

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

**Report on Intact and Degraded Criticality for Selected Plutonium Waste Forms in a
Geologic Repository, Volume II: Immobilized In Ceramic**

Document Identifier: BBA000000-01717-5705-00020 REV 01

October 28, 1998

Prepared for:

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*Corrections were made to the
Reference Section for
accession number format.
06/29/99 P.J.*

Under Contract Number
DE-AC08-91RW00134

Hugh A. Benton 7/9/99

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October 28, 1998

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Corrections were made to the Reference Section
for accession number format.
06/29/99

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History of Change Page

<u>Rev/Change Number</u>	<u>Date</u>	<u>Description and Reason for Change</u>
REV 00	09/21/98	Initial Issue
REV 01	11/18/98	Revisions identified with vertical line in the margin. Revisions incorporate Editorial Changes only.

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EXECUTIVE SUMMARY

As part of the plutonium waste form development and down-select process, repository analyses have been conducted to evaluate the long-term performance of these forms for repository acceptance. Intact and degraded mode criticality analysis of the mixed oxide (MOX) spent fuel is presented in Volume I, while Volume II presents the evaluations of the waste form containing plutonium immobilized in a ceramic matrix.

Although the ceramic immobilization development program is ongoing, and refinements are still being developed and evaluated, this analysis provides value through quick feed-back to this development process, and as preparation for the analysis that will be conducted starting in fiscal year (FY) 1999 in support of the License Application.

While no MOX fuel has been generated in the United States using weapons-usable plutonium, Oak Ridge National Laboratory (ORNL) has conducted calculations on Westinghouse-type reactors to determine the expected characteristics of such a fuel. These spent nuclear fuel (SNF) characteristics have been used to determine the long-term potential for criticality in a repository environment.

In all instances the methodology and scenarios used in these analyses are compatible with those developed and used for Commercial Spent Nuclear Fuel (CSNF) and Defense High Level Waste (DHLW), as tailored for the particular characteristics of the waste forms. This provides a common basis for comparison of the results.

This analysis utilizes dissolution, solubility, and thermodynamic data that are currently available. Additional data on long-term behavior is being developed, and later analyses (FY 99) to support the License Application will use the very latest information that has been generated. Ranges of parameter values are considered to reflect sensitivity to uncertainty. Most of the analysis is focused on those parameter values that produce the worst case results, so that potential licensing issues can be identified.

MOX (Volume I)

This study is concerned with evaluating the criticality potential of the intact and degraded forms of the MOX SNF in waste packages (WPs). Current WP designs for both the 21 PWR WP and the 12 PWR WP are analyzed. Aluminum thermal shunts were used in both designs to enhance the heat flow rate.

This study also includes an evaluation of the structural, thermal, and shielding impacts of the MOX SNF WP's. Although previous analyses showed these impacts to be within regulatory and safety requirements, a more comprehensive evaluation is appropriate at this time to reflect the current MOX design and to prepare for the License Application analysis phase.

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Since the MOX WP's will have criticality performance very similar to the waste packages containing commercial low enriched uranium (LEU) SNF, the criticality evaluations follow the same methodology of initial analysis with the following steps:

1. Criticality evaluation of the intact configuration to demonstrate the effectiveness of the criticality control measures,
2. Criticality evaluation of the same degraded basket configurations that have been used for the commercial LEU SNF,
3. Determination of the configurations having both degraded basket and degraded MOX SNF, using the geochemistry code, EQ6, as has also been done for the commercial LEU SNF, and
4. Criticality evaluation of the combined degraded basket and degraded SNF configurations.

Major Findings, MOX (Volume I)

Based on the current available data and designs for the MOX fuel, we find the following:

1. Assuming that the MOX SNF will be emplaced at least 10 years following discharge, those assemblies having low burnup (≤ 46 GWd/MTHM) can be loaded into the standard commercial 21 PWR WP, and those assemblies having high burnup (> 46 GWd/MTHM) can be loaded into the standard commercial 12 PWR WP. This strategy will meet the maximum thermal output design criteria of 18 kW per package. With the expected distribution of burnups in the MOX SNF, this strategy will result in approximately half the MOX assemblies being placed in each of the two types of waste package. This emplacement strategy will also have the following performance aspects:
 - The MOX SNF waste packages meet all regulatory requirements.
 - There is no credible intact or degradation scenario leading to an internal criticality in the waste packages.
 - Structural, thermal, and shielding impacts are no greater (and may be less) than those of the corresponding commercial SNF waste packages.
2. The most severe structural hazard to the waste package is modeled by a finite element analysis of a tipover accident. It is found that the peak stress in the waste package, resulting from such an event, will be at least 15% less than the ultimate material tensile strength of the material. This shows that the structural behavior of both the 21 PWR WP and the 12 PWR WP will be within design limits. The MOX SNF WP stress values are very similar to values calculated for commercial SNF WP's, as would be expected, since both fuel types have similar SNF assembly weights.
3. Assuming that the MOX SNF will be emplaced at least 10 years following discharge, the maximum initial heating rates for the MOX SNF were 798 watts/assembly for the 21 PWR

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WP and 1070 watts/assembly for the 12 PWR WP. These values are less than the 850 watts/assembly and 1500 watts/assembly used as the thermal design basis (maximum thermal output of 18 kW per disposal container) for commercial LEU PWR SNF, indicating that the MOX assemblies are well within the design envelope of the commercial SNF WP. The peak fuel temperature calculated for the 21 MOX PWR WP was approximately 336°C, and that for the 12 MOX PWR was approximately 302°C. These temperatures are well below the established design limit of 350°C.

