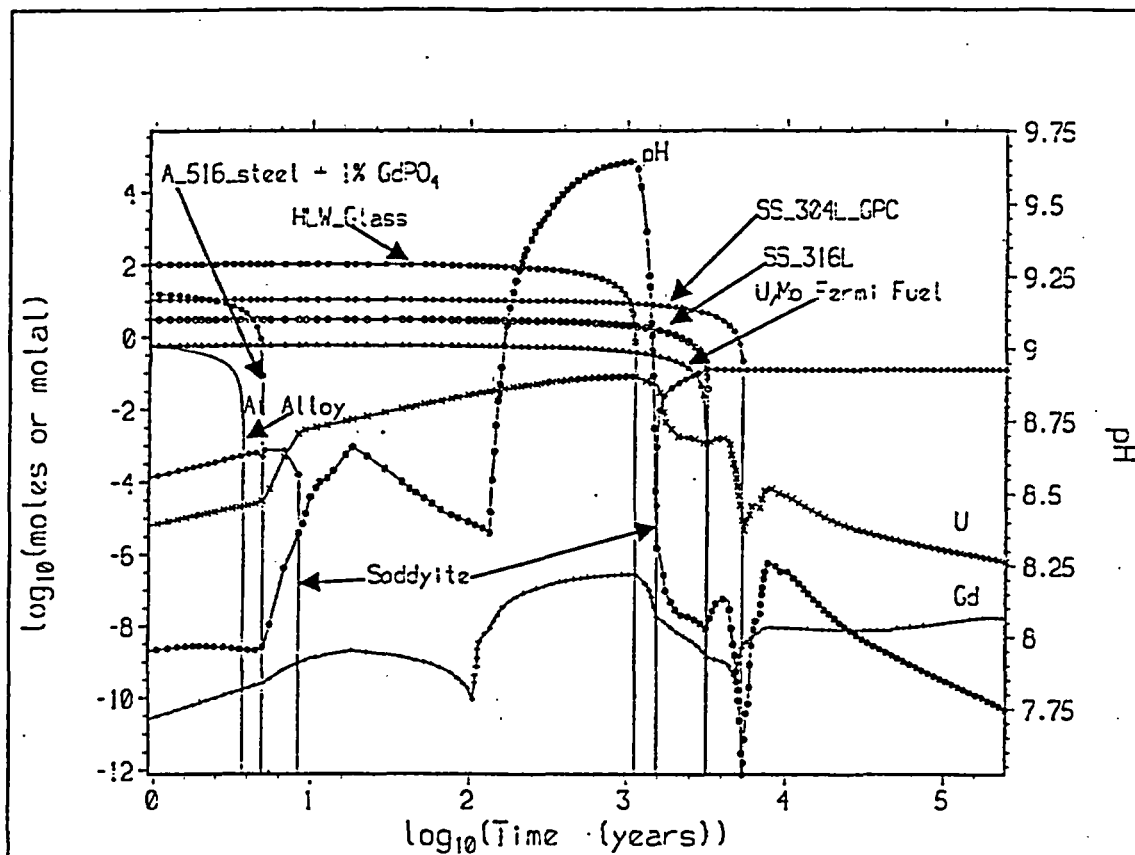


Figure 5-8. Case 8 (N12\_1212): Effects of Reactants (Faster Rate of Degradation for Both Steels and Glass) on pH and Aqueous U and Gd and Sodyite with J-13 Well Water Percolation Rate of 0.015 m<sup>3</sup>/year (molal for aqueous U and Gd and moles for solids)

Figure 5-9 shows EQ6 simulation results for Case 9 (N13\_2112) with combination of faster degradation rates for steel components and average rates of degradation for glass. In this case, the combination of water percolation and HLW glass degradation rates caused the smallest U loss (16.87%) among Cases 7, 8, and 9. In addition, Case 9 (Figure 5-9) exhibited a 1.5% Gd loss (Table 5-12) due to a low pH regime that reached < 3.5 and caused Gd loss as Gd<sup>3+</sup> (Ref. 2, p. 24).

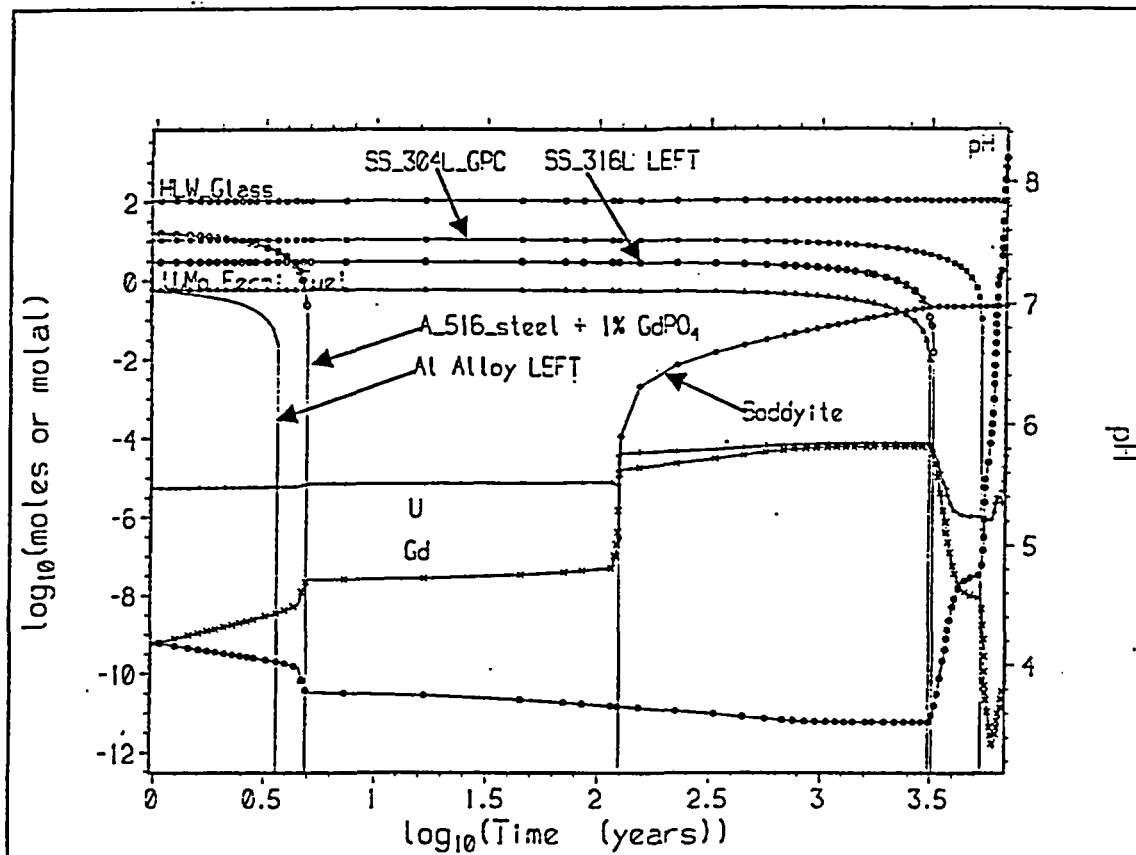


Figure 5-9. Case 9 (N13\_2112): Effects of Reactants (Faster Rate of Degradation for Steel ) on pH and Aqueous U and Gd, and Soddyite with J-13 Well Water Percolation Rate of 0.015 m<sup>3</sup>/year (molal for aqueous U and Gd and moles for solids)

Table 5-12. Total Concentration Changes for U and Gd as Function of Time for Case 9 (N13\_{A,B}211)

Time (years)	U (moles)	Gd (moles)	pH
0.00E+00	6.19E-01	4.34E-02	7.59E+00
1.48E+03	6.18E-01	4.32E-02	3.53E+00
6.59E+03	6.18E-01	4.28E-02	7.42E+00
6.93E+03	6.18E-01	4.28E-02	8.22E+00
2.50E+05	5.14E-01	4.27E-02	8.32E+00

The two-stage simulations with Cases 10, 11, 12, 13, and 14 were all started with the first-stage EQ6 run of N01A2204. In this run a fast rate of degradation for HLW glass, and stainless steel components outside the DOE SNF canister, including the canister's outside surface, was selected. The fastest rate of water percolation was selected (0.5 m<sup>3</sup>/year) to remove sources of high alkalinity rapidly. Figure 5-10 shows that within about 1,200 years most of the HLW glass was dissolved and the pH started to decrease due to acid producing components of remaining

steels, reaching 6.15 by about 3,500 years. Figure 5-11 shows major minerals in this simulation. As expected, major minerals are oxides of iron and silica clays.

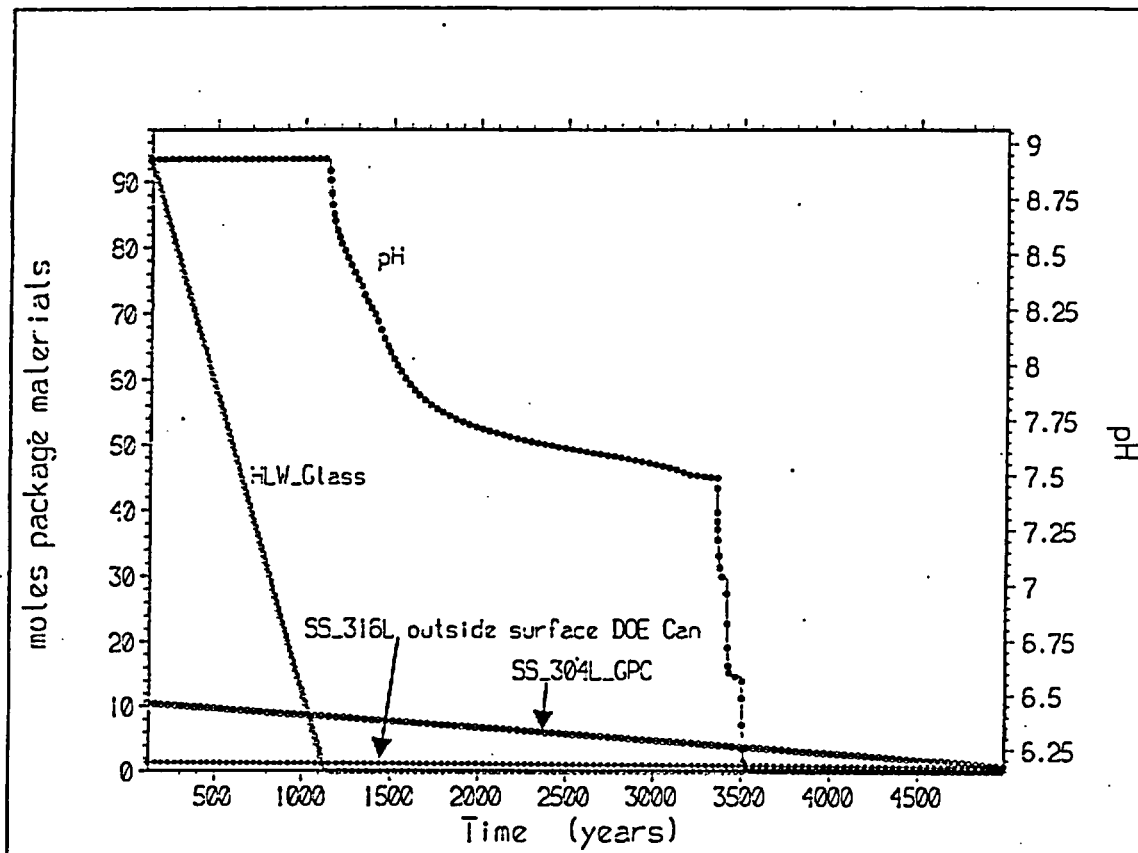


Figure 5-10. Case 10, First Stage (N01A2204): pH and Moles of Package Materials (Outside the DOE SNF Canister), J-13 Well Water Percolation Rate: 0.5 m<sup>3</sup>/year