4. Dose rates from both neutron and gamma radiation were calculated for the 21 PWR WP loaded with the highest burnup MOX SNF and the shortest cooling period after reactor discharge (10 years) to serve as a worst case that would give the highest dose rates. Maximum dose values at the exterior surfaces of the waste package were less than 110 rad/hr. Maximum dose rates from the MOX SNF were much less than from commercial LEU PWR SNF of similar burnup which were calculated to be greater than 150 rad/hr. The 12 MOX PWR WP design has an equivalent amount of shielding with a smaller radiation source, which should result in smaller surface dose rates.

The design limit of 100 rad/h on the surface rate was specified so that no significant increase could occur in the corrosion rate of the waste package barrier due to any radiolytic compounds synthesized from moist air. For both waste packages, the SNF surface dose rate exceeded the design limit only during the period immediately following emplacement when humidity in the external environment is expected to be low. It is concluded, therefore, that no increase in corrosion rates from radiolysis will occur.

5. Criticality evaluations were performed for the 21 PWR MOX SNF WP and the 12 PWR MOX SNF WP for conditions ranging from intact to fully degraded fuel and basket. The peak k_{eff} 's ranged from 0.55 to 0.90 where the 0.90 resulted from a worst case configuration. The following observations on the criticality potential of the PWR MOX SNF can be made:
 - The 12 PWR WP has a higher k_{eff} than the 21 PWR WP for the flooded conditions with intact fuel and basket because the 12 PWR WP has no neutron absorber plates.
 - The 12 PWR WP has a lower k_{eff} than the 21 PWR WP for the flooded conditions with intact fuel, but with degraded basket, because the iron oxide corrosion products displace moderator compensating, in part, for the absence of absorber plates.
 - The worst case k_{eff} is below the criticality limit of 0.92 for any credible configuration and thus a criticality event internal to the waste package is virtually impossible.

Ceramic (Volume II)

For the ceramic waste form the principal criticality control measure is the incorporation of neutron absorbing material in the waste form itself. The potential for criticality is determined primarily by the amount of such neutron absorber material remaining in the waste package if, and when, the waste package is breached, and its contents are thereby exposed to aqueous corrosion. Under such conditions the waste form can be corroded; the fissile material in the

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waste form (either plutonium or its decay product uranium) will remain in the waste package for hundreds of thousands of years, because it is very insoluble under most water chemistry conditions. The neutron absorber hafnium is even less soluble than the fissile material so it will remain in the WP. However, the more neutronically efficient absorber, gadolinium, could become more soluble under some conditions and could eventually be flushed from the waste package.

This study is concerned with evaluating the potential for criticality of the currently defined ceramic waste form. After a few criticality calculations to demonstrate that the intact configuration is safely below the critical limit, the study is focused on identifying those degraded configurations that are most reactive (result in the highest values of the neutron multiplication factor, k_{eff}). The degraded configurations having the greatest potential for criticality are selected out of the range of configurations arising from the set of degradation scenarios analyzed with the geochemistry code, EQ6. The degradation scenarios examined with the geochemistry code are those most likely to lead to a loss of a major fraction of the neutron absorber material, by virtue of an increase in the solubility of that material.

Shielding, thermal, and structural evaluations were not performed explicitly for the immobilized Pu waste package because the comparison cases with the DWPF WP had not yet been completely evaluated. Nevertheless, conservative comparison with previous evaluations of a similar WP concept does support a finding that inclusion of the immobilized plutonium has a negligible repository impact.

Major Findings, Ceramic (Volume II)

Based on the data presently available, and the current canister loading of the current ceramic formulation (28.7 kg of Pu per canister), we find the following:

1. The ceramic plutonium waste form can be emplaced in the repository at a loading of 5 plutonium containing canisters per waste package; this permits the disposal of immobilized plutonium in the same disposal container/waste package as will be used for the disposal of high level waste (HLW) glass.
 - The ceramic plutonium waste package meets all regulatory requirements.
 - There is no credible degradation scenario leading to criticality internal to the waste package.
 - Thermal and shielding impacts are comparable to, or less than, those of the corresponding HLW waste package.
2. The completely intact configuration has virtually no potential for criticality, since the calculated $k_{eff} = 0.12$ for the unbreached waste package, and $k_{eff} = 0.11$ when all of the void space in the waste package is filled with water.

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3. The processes in the expected degradation scenarios will generally have the following sequence:
- breach of the waste package by aqueous corrosion, and wetting of all interior surfaces,
 - breach of the stainless steel canisters containing the HLW filler glass and the plutonium ceramic waste form,
 - dissolution of the filler glass,
 - breach of the inner cans that actually contain the plutonium ceramic disks,
 - corrosion of the stainless steel of the canisters and cans, and
 - dissolution of the ceramic waste form.

Many of these processes will overlap in time. In fact, the overlap of the last two processes (corrosion of the stainless steel and dissolution of the ceramic waste form) is what gives rise to the possibility of gadolinium removal.

4. The degraded configurations are divided into two types:
- intermediate-level degraded, in which the ceramic disks remain intact, while all the other components of the waste package have been degraded or fragmented (and the soluble degradation products are removed from the waste package), and
 - fully collapsed, in which the ceramic disks are also degraded and/or fragmented and all the fragments and insoluble degradation products mixed into a homogeneous layer at the bottom of the waste package.
5. The following are the principal criticality (k_{eff}) results for the worst cases of these two configuration types:
- For the intermediate degraded configurations there will be no significant loss of the principal neutron absorber, gadolinium, and: $k_{eff} < 0.38$.
 - For the fully collapsed configurations there could be as much as a 13% loss of the neutron absorbing gadolinium, but the more dominating effect is the geometry being less favorable to criticality than the intermediate degraded configurations, so that $k_{eff} < 0.33$, which is less than 0.38 for the intermediate degraded configurations.

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1. ACRONYMS

CDA	Controlled Design Assumptions
CRWMS	Civilian Radioactive Waste Management System
CSNF	Commercial Spent Nuclear Fuel
DHLW	Defense High Level Waste
DOE	Department of Energy
DWPF	Defense Waste Processing Facility
FY 99	Fiscal Year 1999
HLW	High Level Waste
LEU	Low Enriched Uranium (used in nuclear fuel)
LLNL	Lawrence Livermore National Laboratory
MOX	Mixed Oxide Fuel
MT	Metric Ton
SNF	Spent Nuclear Fuel
WF	Waste Form
WP	Waste Package

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1. INTRODUCTION AND BACKGROUND

As part of the plutonium waste form development and down-select process, repository analyses have been conducted to evaluate the long-term performance of these waste forms for repository acceptance. This Volume assesses the intact and degraded mode criticality of the waste form containing plutonium immobilized in a ceramic matrix. Volume I presents a similar assessment for the plutonium in the form of a mixed oxide (MOX) spent fuel.

Although the ceramic immobilization development program is ongoing, and refinements are still being developed and evaluated, this analysis provides value through quick feed-back to this development process, and to the continuing analysis in support of the License Application.

In all instances the methodology and scenarios used in these analyses are compatible with those developed and used for the Commercial Spent Nuclear Fuel (CSNF) and Defense High Level Waste (DHLW), as tailored for the particular characteristics of the immobilized plutonium waste forms. This provides a common basis for comparison of the results.

This analysis utilizes dissolution, solubility, and thermodynamic data that are currently available. Long-term data are being developed and later analyses (FY 99) to support the License Application will use the very latest information that has been generated. Where applicable, ranges of values are used to bound the results.

The content of this report is organized as follows:

- Section 2 provides a brief description of the waste package and its contents, particularly the immobilized plutonium waste form. These descriptions include dimensions, masses, chemical compositions, and degradation rates. Summaries of evaluations showing negligible repository impacts for issues not related to criticality (shielding, thermal, and structural) are also given.
- Section 3 describes the analyses used to evaluate criticality. For the intact configuration, only the results of the k_{eff} calculation are given. For the degraded configurations the k_{eff} calculations are supported by descriptions of the degraded configurations, including the geochemistry calculations used to develop the chemical compositions of the material remaining in the waste package after degradation.
- Section 4 summarizes the major findings from this study.

The specific activities involved with the production and review of this document have been performed according to an approved Technical Document Preparation Plan (Ref. 3).

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**2. WASTE PACKAGE MATERIAL AND COMPONENTS: DESCRIPTIONS AND
QUANTITIES**

2.1 Waste Stream Quantities

Of the 200 metric tons of fissile material declared surplus, about 50 metric tons are plutonium. Approximately 18 metric tons of this material contains impurities considered unsuitable for MOX reactor fuel and have been designated for immobilization in ceramic for disposal. In addition, the Department of Energy (DOE) has reserved the option of using the immobilization approach for disposal of all the 50 metric tons of surplus plutonium. The proposed immobilization and disposal methods must be analyzed to identify suitable waste package designs and to demonstrate compliance with criticality requirements.