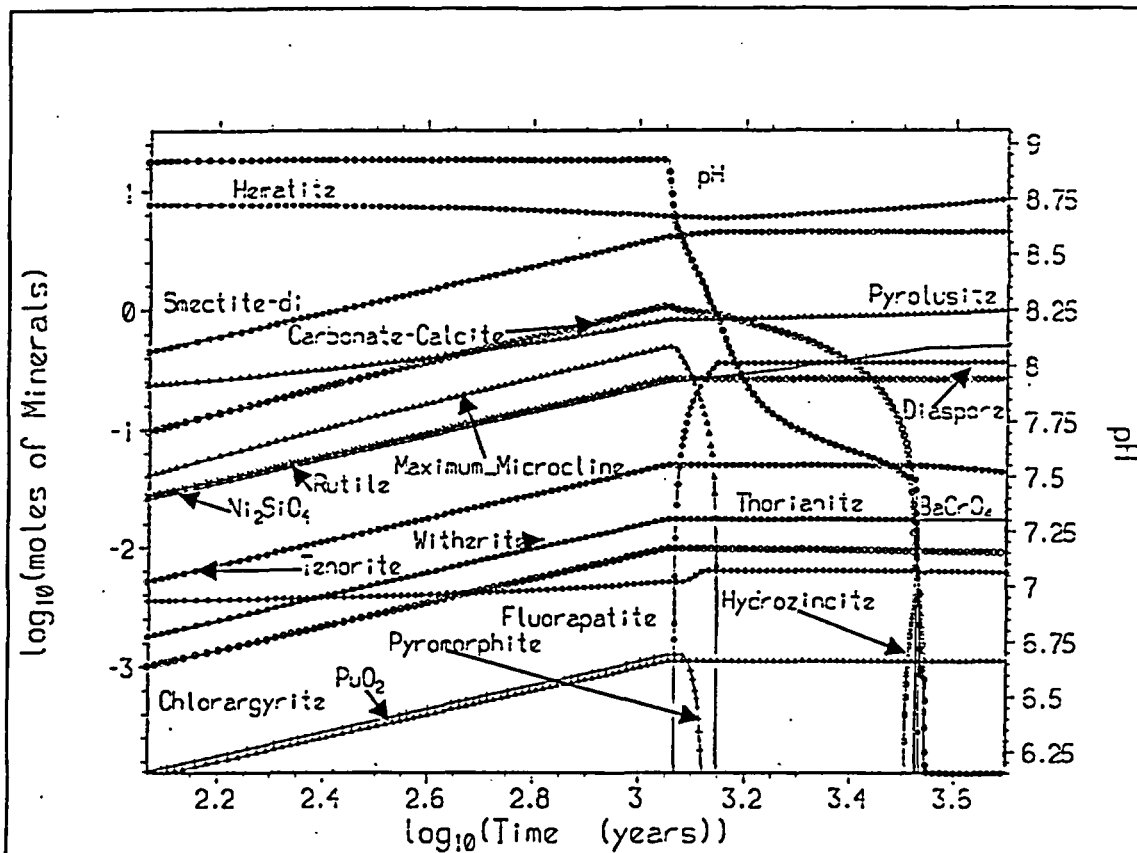


Figure 5-11. Case 10, First Stage (N01A2204): Major Minerals and pH as Function of Time, J-13 Well Water Percolation Rate of 0.5 m<sup>3</sup>/year

Stage two ("B") of the Cases 10 (Figure 5-12), 11, and 12 (N02B1012, N03B1012, N04B1012) corresponds to simulation in which, respectively, 100%, 10%, and 1% of the fuel comes in contact with J-13 well water due to Zr cladding failure. The percolation rate of 0.015 m<sup>3</sup>/yr was selected for these stages. Table 5-9 reveals almost complete retention of U and Gd within the WP. The increase in % loss of uranium in Cases 11 and 12 reflects the fact that smaller total amount of fuel was accessible to percolating water. As a result, losses of uranium in Case 11 and 12 appear to be larger. However, the total amount of uranium loss was negligible (< 0.05%).

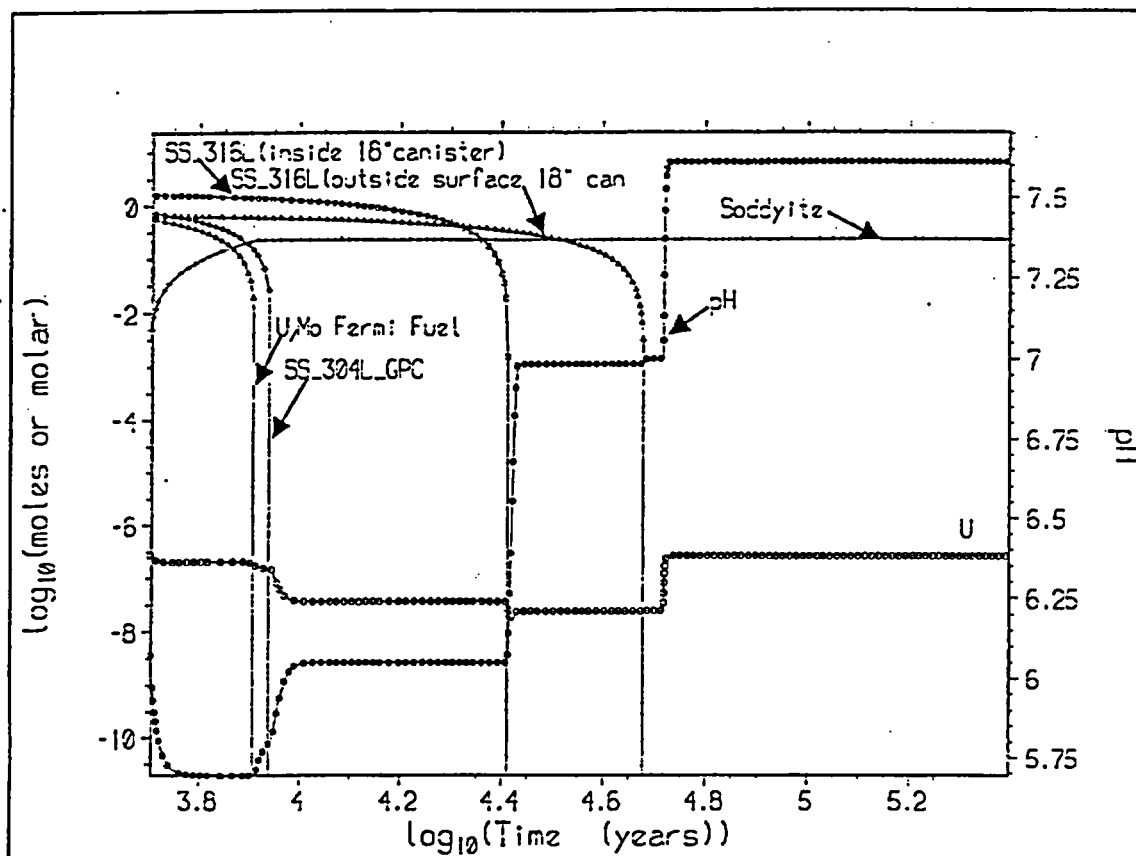


Figure 5-12. Case 10, Second Stage (N02B1012): pH and Moles of Package Materials (Inside the DOE SNF Canister and Remaining from First Stage) as a Function of Time, J-13 Well Water Percolation Rate of 0.015 m<sup>3</sup>/year (molar for aqueous U and Gd and moles for solids)

In Cases 13 (Figure 5-13, N01A2204/N14B2012) and 14 (Figure 5-14, N01A2204/N16B2011), the effects of water percolation rate into the WP were tested by increasing the rate from 0.0015 to 0.015 m<sup>3</sup>/year. Table 5-13 and Figure 5-13 show losses of the U and Gd in both runs were 0%.

Table 5-13. Total Concentration Changes for U and Gd as Function of Time for Case 13 (N01A2204/N14B2012)

Time (years)	U (moles)	Gd (moles)	pH	Remarks
0.00E+00	1.68E-01	1.00E-14	7.59	Beginning of the first-stageEQ6 simulation
1.23E+00	1.68E-01	8.62E-15	8.34	
1.17E+02	1.52E-01	5.32E-21	8.92	
2.74E+02	1.28E-01	1.67E-22	8.93	
5.55E+02	8.68E-02	1.67E-22	8.93	
9.06E+02	3.50E-02	1.67E-22	8.93	
1.05E+03	1.43E-02	1.67E-22	8.93	
1.12E+03	3.92E-03	1.67E-22	8.93	

1.13E+03	1.23E-03	1.67E-22	8.93	
1.59E+03	1.67E-22	1.67E-22	7.92	
5.00E+03	1.67E-22	1.67E-22	6.15	
5.00E+03	4.49E-01	7.08E-03	6.15	Beginning of the second-stage EQ6 simulation
7.63E+03	4.49E-01	7.08E-03	5.61	
9.61E+04	4.49E-01	7.08E-03	6.28	
1.85E+05	4.49E-01	7.08E-03	6.70	
2.50E+05	4.49E-01	7.08E-03	6.99	

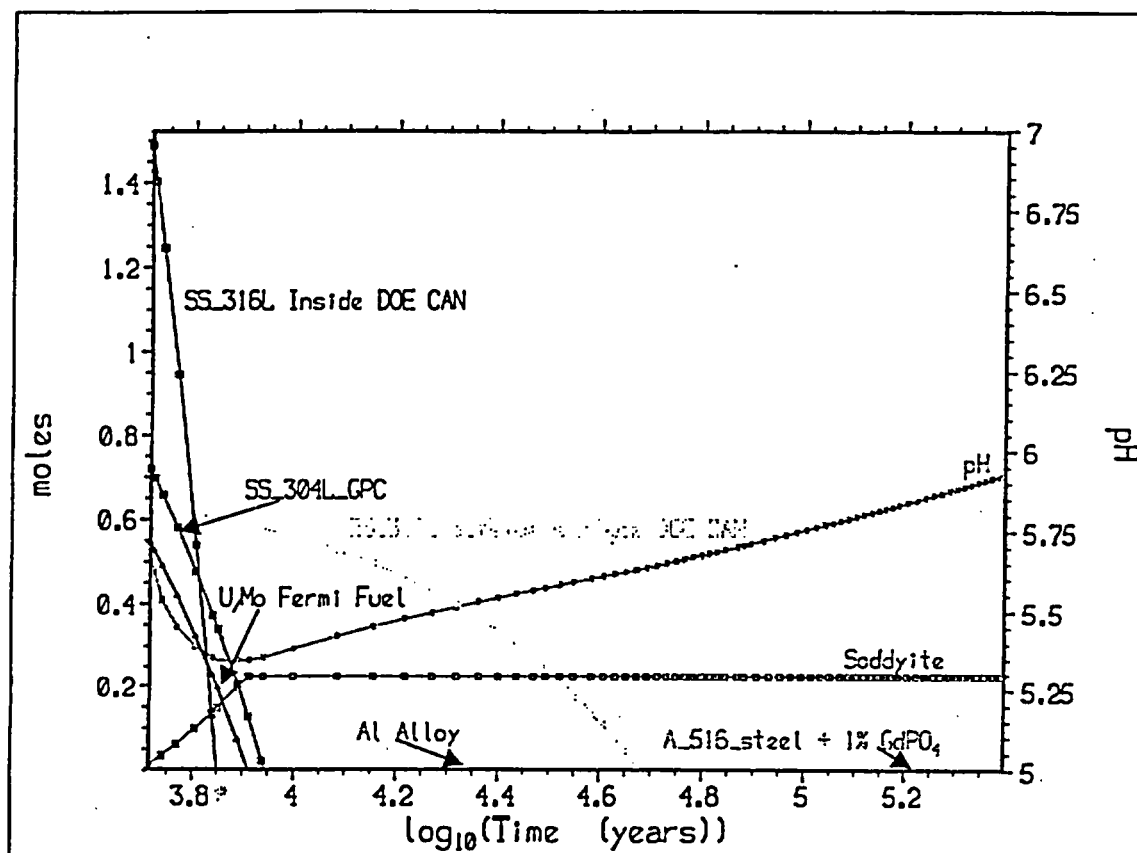


Figure 5-13. Case 14, Second Stage (N16B2011): pH and Moles of Package Materials (Inside the DOE SNF Canister and Remaining from First Stage) as Function of Time with J-13 Well Water Percolation Rate of 0.0015 m<sup>3</sup>/year