2.2 Waste Form Description

The waste form for immobilized plutonium will be a ceramic containing approximately 10.5 wt% plutonium in the +4 valence state, nominally expressed as PuO_2 . The dominant mineral phase is a titania-based pyrochlore. The basic waste form unit will be a cold-pressed disk. This section provides the current dimensions and composition. The final values will be available as the waste form development project, presently in progress at Lawrence Livermore National Laboratory (LLNL), is completed.

The disks are stacked in cans, 20 disks per can. The stainless steel cans are stacked 4 deep in very light tubes, of a material to be specified; there will also be a mechanism to space and separate the cans within these tubes. The weight, volume, and composition of these light tubes and their supports have been neglected in this analysis.

There will be seven of these tubes fastened at the inside wall of a Defense Waste Processing Facility (DWPF) canister. While the final design has not yet been specified, a sketch of a likely arrangement is given in Figure 2.2-1. This results in a total of 28 cans, or 560 disks, per canister.

2.2.1 Dimensions

Ceramic Disk: 1 inch thick and 2.625 inches in diameter, yielding a volume of 5.412 cubic inches, or 88.69 cm^3 . The 20 disks per can will occupy a volume of 108.24 cubic inches, or 1773.7 cm^3

Can: Cylindrical shell 21 inches length by 3 inches outside diameter x 0.125 inch thick. The can will displace a volume of 148.4 cubic inches, or 2432.5 cm^3 .

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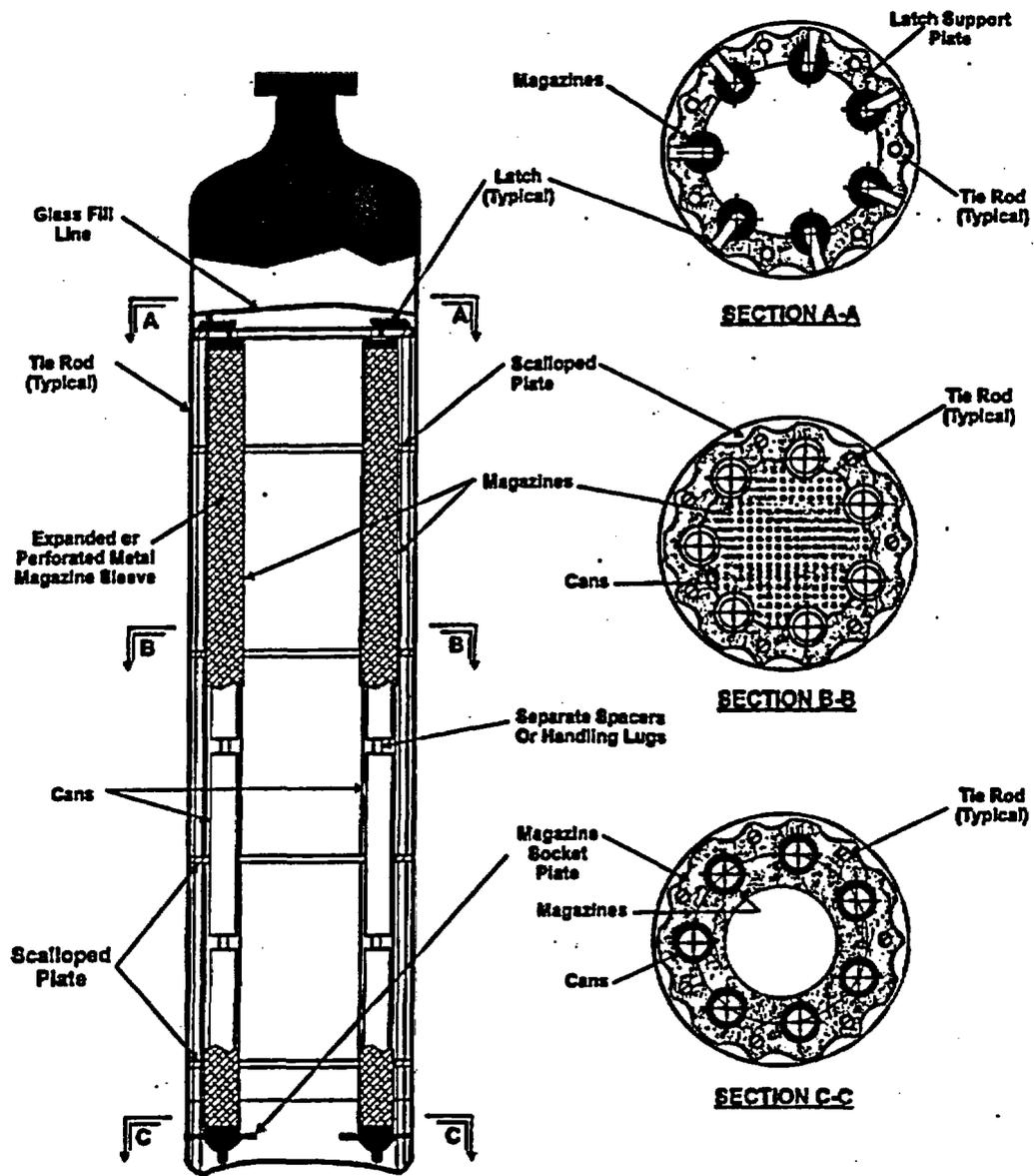


Figure 2.2-1. Can-in-Canister sketch from SRS showing cross section with 4 cans in a tube and 7 tubes in a DWPF canister

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2.2.2 Mass

The WF mass is determined from the above dimensions and an approximate density of the ceramic material, $\rho = 5.5 \text{ g/cm}^3$, resulting in 9.755 kg of ceramic per can.

2.2.3 Chemical/Isotopic Composition of the Ceramic Waste Form

The principal chemical components of the waste form are specified in Table 2.2.3-1, below. The average concentration of impurities in the Pu stream that will be in the final ceramic (i.e., that survive the ceramic formation process) is specified in Table 2.2.3-2. The impurities, plus oxygen, are 27.2wt% of the total Pu feed, with 72.8wt% of the feed being Pu. Since the amount of feed is always adjusted so the Pu will be 10.5wt% of the total ceramic, the impurities in the Pu feed will constitute 3.92wt% of the total ceramic weight ($= 27.2 \times 10.5/72.8$), for the 18 metric ton (MT) case. Note that the value of the Pu wt% (10.5) is used in this calculation, rather than the value of PuO_2 wt% (11.9) to be consistent with the oxygen of PuO_2 already having been included in the non-Pu component of the feed.

Table 2.2.3-1. Principal chemical components of the ceramic waste form

Component	Raw Wt % ⁽²⁾	Wt% adjusted(18 MT) ⁽³⁾	Wt% adjusted(50 MT) ⁽³⁾
CaO	10.0	9.6	9.8
HfO ₂	10.6	10.1	10.4
UO ₂ ⁽⁴⁾	23.7	22.6	23.3
PuO ₂ ⁽¹⁾	11.9	11.9	11.9
Gd ₂ O ₃	7.9	7.5	7.8
TiO ₂	35.9	34.3	35.3
Impurities	N/A	3.92	1.43

⁽¹⁾ Represents total fissile oxide; enriched uranium may be substituted for plutonium, which will increase the uranium oxide percent above that given in the table.

⁽²⁾ Nominal weight percents of the principal components without correction for the impurities in the plutonium feed (Ref. 13, p. 8).

⁽³⁾ Weights of the non-fissile components are adjusted for the impurities (including oxygen) which are 27.2wt% of the Pu feed, or 3.92wt% of the total ceramic. Therefore, the adjustment factor for each non-fissile component is $(100-11.9-3.92)/(100-11.9)$.

⁽⁴⁾ Consists of depleted uranium with ²³⁵U enrichment of 0.2%, which is included in the criticality calculation.

⁽⁵⁾ In the 50 MT immobilized case, the principal impurities will come from the 18.2 MT of the non-weapons grade Pu, and will, therefore be diluted by the weapons grade Pu to 1.43% of the total ceramic ($= 3.92 \times 18.2/50$). [The weapons grade Pu actually has some gallium impurity not found in the non-weapons grade Pu, but the amount is uncertain, and gallium is not a neutronically significant element.]

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Table 2.2.3-2. Impurities in the Pu process input stream

Element	Wt% of Pu stream	Wt% of total ceramic ⁽¹⁾
Al	1.86	0.268
Am	1.58	0.228
B	0.09	0.013
Ba	0.21	0.030
Ce	0.09	0.013
Cr	0.14	0.020
Cu	0.09	0.014
Fe	0.62	0.090
Ga	0.50	0.071
K	0.71	0.103
La	0.03	0.004
Mg	1.14	0.165
Mo	0.62	0.090
Na	0.36	0.052
Ni	0.29	0.042
Nd	0.58	0.084
Np	0.05	0.008
O ⁽²⁾	15.42	2.223
Pb	0.01	0.001
Si	1.05	0.152
Sn	0.00	0.000
Ta	0.96	0.139
W	0.02	0.003
Zn	0.09	0.013
Unknown	0.67	0.096
Total	27.18	3.919

⁽¹⁾ From Ref 13; percent of total ceramic has one more significant figure than percent of Pu feed because the Pu feed is approximately 10wt% of the total ceramic (actually 10.5%) so the Pu feed weight percents are shifted right by approximately one decimal place to make up the total ceramic weight percents. $Wt\% \text{ Total Ceramic} = (wt\% \text{ Pu stream}) \times (wt\% \text{ Pu Total Ceramic}) / (wt\% \text{ Pu in feed})$.

⁽²⁾ Includes oxygen of PuO₂.

The average initial Pu-related isotopic composition of the feed stream is given in Table 2.2.3-3. The data are taken from Table 4.3 of the LLNL report (Ref. 13, p. 15). It should be noted that by the time of any potential criticality, much of the ²³⁹Pu will have decayed into ²³⁵U. A conservative estimate of this decay at the time of potential criticality is given in with the description of the configurations which are likely to have criticality potential (Section 3.3.1).