In most EQ6 runs, we have suppressed minerals that generally do not form at low temperature; such mineral phases include muscovite, mica, which are thermodynamically stable, but kinetically inhibited relative to clays. A complete list of such minerals is listed in each EQ6-input file. In some cases, hematite (the thermodynamically stable phase) was suppressed to cause



formation of goethite; both phases form in rust. In Case 15 (Figure 5-14), goethite was simulated to form instead of hematite, otherwise, Case 15 is identical to Case 13. The two cases show minor differences in solution chemistry such as pH that could cause major effects on solubility of fissile and neutron absorber. However, one needs to consider that molar volume of hematite is about 30% higher than goethite, which could change effective void volume in the WP (Ref. 2).

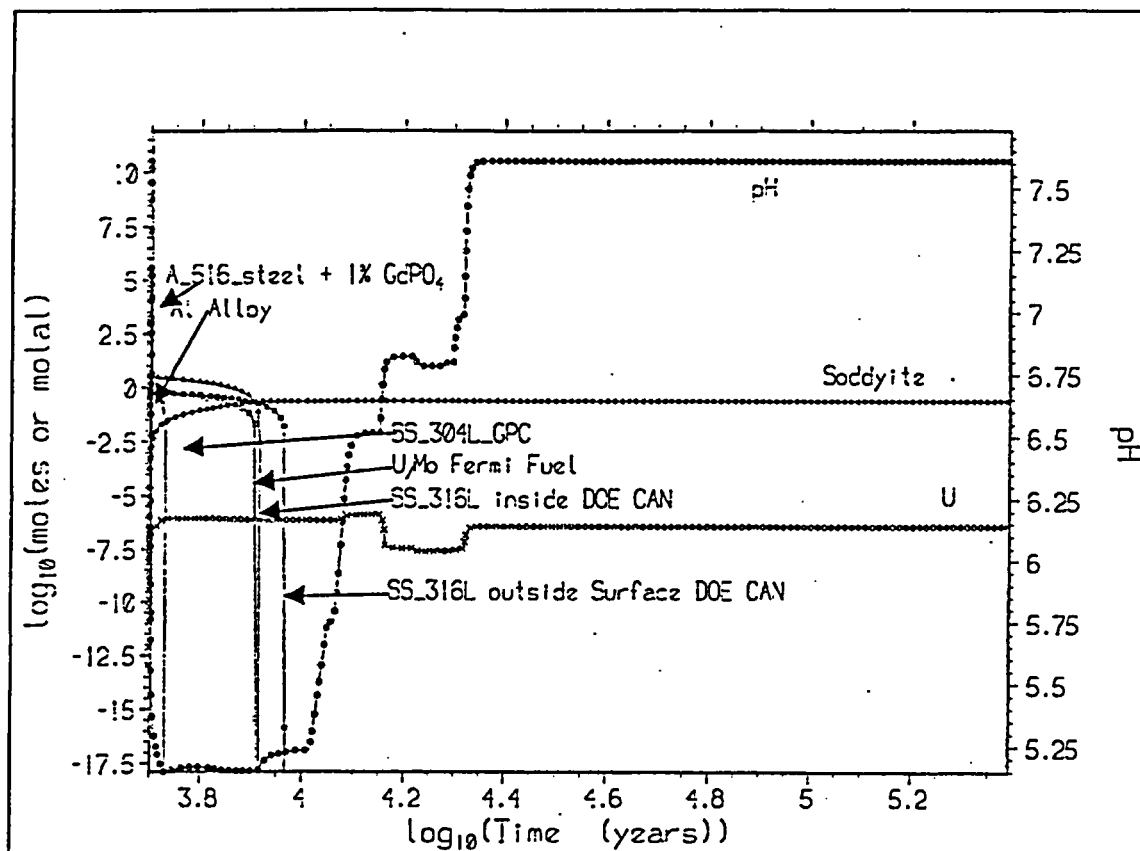


Figure 5-14. Case 15, Second Stage (NH2B2012): pH and Moles of Package Materials (Inside the DOE SNF Canister and Remaining from First Stage) and Aqueous U and Soddyite as a Function of Time (Hematite Suppressed), J-13 Well Water Percolation Rate of 0.015 m<sup>3</sup>/year (molal for aqueous U and moles for solids)

Case 16 (N17A1203/N17{B,C}1011) consisted of a stage "A" in which steels degrade at an average rate and water percolation rate was set at 0.15 m<sup>3</sup>/year, in contrast with previous first-stage runs (stage "A" of Cases 10 through 15) where steel degraded at high rates and water flux was at the rate of 0.5 m<sup>3</sup>/year (Figure 5-15). The second-stage of simulation was extended to 500,000 years. The simulation calculated practically no loss of U and Gd. The fast rate of glass degradation resulted in disappearance of HLW glass in about 1,400 years. In the later part of stage "A," and in early part of stage "B" the pH of the system was controlled by oxidation of Cr and Ni components of the WP's steel components. However, the pH did not get low enough to

initiate dissolution of  $\text{GdPO}_4$  (Figure 5-16).

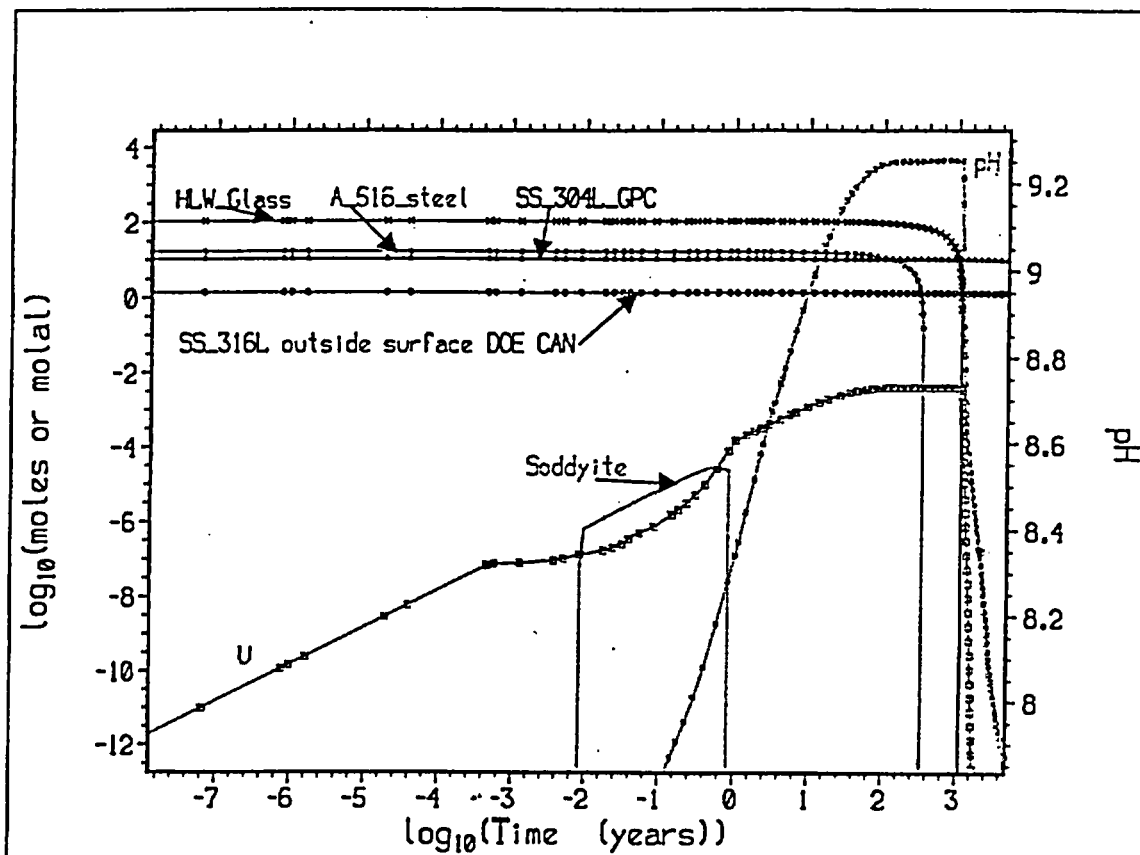


Figure 5-15. Case 16, First Stage (N17A1203): pH, Aqueous U, Soddyite and Moles Package Materials (Outside the DOE SNF Canister) as a Function of Time, J-13 Well Water Percolation Rate of  $0.15 \text{ m}^3/\text{year}$  (molal for aqueous U and moles for solids)

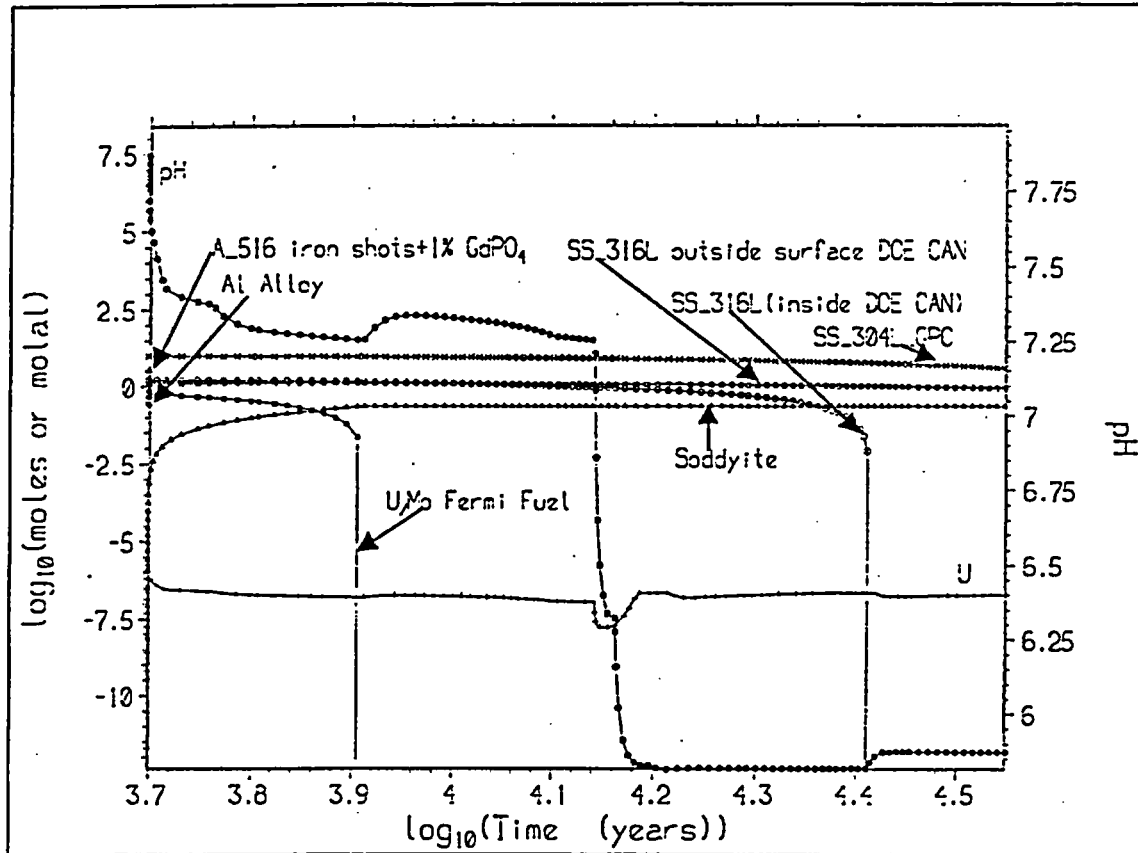


Figure 5-16. Case 16, Second Stage (N17B1011): pH, Aqueous U, Soddyite and Moles Package Materials (Inside the DOE SNF Canister and Remaining from First Stage) as a Function of Time, J-13 Well Water Percolation Rate of  $0.015 \text{ m}^3/\text{year}$  (molal for aqueous U and moles for solids)

Case 17 (N18A1103/N18{B,C,D}1012) simulated a first-stage run in which steel components and HLW glass degraded at the average rates with water percolation rate of  $0.15 \text{ m}^3/\text{yr}$ . The second stage started with large amounts of HLW glass and steels left over from the first stage. Similar to Case 16, even when all steel components are degraded, the pH increased. However, the solution was not alkaline enough to dissolve principal uranium phase (soddyite). The second stage simulation calculated no loss of U and Gd.

In an effort to calculate the effects of HLW glass on losses of U and Gd, Case 18 (N19A2004/N19{B,C,D}1112) was initiated. At stage one of this case water came in contact with steel components outside the DOE SNF canister. The second stage started with water coming in contact with HLW glass and all other components inside the 18-inch SNF canister with percolation rate of  $0.015 \text{ m}^3/\text{year}$ . Figures 5-17 and 5-18 show that the pH of the water reached 7.8 with no steel left to buffer. The pH was controlled with rate of water flow through the WP. There was no loss of U and Gd.

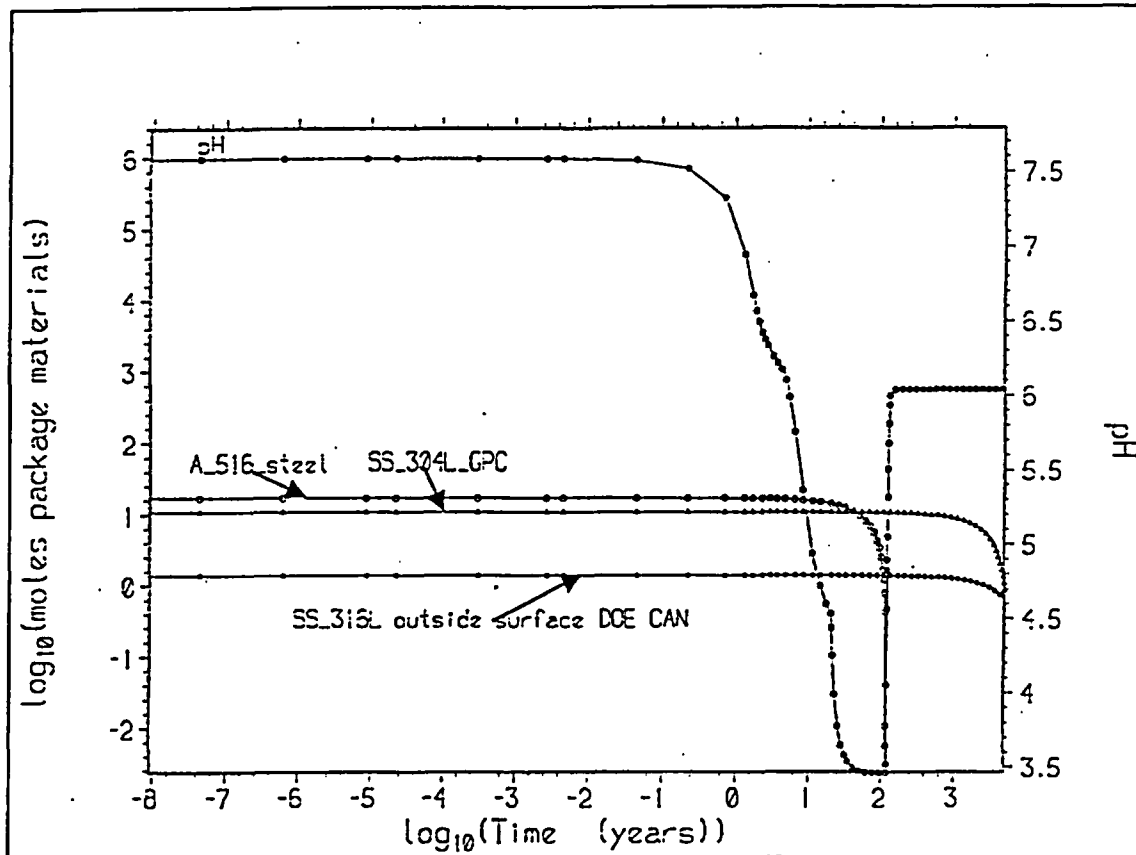


Figure 5-17. Case 18, First Stage (N19A2004): pH, Aqueous U, Soddyite and Moles Package Materials (Outside the DOE SNF Canister) as a Function of Time, J-13 Well Water Percolation Rate of  $0.5 \text{ m}^3/\text{year}$  (molal for aqueous U and moles for solids)

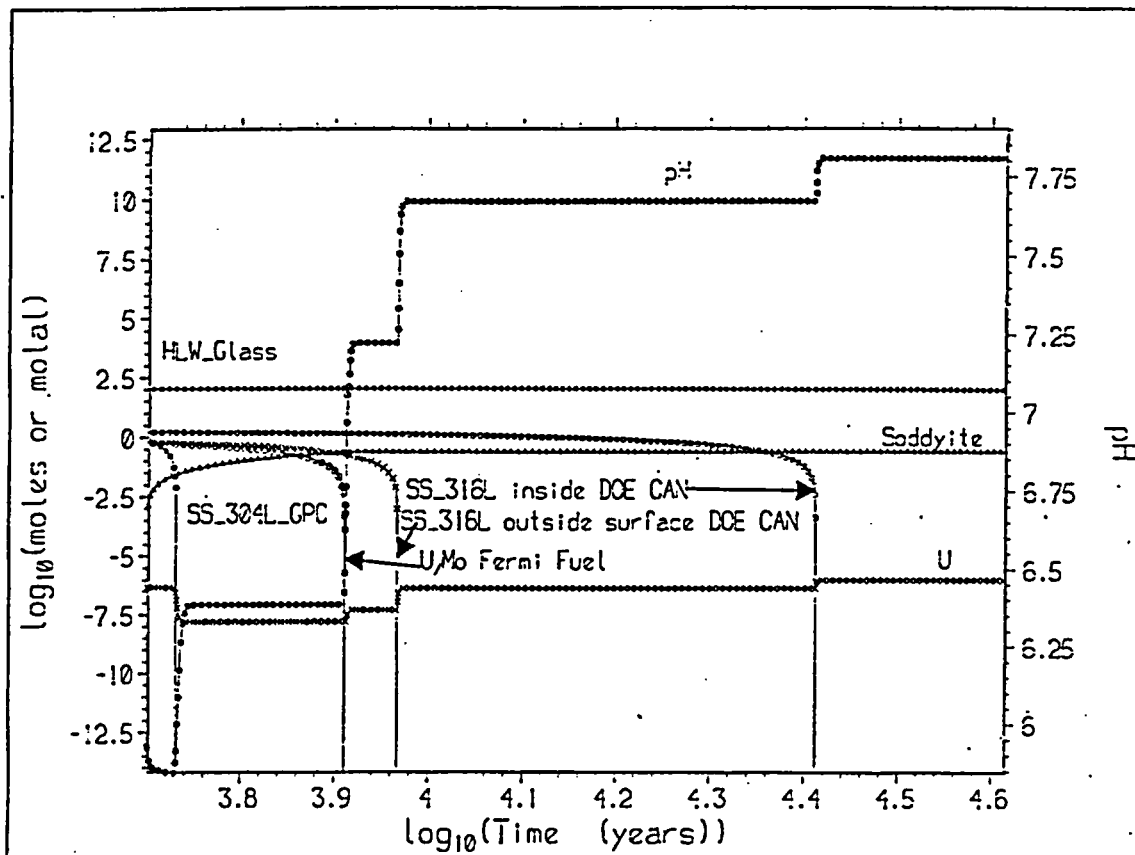


Figure 5-18. Case 18, Second stage (N19B1011): pH, Aqueous U, Soddyite and Moles Package Materials (Inside the DOE SNF Canister and Remaining from First Stage) as Function of Time, J-13 Well Water Percolation Rate of  $0.015 \text{ m}^3/\text{year}$  (molal, moles/kg, for ionic species and moles for solids)

## 6. RESULTS

### 6.1 SUMMARY OF THE RESULTS

A principal objective of these calculations was to assess the chemical circumstances that could lead to removal of neutron absorbers (Gd) from the waste package, while fissile materials (U) remaining behind. Such circumstances could increase the probability of a nuclear criticality occurrence within the waste package. Gadolinium is assumed to be present as  $\text{GdPO}_4$  that is combined with iron shot to produce Gd-doped iron shot which is distributed among the 4-inch stainless steel pipes containing the fuel pins in the 18-inch DOE SNF canister. Water with composition of J-13 well water is assumed to drip in through an opening at the top of the WP, pooling inside and eventually overflowing, allowing removal of soluble components through continual dilution. This calculation selected 18 EQ6 cases and examined the results to identify the reasons for the chemical changes during degradation of waste package materials and flushing by J-13 well water. It appeared that, even in unusual conditions, loss of Gd was insignificant, when the element was present in the package as solid  $\text{GdPO}_4$ . The scenarios and conditions of EQ6 were chosen to emphasize conditions that could create either acid or alkaline conditions, and to determine if these conditions are of sufficient duration to induce Gd loss. Nevertheless, the differences in the results were in all instances small.

Eighteen EQ6 reaction-path cases were constructed to span the range of possible Gd and fuel corrosion (Tables 5-8 and 5-9). Two general EQ6 scenarios were selected: single- and multiple-stages. Cases 1 through 9 were single-stage cases, where high pH was achieved by simultaneous exposure of fuel to degrading glass. The single-stage EQ6 Cases 1 through 9 produced insignificant Gd loss; the total loss was  $\leq 2.3\%$  in  $\geq 2.5 \times 10^5$  years. Furthermore, when the HLW glass was allowed to degrade rapidly, the alkaline conditions produced high U loss (Table 5-9, Cases 3 through 7), reducing the chances of internal criticality. Some of these "alkaline" cases actually produced short-lived, very low pH ( $\sim 3$ ) when glass corrosion rates were set to low values, but steel corrosion rates were set to high values. These low-pH values may not be realistic, since the simple glass corrosion model does not allow a feedback between pH and corrosion rate (which would tend to increase pH).