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Table 2.2.3-3. Average wt% isotopic composition of the Pu feed in 2010

Isotope	18 MT case	50 MT case
²³⁸ Pu	0.02	0.01
²³⁹ Pu	90.59	92.84
²⁴⁰ Pu	8.41	6.57
²⁴¹ (Pu + Am) ⁽¹⁾	0.89	0.54
²⁴² Pu	0.09	0.04

⁽¹⁾ Since ²⁴¹Pu has a half-life of only 14 years, all the ²⁴¹Pu will have decayed into ²⁴¹Am by the time there is any possibility of criticality (upwards of 10,000 years).

For the canister containing immobilized plutonium, the principal source of radiation during preclosure (up to 300 years) is the high level waste (HLW) glass in which the plutonium cans are embedded; there is approximately 1478 kg of HLW per canister. Any shielding requirements will, therefore, be less than, or approximately the same as, what is already required for the DWPF glass waste package (as explained further in Section 2.6.1).

The only significant radioactivity in the waste form itself derives from the Pu feed, and will have approximately the distribution indicated in Table 2.2.3-4 in the year 2010. This table lists Curies per kg of (Pu + Am) in the feed. This table is taken from Table 4.4 of the LLNL report (Ref. 13, p. 15)

Table 2.2.3-4. Curies per kg of total Plutonium plus Americium

Isotope	Activity (Ci per kg of Pu+Am)	
	50-MetricTon Case	18-Metric Ton Case
²³⁸ Pu	2.1	4.2
²³⁹ Pu	57.7	56.3
²⁴⁰ Pu	15.0	19.2
²⁴¹ Pu	99.3	165.
²⁴¹ Am	15.1	25.0
²⁴² Pu	0.00161	0.0034
Total	189.	270.

2.2.4 Composition of HLW Filler Glass

The chemical composition of the HLW filler glass used for the degradation calculations is given in Table 2.2.4-1.

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Table 2.2.4-1. HLW Filler Glass Composition

Component ⁽¹⁾	Weight %
Ag	0.05
Al ₂ O ₃	3.96
B ₂ O ₃	10.28
BaSO ₄	0.14
Ca ₃ (PO ₄) ₂	0.07
CaO	0.85
CaSO ₄	0.08
Cr ₂ O ₃	0.12
Cs ₂ O ⁽²⁾	0.08
CuO	0.19
Fe ₂ O ₃	7.04
FeO	3.12
K ₂ O	3.58
Li ₂ O	3.16
MgO	1.36
MnO	2.00
Na ₂ O	11.00
Na ₂ SO ₄	0.36
NaCl	0.19
NaF	0.07
NiO	0.93
PbS	0.07
SiO ₂	45.57
ThO ₂ ⁽³⁾	0.21
TiO ₂ ⁽⁴⁾	0.99
U ₃ O ₈ ⁽⁵⁾	2.20
Zeolite ⁽⁶⁾	1.67
ZnO ⁽⁷⁾	0.08
²³⁷ Np ⁽⁸⁾	0.000751
²³⁹ Pu ⁽⁸⁾	0.012342
Tc ⁽⁸⁾	0.010797
Zr ⁽⁸⁾	0.026415

⁽¹⁾ Ref. 14 (Attachment I, Table 3.3.8, except as explained in note 4 below).

⁽²⁾ Not carried through EQ6 calculation, due to small amount relative to other WP components, or judgement of little significance.

⁽³⁾ Assumed to be analcime, due to high pour temperature of glass and high Na content.

⁽⁴⁾ Obtained by taking the "Grams/canister" entry of Ref. 14 (Attachment I, Table 3.3.3), multiplying by 100% and dividing by the presumed mass/canister of 1682 kg (Ref. 14, Attachment I, footnote to Table 3.3.3). All Tc presumed to be ⁹⁹Tc; all Zr presumed to be ⁹³Zr.

⁽⁵⁾ Contains approximately 0.5% ²³⁵U.

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2.2.5 Corrosion Rates

The range of corrosion rates for the waste package solid components used in the EQ6 runs are summarized in Table 2.2.5-1; these rates were taken from Table 5.1.1.6-1 of Ref. 6. The values actually used in the geochemistry calculations are identified, and justified, in Section 3.3.1.

Table 2.2.5-1. Corrosion Rates Used for EQ6 Analyses

Material	Rate
Pu-ceramic:⁽¹⁾	
Very high (pH 4, 50 °C)	0.4 g/m ² /day
High (pH 6, 50 °C)	4×10 ⁻² g/m ² /day
Average (pH ≥ 7, 25 °C)	2×10 ⁻³ g/m ² /day
Stainless Steel (316L, 304L):⁽²⁾	
High	1 μm/yr ⁽³⁾
Average	0.1 μm/yr ⁽³⁾
HLW Glass:⁽²⁾	
High	2.8×10 ⁻⁴ g/m ² /day
Average	2×10 ⁻⁴ g/m ² /day

⁽¹⁾ Originally from Ref. 13, under the metamict assumption

⁽²⁾ Originally from Ref. 16; in the actual analysis this value is multiplied by a factor somewhat greater than 30 to reflect internal fracturing.