Multiple-stage cases were Cases 10 through 18 of Table 5-9. These cases tested the effect of exposing the Gd and U to long-lived acidic conditions (pH  $\sim 5$  to 6). The highest level of acidity was achieved during first-stage EQ6 simulations. In the first stage it was assumed that the DOE SNF canister was intact, and only the HLW glass and its container, the A516 outer web structure, and the outside surface of the DOE SNF canister were allowed to interact with the water dripping into the package. With a sufficiently high drip rate, the alkaline components of the glass are removed during this stage. In the second stage, the Gd-doped iron shot, fuel, and other components within the DOE SNF canister are exposed to J-13 well water at a much lower drip rate, allowing pH to drop. When hematite formation was suppressed (in favor of goethite); somewhat lower pH was achieved. Cases 9 through 12 resulted in no significant loss of Gd, but a few percent loss of U (Table 5-9). However, in all cases the predicted major corrosion products are: an Fe-rich smectite clay (nontronite); hematite or goethite; pyrolusite; rutile; and

$\text{Ni}_2\text{SiO}_4$  or  $\text{NiFe}_2\text{O}_4$ . The smectite and Fe oxide typically comprise over 90% of the corrosion product volume. The Gd enters into rhabdophane (hydrated  $\text{GdPO}_4$ ) as the iron shot corrodes, and the dominant U solid is soddyite ( $(\text{UO}_2)_2(\text{SiO}_4) \cdot 2\text{H}_2\text{O}$ ). The detail of each run is explained in Section 5.3.

## **6.2 TBV DISCLAIMER**

Existing data were used in the development of the results presented in this section. Therefore, the use of any data from this calculation for input into documents supporting procurement, fabrication, or construction is required to be identified and tracked as TBV in accordance with appropriate procedures.

**7. REFERENCES**

- 1 Department of Energy (DOE), Office of Environmental Management 1999. *Fermi (U-Mo) Fuel Characteristics for Disposal Criticality Analysis*. DOE/SNF/REP-035 Revision 0. Idaho Falls, Idaho: Idaho National Engineering and Environmental Laboratory. TIC: 242461.
- 2 Civilian Radioactive Waste Management System (CRWMS) Management & Operating Contractor (M&O) 1998. *EQ6 Calculation for Chemical Degradation of Fast Flux Test Facility (FFTF) Waste Packages*. BBA000000-01717-0210-00028 REV 00. Las Vegas, Nevada: M&O. ACC: MOL.19981229.0081.
- 3 CRWMS M&O 1998. *Total System Performance Assessment-Viability Assessment (TSPA-VA) Analyses Technical Basis Document. Chapter 10, Disruptive Events*. B00000000-01717-4301-00010 REV 00. Las Vegas, Nevada: M&O. ACC: MOL.19980724.0399.
- 4 CRWMS M&O 1998. *Evaluation of Codisposal Viability for Aluminum-Clad DOE-Owned Spent Fuel: Phase II. Degraded Codisposal Waste Package Internal Criticality*. BBA000000-01717-5705-00017 REV 01. Las Vegas, Nevada: M&O. ACC: MOL.19980616.0098.
- 5 National Research Council of the National Academy of Sciences 1995. *Technical Bases for Yucca Mountain Standards*. Washington, D.C.: National Academy Press. TIC: 104273.
- 6 Harrar, J.E.; Carley, J.F.; Isherwood, W.F.; and Raber, E. 1990. *Report of the Committee to Review the Use of J-13 Well Water in Nevada Nuclear Waste Storage Investigations*. UCID-21867. Livermore, California: Lawrence Livermore National Laboratory (LLNL). ACC: MOL.19980416.0660.
- 7 Wolery, T.J. 1992. *EQ3/6, A Software Package for Geochemical Modeling of Aqueous Systems: Package Overview and Installation Guide (Version 7.0)*. UCRL-MA-110662 PT I. Livermore, California: LLNL. TIC: 205087.
- 8 Daveler, S.A. and Wolery, T.J. 1992. *EQPT, A Data File Preprocessor for the EQ3/6 Software Package: User's Guide, and Related Documentation (Version 7.0)*. UCRL-MA-110662 PT II. Livermore, California: LLNL. TIC: 205240.
- 9 Wolery, T.J. 1992. *EQ3NR, A Computer Program for Geochemical Aqueous Speciation-Solubility Calculations: Theoretical Manual, User's Guide, and Related Documentation (Version 7.0)*. UCRL-MA-110662 PT III. Livermore, California: LLNL. TIC: 205154.



- 
- 10 Wolery, T.J. and Daveler, S.A. 1992. *EQ6, A Computer Program for Reaction Path Modeling of Aqueous Geochemical Systems: Theoretical Manual, User's Guide, and Related Documentation (Version 7.0)*. UCRL-MA-110662 PT IV. Livermore, California: LLNL. TIC: 205002.
  - 11 Spahiu, K. and Bruno, J. 1995. *A Selected Thermodynamic Database for REE to be Used in HLNW Performance Assessment Exercises*. SKB Technical Report 95-35. Stockholm, Sweden: Swedish Nuclear Fuel and Waste Management Co. TIC: 225493.
  - 12 CRWMS M&O 1998. *Electronic Media (CD): The Calculation Files for EQ6 Calculation for Chemical Degradation of Enrico Fermi Spent Nuclear Fuel Waste Packages*. BBA000000-01717-0210-00029 REV 00. Las Vegas, Nevada: M&O. ACC: MOL.19990507.0237.
  - 13 CRWMS M&O 1998. *Viability Assessment of a Repository at Yucca Mountain. Volume 3: Total system Performance Assessment*. B00000000-01717-4301-00003 REV 01. Las Vegas, Nevada: M&O. ACC: MOL.19981007.0030.
  - 14 Firsching, F.H. and Brune, S.N. 1991. "Solubility Products of the Trivalent Rare-Earth Phosphates." *Jour. Chem. Eng. Data*, 36, 93-95. American Chemical Society. TIC: 240863.
  - 15 Yang, I.C.; Rattray, G.W.; and Yu, P. 1996. *Interpretation of Chemical and Isotopic Data from Boreholes in the Unsaturated-Zone at Yucca Mountain, Nevada*. Water Resources Investigations Report 96-4058. Denver, Colorado: U.S. Geological Survey. ACC: MOL.19980528.0216.
  - 16 Weast, R.C., ed. 1977. *CRC Handbook of Chemistry and Physics, 58th Ed.* Cleveland, Ohio: CRC Press, Inc. TIC: 242376.
  - 17 CRWMS M&O 1996. *Second Waste Package Probabilistic Criticality Analysis: Generation and Evaluation of Internal Criticality Configurations*. BBA000000-01717-2200-00005 REV 00. Las Vegas, Nevada: M&O. ACC: MOL.19960924.0193.
  - 18 Hillner, E.; Franklin D.G.; and Smee J.D. 1994. *The Corrosion of Zircaloy-Clad Fuel Assemblies in a Geologic Repository Environment*. West Mifflin, Pennsylvania: Bettis Atomic Power Laboratory. TIC: 237127.
  - 19 CRWMS M&O 1998. *EQ6 Calculations for Chemical Degradation of Pu-Ceramic Waste Packages*. BBA000000-01717-0210-00018 REV 00. Las Vegas, Nevada: M&O. ACC: MOL.19980918.0004.

## Waste Package Operations

## Calculation

Title: EQ6 Calculations for Chemical Degradation of Enrico Fermi Spent Nuclear Fuel Waste Packages

Document Identifier: BBA000000-01717-0210-00029 REV 00

Page 50 of 51

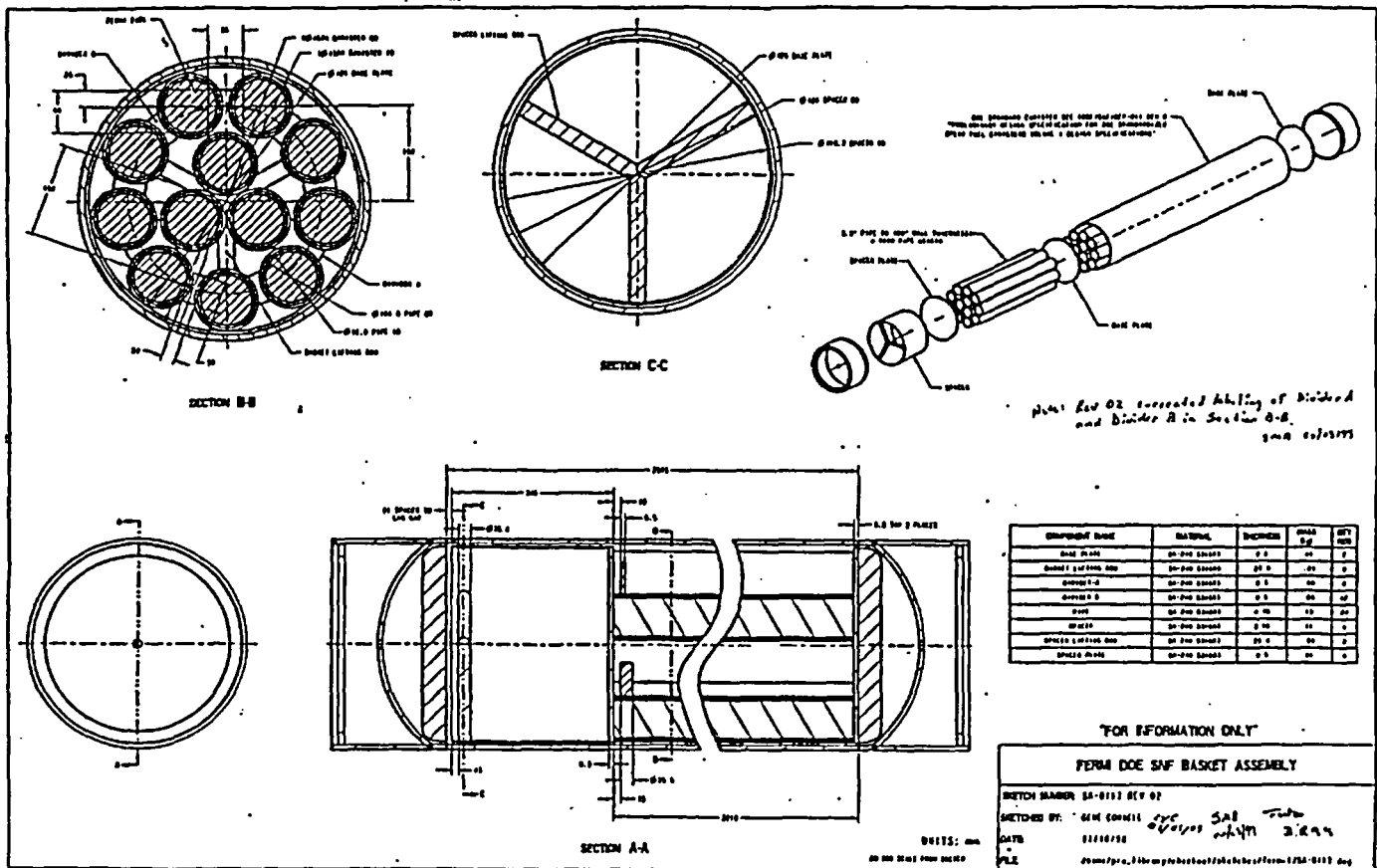
- 20 CRWMS M&O 1998. *EQ3/6 Software Installation and Testing Report for Pentium Based Personal Computers (PCs)*. CSCI: LLYMP9602100. Las Vegas, Nevada: M&O. ACC: MOL.19980813.0191.
- 21 CRWMS M&O 1998. *EQ6 Calculations for Chemical Degradation of PWR and MOX Spent Fuel Waste Packages*. BBA000000-01717-0210-00009 REV 00. Las Vegas, Nevada: M&O. ACC: MOL.19980701.0483.
- 22 CRWMS M&O 1999. *DOE SRS HLW Glass Chemical Composition*. BBA000000-01717-0210-00038 REV 00. Las Vegas, Nevada: M&O. ACC: MOL.19990215.0397.
- 23 DOE/RW 1992. *Characteristics of Potential Repository Wastes*. DOE/RW-0184-R1 vol. 1, p. 3.3-15, Table 3.3.8. Oak Ridge, Tennessee: Martin Marietta Energy Systems, Inc. ACC: HQO.19920827.0001.
- 24 CRWMS M&O 1995. *Total System Performance Assessment - 1995: An Evaluation of the Potential Yucca Mountain Repository*. B00000000-01717-2200-00136 REV 01. Las Vegas, Nevada: M&O. ACC: MOL.19960724.0188.
- 25 CRWMS M&O 1998. *Unsaturated-Zone Flow: Preliminary Draft Section 2.3 of TSPA-VA Document*. B00000000-01717-2200-00201. Las Vegas, Nevada: M&O. ACC: MOL.19980428.0202.
- 26 CRWMS M&O 1996. *Status Report on Degraded Mode Criticality Analysis of Immobilized Plutonium Waste Forms in a Geologic Repository*. A00000000-01717-5705-00013 REV 00. Vienna, Virginia: M&O. ACC: MOL.19970324.0023.
- 27 CRWMS M&O 1997. *Degraded Mode Criticality Analysis of Immobilized Plutonium Waste Forms in a Geologic Repository*. A00000000-01717-5705-00014 REV 01. Las Vegas, Nevada: M&O. ACC: MOL.19980422.0911.
- 28 Roberts, W.L.; Rapp, Jr., G.R.; and Weber, J. 1974. *Encyclopedia of Minerals*. New York, New York: van Nostrand Reinhold Co. TIC: 238571.
- 29 CRWMS M&O 1996. *Material Compositions and Number Densities For Neutronics Calculations*. BBA000000-01717-0200-00002 REV 00. Las Vegas, Nevada: M&O. ACC: MOL.19960624.0023.
- 30 Walker, F.W.; Parrington, J.R.; and Feiner, F. 1989. *Nuclides and Isotopes, 14th ed., Chart of the Nuclides*. San Jose, California: General Electric Co. TIC: 201637.
- 31 CRWMS M&O 1998. *Disposal Criticality Analysis Methodology Topical Report*. B00000000-01717-5705-00095 REV 00. Las Vegas, Nevada: M&O. ACC: MOL.19980918.0005.

**8. ATTACHMENTS**

**Attachment I. Sketch SK-0117 REV 01 (1 page)**

**Attachment II. Sketch SK-0069 REV 02 (1 page)**

**Attachment III. Directory Listing of Files on Electronic Media (6 pages)**



FOR INFORMATION ONLY

5-DHLN/DOE SPENT FUEL DISPOSAL CONTAINER

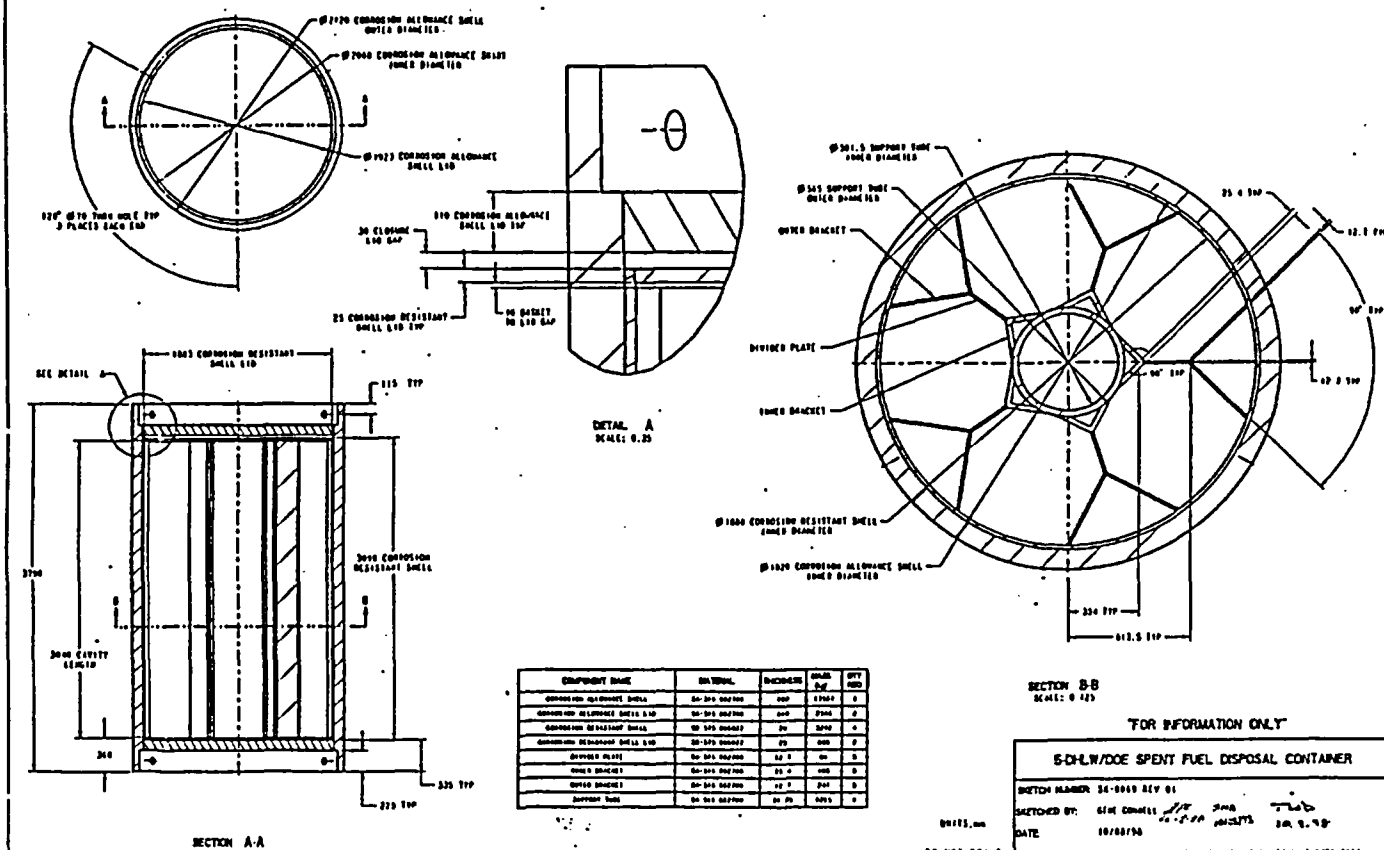
DETROIT NUMBER 34-8049 2(V 01

SKETCHED BY: GIM COMELL *1/18* JMB *7-60*  
DATE: 10/22/76 *10-2-76* MJC/JS *10 9 78*

FILE #bom/po.0.2b:wp/1:bas/001/pd/000001/dato.204/20-0011 dm

gniff.no

DO NOT SCALE



### Attachment III. Directory Listing of Files on Electronic Media

This attachment contains the MS-DOS directory listing of the electronic media (Ref. 12).

Following file types are in the main directory

- 1) Excel files (extension = xls), called out in the text and tables;
- 2) A draft copy of this calculation document, 315F.doc as of 05-02-99.

Following file types are in the "CD Files" directory

- 1) EQ6 input files (extension = 6i), as discussed in Section 5.3.1, have 8-character names N???????6i;
- 2) EQ6 output files (text, extension = 6o);
- 3) Tab-delimited text files (extension = txt), with names N???????elem????txt. as discussed in Section 5.3.2; these contain total aqueous moles (\*.elem\_aqu.txt), total moles in minerals and aqueous phase (\*.elem\_m\_a.txt), total moles in minerals, aqueous phase, and remaining special reactants (\*.elem\_tot.txt), and the total moles in minerals alone (\*.elem\_min.txt). The \*.elem\_tot.txt and \*.elem\_min.txt also have the volume in cm<sup>3</sup> of the minerals and total solids (including special reactants) in the system;
- 4) FORTRAN source files (extension = for) for the version of EQ6 used in the calculations;
- 5) MS-DOS/Win95/Win98 executables (extension = exe) for the version of EQ6 and runeq6 used in the calculations, and the autoexec.bat file that sets up the environment; and
- 6) EQ6 data files used for the calculations, with the text file data0.nuc.R8a, and the binary version data1.nuc.

Directory of E:\

```
315F      DOC      5,102,592  05-04-99  1:05p 315F.doc
CDFILE-5   <DIR>           05-10-99  2:39p cd files
FERMI-24  XLS      153,088   03-24-99  4:23p Fermi_Fuel_kz.xls
          2 file(s)      5,255,680 bytes
```

Directory of E:\cd files

```
.          <DIR>           03-24-99  4:23p .
..         <DIR>           03-24-99  4:23p ..
EQ6NEW    EXE      1,056,469  11-25-98  1:46p EQ6NEW.EXE
EQ6NEW    FOR      1,322,426  11-25-98  12:49p eq6new.for
EQ6NEW1A  EXE      690,635   11-23-98  3:59p eq6new1A.exe
EQ6NEW1B  EXE      376,832   11-23-98  3:58p eq6new1B.exe
EQLIBNEW  FOR      492,613   07-01-98  6:34p eqlibnew.for
EXTERNAL  FNT       9,900    06-29-95  8:27p EXTERNAL.FNT
HELP_PP   PP       50,724    03-31-98  6:04p HELP_PP
N!1A2204  6I       39,695    02-08-99  10:53a n!1a2204.6i
N!1A2204  6O      4,210,179   02-16-99  1:23p n!1a2204.6o
N!1A2-48  TXT       37,001   02-16-99  1:23p N!1A2204.elem_aqu.txt
N!1A2-50  TXT       35,264   02-16-99  1:23p N!1A2204.elem_m_a.txt
N!1A2-52  TXT       35,256   02-16-99  1:23p N!1A2204.elem_min.txt
N!1A2-54  TXT       35,269   02-16-99  1:23p N!1A2204.elem_tot.txt
N01A2204  6I      40,702    02-08-99  10:26a N01A2204.6i
```