⁽³⁾ This is the standard unit for corrosion of steel, assuming a flat plate geometry; to convert to g/m²/day, multiply by the density of steel (in kg/m³), by 1000 (to convert kg to g), by 10⁻⁶ (to convert microns to meters), and divide by 365 (to convert years to days).

It should be noted that the aqueous corrosion (or degradation) of individual solid waste package components does not necessarily lead directly to removal from the waste package of elements or ions from those corroded components. Individual elements may remain in a solid altered state, or precipitate in some insoluble mineral. In particular, the evidence to be discussed in the following sections shows that the primary neutron absorber, gadolinium, is nearly insoluble over most of the time period and water chemistry of interest, while the secondary neutron absorber, hafnium, is completely insoluble over the same parameter range.

2.3 Plutonium Disposition Canister

The waste forms are contained within the waste packages in stainless steel canisters approximately 3 meters overall length, 61 cm outer diameter and 1 cm thick.

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2.3.1 Canister Dimensions

HLW glass mass (baseline formulation) per DWPF canister: 1680 kg.
% HLW glass displaced by Pu waste form cans: 11%
% HLW glass displaced by rack for cans: 1%
Mass of DWPF canister (empty): 499 kg

With the density of 316 stainless steel = 7.95 g/cm^3 , the following are calculated:

Ceramic mass per canister: 273.15 kg
Mass of rack: 58.5 kg
Steel can mass per canister: 96.7 kg
HLW glass per canister: 1478.4 kg

2.3.2 Canister Mass

With these parameters the total loaded canister masses are:

Ceramic canister: 2405 kg
DWPF canister: 2179 kg

2.4 Waste Package Description

The disposal container will be the same 5-canister design as is planned for the ordinary DWPF HLW canisters. An isometric view of the 5-canister package is given in Figure 2.4-1, with the lids removed, and showing the inner and outer barriers. The nominal Pu loading per waste package is 5 Pu loaded canisters per waste package. Previous analyses of ceramic formulations (Ref. 4) have suggested that criticality prevention would be enhanced by limiting the number of Pu loaded canisters to 1 or 2 per package. However, the results of this study will show that the performance of the current formulation will prevent criticality, even if all 5 canisters are loaded with plutonium ceramic.

The disposal container consists primarily of a corrosion allowance outer barrier and a corrosion-resistant inner barrier. The corrosion-allowance outer barrier will likely be carbon steel 10 cm thick as is used in the Civilian Radioactive Waste Management System (CRWMS) current design for the commercial spent nuclear fuel waste package. The inner barrier will be corrosion resistant, high nickel, Alloy-22, 2 cm thick, also corresponding to that planned for the commercial SNF WP. The dimensions and compositions of the intact WP components are provided in Table 2.4-1 (Ref. 12, p. 10).

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**Table 2.4-1. The Physical Characteristics of the Main Components of the Five High-Level
Waste Canister Waste Package**

Component	Number	Material	Inner Diameter (cm)	Outer Diameter (cm)	Thickness (cm)	Inner Height (cm)	Outer Height (cm)
Outer Barrier	1	ASTM A 516 Carbon Steel	177	197	10.0	-----	331
Outer Barrier Lid	2 (top and bottom)	ASTM A 516 Carbon Steel	-----	177.3	11.0	-----	-----
Inner Barrier	1	ASTM B 575 N06022 (Alloy 22)	173	177	2.0	304 ^w	-----
Inner Barrier Lid	2 (top and bottom)	ASTM B 575 N06022 (Alloy 22)	-----	173.3	2.5	-----	-----
Canister	5	ASTM A312 Type 304L Stainless Steel	59.055	60.96	0.9525	-----	299.72