N01A2204	60	1,198,719	02-08-99	10:46a	n01a2204.6o
N01A2-64	TXT	10,741	02-07-99	2:44p	N01A2204.elem_aqu.txt
N01A2-66	TXT	10,252	02-07-99	2:44p	N01A2204.elem_m_a.txt
N01A2-68	TXT	10,244	02-07-99	2:44p	N01A2204.elem_min.txt
N01A2-70	TXT	10,257	02-07-99	2:44p	N01A2204.elem_tot.txt
N02B1012	6I	42,572	02-08-99	3:23p	N02B1012.6i
N02B1012	60	5,658,001	02-08-99	8:07p	n02b1012.6o
N02B1-92	TXT	50,636	02-08-99	8:07p	N02B1012.elem_aqu.txt
N02B1-96	TXT	48,251	02-08-99	8:07p	N02B1012.elem_m_a.txt
N02B1-98	TXT	48,243	02-08-99	8:07p	N02B1012.elem_min.txt
N02B-100	TXT	48,256	02-08-99	8:07p	N02B1012.elem_tot.txt
N03B1012	6I	42,572	02-08-99	3:23p	N03B1012.6i
N03B1012	60	2,020,300	02-08-99	8:25p	n03b1012.6o
N03B-112	TXT	19,831	02-08-99	8:25p	N03B1012.elem_aqu.txt
N03B-114	TXT	18,910	02-08-99	8:25p	N03B1012.elem_m_a.txt
N03B-116	TXT	18,902	02-08-99	8:25p	N03B1012.elem_min.txt
N03B-118	TXT	18,915	02-08-99	8:25p	N03B1012.elem_tot.txt
N03C1012	6I	34,160	02-09-99	1:57p	N03C1012.6i
N03C1012	60	3,355,475	02-09-99	8:13p	n03c1012.6o
N03C-134	TXT	30,436	02-09-99	8:13p	N03C1012.elem_aqu.txt
N03C-136	TXT	29,011	02-09-99	8:13p	N03C1012.elem_m_a.txt
N03C-138	TXT	29,003	02-09-99	8:13p	N03C1012.elem_min.txt
N03C-140	TXT	29,016	02-09-99	8:13p	N03C1012.elem_tot.txt
N04^1012	6I	34,234	02-12-99	10:41a	N04^1012.6i
N04^1012	60	3,789,788	02-12-99	12:28p	n04^1012.6o
N04^-158	TXT	33,466	02-12-99	12:28p	n04^1012.elem_aqu.txt
N04^-160	TXT	31,897	02-12-99	12:28p	n04^1012.elem_m_a.txt
N04^-162	TXT	31,889	02-12-99	12:28p	n04^1012.elem_min.txt
N04^-164	TXT	31,902	02-12-99	12:28p	n04^1012.elem_tot.txt
N04B1012	6I	42,572	02-08-99	3:23p	N04B1012.6i
N04B1012	60	2,032,675	02-08-99	8:44p	n04b1012.6o
N04B-176	TXT	19,831	02-08-99	8:44p	N04B1012.elem_aqu.txt
N04B-178	TXT	18,910	02-08-99	8:44p	N04B1012.elem_m_a.txt
N04B-180	TXT	18,902	02-08-99	8:44p	N04B1012.elem_min.txt
N04B-182	TXT	18,915	02-08-99	8:44p	N04B1012.elem_tot.txt
N04C1012	6I	34,160	02-09-99	1:57p	N04C1012.6i
N04C1012	60	254,561	02-09-99	8:15p	n04c1012.6o
N04C-188	TXT	2,661	02-09-99	8:15p	N04C1012.elem_aqu.txt
N04C-190	TXT	2,556	02-09-99	8:15p	N04C1012.elem_m_a.txt
N04C-192	TXT	2,548	02-09-99	8:15p	N04C1012.elem_min.txt
N04C-194	TXT	2,561	02-09-99	8:15p	N04C1012.elem_tot.txt
N06_1113	6I	42,508	02-05-99	3:44p	N06_1113.6i
N06_1113	60	7,502,688	02-06-99	5:40p	n06_1113.6o
N06_-222	TXT	70,836	02-06-99	5:40p	N06_1113.elem_aqu.txt
N06_-226	TXT	67,491	02-06-99	5:40p	N06_1113.elem_m_a.txt
N06_-228	TXT	67,483	02-06-99	5:40p	N06_1113.elem_min.txt
N06_-230	TXT	67,496	02-06-99	5:40p	N06_1113.elem_tot.txt
N07_1111	6I	42,508	02-05-99	3:48p	N07_1111.6i
N07_1111	60	4,829,204	02-06-99	6:12p	n07_1111.6o
N07_-250	TXT	48,616	02-06-99	6:12p	N07_1111.elem_aqu.txt
N07_-252	TXT	46,327	02-06-99	6:12p	N07_1111.elem_m_a.txt
N07_-254	TXT	46,319	02-06-99	6:12p	N07_1111.elem_min.txt
N07_-256	TXT	46,332	02-06-99	6:12p	N07_1111.elem_tot.txt
N08_1211	6I	42,585	02-05-99	3:49p	N08_1211.6i
N08_1211	60	4,129,755	02-06-99	6:52p	n08_1211.6o
N08_-276	TXT	41,041	02-06-99	6:52p	N08_1211.elem_aqu.txt
N08_-278	TXT	39,112	02-06-99	6:52p	N08_1211.elem_m_a.txt

N08_-280 TXT	39,104	02-06-99	6:52p	N08_1211.elem_min.txt
N08_-282 TXT	39,117	02-06-99	6:52p	N08_1211.elem_tot.txt
N09_2211 6I	42,585	02-05-99	3:50p	N09_2211.6i
N09_2211 6O	4,824,485	02-06-99	7:37p	n09_2211.6o
N09_-302 TXT	48,111	02-06-99	7:37p	N09_2211.elem_aqu.txt
N09_-304 TXT	45,846	02-06-99	7:37p	N09_2211.elem_m_a.txt
N09_-306 TXT	45,838	02-06-99	7:37p	N09_2211.elem_min.txt
N09_-308 TXT	45,851	02-06-99	7:37p	N09_2211.elem_tot.txt
N10_2111 6I	42,587	02-05-99	3:51p	N10_2111.6i
N10_2111 6O	4,889,780	02-06-99	8:08p	n10_2111.6o
N10_-328 TXT	49,626	02-06-99	8:08p	N10_2111.elem_aqu.txt
N10_-332 TXT	47,289	02-06-99	8:08p	N10_2111.elem_m_a.txt
N10_-334 TXT	47,281	02-06-99	8:08p	N10_2111.elem_min.txt
N10_-336 TXT	47,294	02-06-99	8:08p	N10_2111.elem_tot.txt
N11_1212 6I	42,585	02-05-99	3:53p	N11_1212.6i
N11_1212 6O	4,708,735	02-20-99	10:27a	n11_1212.6o
N11_-356 TXT	46,091	02-06-99	8:56p	N11_1212.elem_aqu.txt
N11_-358 TXT	43,922	02-06-99	8:56p	N11_1212.elem_m_a.txt
N11_-360 TXT	43,914	02-06-99	8:56p	N11_1212.elem_min.txt
N11_-362 TXT	43,927	02-06-99	8:56p	N11_1212.elem_tot.txt
N11_B121 6I	34,074	02-21-99	4:40p	N11_B121.6i
N11_B121 6O	2,685,215	02-21-99	5:51p	n11_b121.6o
N11_-376 TXT	25,891	02-21-99	5:51p	N11_B121.elem_aqu.txt
N11_-378 TXT	24,682	02-21-99	5:51p	N11_B121.elem_m_a.txt
N11_-380 TXT	24,674	02-21-99	5:51p	N11_B121.elem_min.txt
N11_-382 TXT	24,687	02-21-99	5:51p	N11_B121.elem_tot.txt
N12_2212 6I	42,585	02-05-99	3:54p	N12_2212.6i
N12_2212 6O	7,902,655	02-06-99	10:06p	n12_2212.6o
N12_-412 TXT	74,371	02-06-99	10:06p	N12_2212.elem_aqu.txt
N12_-414 TXT	70,858	02-06-99	10:06p	N12_2212.elem_m_a.txt
N12_-416 TXT	70,850	02-06-99	10:06p	N12_2212.elem_min.txt
N12_-418 TXT	70,863	02-06-99	10:06p	N12_2212.elem_tot.txt
N13_2112 6I	42,585	02-05-99	3:56p	N13_2112.6i
N13_2112 6O	3,304,413	02-06-99	10:24p	n13_2112.6o
N13_-434 TXT	34,981	02-06-99	10:24p	N13_2112.elem_aqu.txt
N13_-436 TXT	33,340	02-06-99	10:24p	N13_2112.elem_m_a.txt
N13_-438 TXT	33,332	02-06-99	10:24p	N13_2112.elem_min.txt
N13_-440 TXT	33,345	02-06-99	10:24p	N13_2112.elem_tot.txt
N13_A112 6I	42,759	02-08-99	9:53a	N13_A112.6i
N13_A112 6O	3,342,121	02-11-99	2:15p	n13_a112.6o
N13_-456 TXT	35,486	02-11-99	2:15p	N13_A112.elem_aqu.txt
N13_-458 TXT	33,821	02-11-99	2:15p	N13_A112.elem_m_a.txt
N13_-460 TXT	33,813	02-11-99	2:15p	N13_A112.elem_min.txt
N13_-462 TXT	33,826	02-11-99	2:15p	N13_A112.elem_tot.txt
N13_B112 6I	37,019	02-15-99	10:00a	N13_B112.6i
N13_B112 6O	4,229,452	02-15-99	3:52p	n13_b112.6o
N13_-482 TXT	37,506	02-15-99	3:51p	N13_B112.elem_aqu.txt
N13_-484 TXT	35,745	02-15-99	3:51p	N13_B112.elem_m_a.txt
N13_-486 TXT	35,737	02-15-99	3:51p	N13_B112.elem_min.txt
N13_-488 TXT	35,750	02-15-99	3:51p	N13_B112.elem_tot.txt
N14B2012 6I	43,707	02-08-99	3:23p	N14B2012.6i
N14B2012 6O	5,099,083	02-09-99	9:03p	n14b2012.6o
N14B-508 TXT	47,101	02-09-99	9:03p	N14B2012.elem_aqu.txt
N14B-510 TXT	44,884	02-09-99	9:03p	N14B2012.elem_m_a.txt
N14B-514 TXT	44,876	02-09-99	9:03p	N14B2012.elem_min.txt
N14B-516 TXT	44,889	02-09-99	9:03p	N14B2012.elem_tot.txt
N16B2011 6I	43,707	02-08-99	3:23p	N16B2011.6i



N16B2011	60	1,940,773	02-09-99	9:17p	n16b2011.6o
N16B-528	TXT	19,326	02-09-99	9:17p	N16B2011.elem_aqu.txt
N16B-530	TXT	18,429	02-09-99	9:17p	N16B2011.elem_m_a.txt
N16B-532	TXT	18,421	02-09-99	9:17p	N16B2011.elem_min.txt
N16B-534	TXT	18,434	02-09-99	9:17p	N16B2011.elem_tot.txt
N17A1203	6I	40,831	02-08-99	2:44p	N17A1203.6i
N17A1203	60	2,746,508	02-17-99	5:43p	n17a1203.6o
N17A-548	TXT	26,901	02-17-99	5:43p	N17A1203.elem_aqu.txt
N17A-550	TXT	25,644	02-17-99	5:43p	N17A1203.elem_m_a.txt
N17A-552	TXT	25,636	02-17-99	5:43p	N17A1203.elem_min.txt
N17A-554	TXT	25,649	02-17-99	5:43p	N17A1203.elem_tot.txt
N17B1011	6I	42,908	02-10-99	5:01p	N17B1011.6i
N17B1011	60	1,686,019	02-11-99	1:03p	n17b1011.6o
N17B-566	TXT	16,296	02-11-99	1:03p	N17B1011.elem_aqu.txt
N17B-568	TXT	15,543	02-11-99	1:03p	N17B1011.elem_m_a.txt
N17B-570	TXT	15,535	02-11-99	1:03p	N17B1011.elem_min.txt
N17B-572	TXT	15,548	02-11-99	1:03p	N17B1011.elem_tot.txt
N17C1011	6I	37,050	02-18-99	1:20p	N17C1011.6i
N17C1011	60	7,274,255	02-15-99	1:53p	n17c1011.6o
N17C-598	TXT	64,776	02-15-99	1:53p	N17C1011.elem_aqu.txt
N17C-602	TXT	61,719	02-15-99	1:53p	N17C1011.elem_m_a.txt
N17C-604	TXT	61,711	02-15-99	1:53p	N17C1011.elem_min.txt
N17C-606	TXT	61,724	02-15-99	1:53p	N17C1011.elem_tot.txt
N18A1103	6I	40,776	02-05-99	4:02p	N18A1103.6i
N18A1103	60	2,867,982	02-05-99	10:45p	n18a1103.6o
N18A-620	TXT	30,436	02-05-99	10:45p	N18A1103.elem_aqu.txt
N18A-622	TXT	29,011	02-05-99	10:45p	N18A1103.elem_m_a.txt
N18A-624	TXT	29,003	02-05-99	10:45p	N18A1103.elem_min.txt
N18A-626	TXT	29,016	02-05-99	10:45p	N18A1103.elem_tot.txt
N18B1012	6I	45,505	02-06-99	12:32p	N18B1012.6i
N18B1012	60	7,904,678	02-06-99	11:40p	n18b1012.6o
N18B-656	TXT	68,816	02-06-99	11:40p	N18B1012.elem_aqu.txt
N18B-658	TXT	65,567	02-06-99	11:40p	N18B1012.elem_m_a.txt
N18B-660	TXT	65,559	02-06-99	11:40p	N18B1012.elem_min.txt
N18B-662	TXT	65,572	02-06-99	11:40p	N18B1012.elem_tot.txt
N18C1012	6I	39,975	02-08-99	9:35a	N18C1012.6i
N18C1012	60	6,999,417	02-08-99	9:51p	n18c1012.6o
N18C-690	TXT	57,706	02-08-99	9:50p	N18C1012.elem_aqu.txt
N18C-692	TXT	54,985	02-08-99	9:50p	N18C1012.elem_m_a.txt
N18C-694	TXT	54,977	02-08-99	9:50p	N18C1012.elem_min.txt
N18C-696	TXT	54,990	02-08-99	9:50p	N18C1012.elem_tot.txt
N18D1012	6I	40,271	02-09-99	1:48p	N18D1012.6i
N18D1012	60	6,576,284	02-09-99	10:14p	n18d1012.6o
N18D-722	TXT	52,151	02-09-99	10:14p	N18D1012.elem_aqu.txt
N18D-724	TXT	49,694	02-09-99	10:14p	N18D1012.elem_m_a.txt
N18D-726	TXT	49,686	02-09-99	10:14p	N18D1012.elem_min.txt
N18D-728	TXT	49,699	02-09-99	10:14p	N18D1012.elem_tot.txt
N19A2004	6I	37,816	02-05-99	4:03p	N19A2004.6i
N19A2004	60	3,180,541	02-05-99	9:56p	n19a2004.6o
N19A-744	TXT	33,466	02-05-99	9:56p	N19A2004.elem_aqu.txt
N19A-746	TXT	31,897	02-05-99	9:56p	N19A2004.elem_m_a.txt
N19A-748	TXT	31,889	02-05-99	9:56p	N19A2004.elem_min.txt
N19A-750	TXT	31,902	02-05-99	9:56p	N19A2004.elem_tot.txt
N19B1112	6I	43,865	02-06-99	12:38p	N19B1112.6i
N19B1112	60	7,943,000	02-07-99	12:56a	n19b1112.6o
N19B-778	TXT	69,826	02-07-99	12:56a	N19B1112.elem_aqu.txt
N19B-780	TXT	66,529	02-07-99	12:56a	N19B1112.elem_m_a.txt

N19B-782 TXT	66,521	02-07-99	12:56a	N19B1112.elem_min.txt
N19B-784 TXT	66,534	02-07-99	12:56a	N19B1112.elem_tot.txt
N19C1112 6I	37,151	02-08-99	9:35a	N19C1112.6i
N19C1112 6O	6,902,402	02-08-99	10:57p	n19c1112.6o
N19C-810 TXT	57,201	02-08-99	10:57p	N19C1112.elem_aqu.txt
N19C-812 TXT	54,504	02-08-99	10:57p	N19C1112.elem_m_a.txt
N19C-814 TXT	54,496	02-08-99	10:57p	N19C1112.elem_min.txt
N19C-816 TXT	54,509	02-08-99	10:57p	N19C1112.elem_tot.txt
N19D1112 6I	37,403	02-09-99	1:46p	N19D1112.6i
N19D1112 6O	6,381,646	02-09-99	11:12p	n19d1112.6o
N19D-840 TXT	50,636	02-09-99	11:11p	N19D1112.elem_aqu.txt
N19D-842 TXT	48,251	02-09-99	11:11p	N19D1112.elem_m_a.txt
N19D-844 TXT	48,243	02-09-99	11:11p	N19D1112.elem_min.txt
N19D-846 TXT	48,256	02-09-99	11:11p	N19D1112.elem_tot.txt
N5_A1114 6I	42,582	02-09-99	11:51a	N5_A1114.6i
N5_A1114 6O	8,105,217	02-19-99	8:00p	n5_a1114.6o
N5_A-876 TXT	76,391	02-19-99	8:00p	N5_A1114.elem_aqu.txt
N5_A-878 TXT	72,782	02-19-99	8:00p	N5_A1114.elem_m_a.txt
N5_A-880 TXT	72,774	02-19-99	8:00p	N5_A1114.elem_min.txt
N5_A-884 TXT	72,787	02-19-99	8:00p	N5_A1114.elem_tot.txt
N5_B1114 6I	39,351	02-10-99	9:41a	N5_B1114.6i
N5_B1114 6O	5,296,764	02-19-99	10:05p	n5_b1114.6o
N5_B-904 TXT	43,061	02-19-99	10:05p	N5_B1114.elem_aqu.txt
N5_B-906 TXT	41,036	02-19-99	10:05p	N5_B1114.elem_m_a.txt
N5_B-910 TXT	41,028	02-19-99	10:05p	N5_B1114.elem_min.txt
N5_B-912 TXT	41,041	02-19-99	10:05p	N5_B1114.elem_tot.txt
N5_C1114 6I	39,467	02-10-99	1:49p	N5_C1114.6i
N5_C1114 6O	6,364,301	02-20-99	12:37a	n5_c1114.6o
N5_C-936 TXT	50,636	02-20-99	12:37a	N5_C1114.elem_aqu.txt
N5_C-938 TXT	48,251	02-20-99	12:37a	N5_C1114.elem_m_a.txt
N5_C-940 TXT	48,243	02-20-99	12:37a	N5_C1114.elem_min.txt
N5_C-942 TXT	48,256	02-20-99	12:37a	N5_C1114.elem_tot.txt
N5_D1114 6I	39,464	02-10-99	5:18p	N5_D1114.6i
N5_D1114 6O	6,405,422	02-20-99	3:09a	n5_d1114.6o
N5_D-968 TXT	51,141	02-20-99	3:08a	N5_D1114.elem_aqu.txt
N5_D-970 TXT	48,732	02-20-99	3:08a	N5_D1114.elem_m_a.txt
N5_D-972 TXT	48,724	02-20-99	3:08a	N5_D1114.elem_min.txt
N5_D-974 TXT	48,737	02-20-99	3:08a	N5_D1114.elem_tot.txt
N5_E1114 6I	38,122	02-11-99	8:57a	N5_E1114.6i
N5_E1114 6O	6,340,325	02-20-99	5:40a	n5_e1114.6o
N5_E-998 TXT	50,636	02-20-99	5:39a	N5_E1114.elem_aqu.txt
N5_-1000 TXT	48,251	02-20-99	5:39a	N5_E1114.elem_m_a.txt
N5_-1004 TXT	48,243	02-20-99	5:39a	N5_E1114.elem_min.txt
N5_-1006 TXT	48,256	02-20-99	5:39a	N5_E1114.elem_tot.txt
N5_F1114 6I	38,450	02-11-99	12:14p	N5_F1114.6i
N5_F1114 6O	6,381,075	02-20-99	8:17a	n5_f1114.6o
N5_-1030 TXT	51,141	02-20-99	8:17a	N5_F1114.elem_aqu.txt
N5_-1032 TXT	48,732	02-20-99	8:17a	N5_F1114.elem_m_a.txt
N5_-1034 TXT	48,724	02-20-99	8:17a	N5_F1114.elem_min.txt
N5_-1036 TXT	48,737	02-20-99	8:17a	N5_F1114.elem_tot.txt
N5_G1114 6I	38,746	02-15-99	4:20p	N5_G1114.6i
N5_G1114 6O	6,452,423	02-15-99	6:56p	n5_g1114.6o
N5_-1062 TXT	51,646	02-15-99	6:55p	N5_G1114.elem_aqu.txt
N5_-1064 TXT	49,213	02-15-99	6:55p	N5_G1114.elem_m_a.txt
N5_-1066 TXT	49,205	02-15-99	6:55p	N5_G1114.elem_min.txt
N5_-1068 TXT	49,218	02-15-99	6:55p	N5_G1114.elem_tot.txt
N5_H1114 6I	37,595	02-18-99	1:13p	N5_H1114.6i

```

N5_H1114 6O      6,914,229 02-18-99 4:15p n5_h1114.6o
N5_-1094 TXT      57,706 02-18-99 4:14p N5_H1114.elem_aqu.txt
N5_-1096 TXT      54,985 02-18-99 4:14p N5_H1114.elem_m_a.txt
N5_-1100 TXT      54,977 02-18-99 4:14p N5_H1114.elem_min.txt
N5_-1102 TXT      54,990 02-18-99 4:14p N5_H1114.elem_tot.txt
NH1A2204 6I      40,850 02-06-99 11:46a NH1A2204.6i
NH1A2204 6O      4,805,315 02-08-99 4:41p nh1a2204.6o
NH1-1122 TXT      64,271 02-05-99 8:44p NH1A2204.elem_aqu.txt
NH1-1124 TXT      61,238 02-05-99 8:44p NH1A2204.elem_m_a.txt
NH1-1126 TXT      61,230 02-05-99 8:44p NH1A2204.elem_min.txt
NH1-1128 TXT      61,243 02-05-99 8:44p NH1A2204.elem_tot.txt
NH2B2012 6I      45,339 02-10-99 4:54p NH2B2012.6i
NH2B2012 6O      5,866,641 02-11-99 1:57p nh2b2012.6o
NH2-1152 TXT      56,696 02-11-99 1:57p NH2B2012.elem_aqu.txt
NH2-1154 TXT      54,023 02-11-99 1:57p NH2B2012.elem_m_a.txt
NH2-1156 TXT      54,015 02-11-99 1:57p NH2B2012.elem_min.txt
NH2-1158 TXT      54,028 02-11-99 1:57p NH2B2012.elem_tot.txt
PP      EXE      308,593 07-05-98 3:00p PP.EXE
PREFER PP          64 03-14-99 4:15p PREFER.PP
-MSSETUP T      <DIR>      05-10-99 3:13p -MSSETUP.T
      261 file(s) . . 218,503,883 bytes

```

Directory of E:\cd files\ -MSSETUP.T

```

.      <DIR>      05-10-99 3:13p .
..     <DIR>      05-10-99 3:13p ..
-MSSTFOF T      <DIR>      05-10-99 3:13p -MSSTFOF.T
      0 file(s)      0 bytes

```

Directory of E:\cd files\ -MSSETUP.T\ -MSSTFOF.T

```

.      <DIR>      05-10-99 3:13p .
..     <DIR>      05-10-99 3:13p ..
      0 file(s)      0 bytes

```

Total files listed:

```

      263 file(s)      223,759,563 bytes
      9 dir(s)      0 bytes free

```