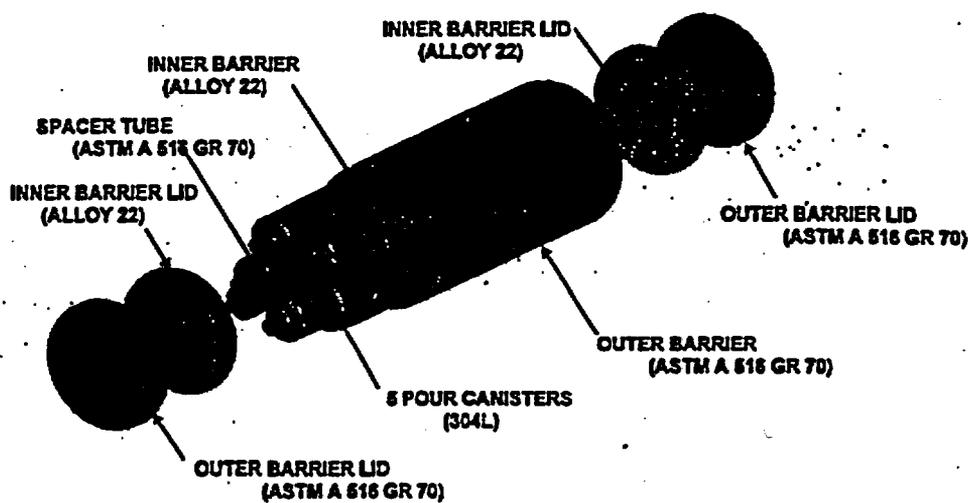


Figure 2.4-1. Five Canister Waste Package for Plutonium Immobilized in Ceramic

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2.5 Waste Package and Canister Quantities

For the waste form composition given in Table 2.2.3-1, and the loading of 20 disks per can and 28 cans per canister, the total mass of Pu per canister will be 28.68 kg. The total number of canisters required for disposal is summarized in Table 2.5-1. Also given in the table is the number of waste packages required at 5 canisters per waste package.

Table 2.5-1. Canisters Required for Immobilized Plutonium Disposal

	18 M Ton case	50 M Ton case
Number of Pu containing canisters	635	1744
Net additional canisters to accommodate DHLW filler displaced by the Pu ceramic	77	210
Net additional as a % of total DWPF canisters (~12000)	0.64%	1.75%
Number of waste packages containing Pu	128	348
Net additional waste packages	16	42

It should be noted that since the plutonium bearing canisters contain 88% of their maximum capacity for HLW glass, the impact of immobilized Pu disposal on the number of waste packages is only the net additional canisters required to make up for the 12% of the HLW displaced by the plutonium bearing cans and their accompanying structure. This net increment is shown for canisters by the second line of Table 2.5-1, and for waste packages by the fifth line.

2.6 Properties and Behavior Not Related to Criticality

A previous study (Ref 17, Section 8) provided preliminary evaluations of the shielding, thermal, and structural impacts of an immobilized plutonium waste form using the can-in-canister concept. In that study the waste form matrix carrying the plutonium was glass, instead of the current ceramic; other significant differences were:

- Higher Pu loading per canister in the previous study (approximately 51 kg versus approximately 29 kg in the present study)
- 4 Pu bearing canisters per WP compared with the present baseline of 5.
- 1330 kg of DWPF filler glass per Pu bearing canister compared with the present 1478 kg.

These differences permit a conservative estimate of the upper bound of the non-criticality impacts of the present immobilized Pu waste, by comparison with the previous study. The specific justifications are given in the following sub-sections.

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2.6.1 Shielding

The comparison of the dose rates from the immobilized Pu WP with those for the DWPF glass WP given in Ref 17, Table 8-5 showed the former to have less half the dose rate of the latter. This ratio between immobilized Pu and DWPF glass waste package dose rate (less than 0.5) should remain approximately the same for the present case in which the number of canisters is increased from 4 to 5 per waste package. The fact that the current Pu disposal canister has approximately 10% more filler glass would tend to increase the ratio, since the dominant radiation source at emplacement is the filler glass. However, the magnitude of the increase in the 0.5 dose ratio will be less than this 10% because of the smaller Pu loading per canister in the present case (143 kg Pu compared with 204 kg Pu in the previous study). In any event, the shielding required for immobilized Pu WP will still be less than that required for the DWPF waste package.

2.6.2 Thermal

The comparison of the peak waste form temperatures and the peak surface temperatures from the immobilized Pu WP with those for the DWPF glass WP were given in Ref 17, Tables 8-7 and 8-8, respectively, for the previous immobilized Pu waste form. This data showed the immobilized Pu WP to have approximately the same, or slightly larger, temperatures as the DWPF WP (with the maximum excess temperature for the immobilized Pu WP being less than 5°C). By the time the peak temperatures occur (approximately 30 years after emplacement for the peak fuel temperature and approximately 60 years after emplacement for the peak WP surface temperature) much of the radioactivity in the HLW has decayed so the principal remaining heat source in the WP is Pu (as is explained in Ref 17, Section 8.3.3.3). Therefore, the temperature comparison between the immobilized Pu WP and DWPF WP should be more favorable to the former in the present case than it was in the previous study, because the present case has a much smaller Pu loading per canister and per WP.

2.6.3 Structural

As explained in Ref 17, Section 8.3.3.4, the design basis structural hazard for this type of WP is a rockfall; this event has the same impact for both the immobilized Pu WP and the DWPF WP. The present waste package design for HLW show satisfactory performance for both cases.

3. CRITICALITY EVALUATIONS

3.1 Methodology

3.1.1 Methodology for Specifying Degradation Processes and Configurations

The methodology that was used for the analysis of the degradation processes was an extension of the methodology used in the previous study of the potential for criticality of the immobilized plutonium waste forms, Ref. 4. That methodology was also used in the most recent evaluation of degraded mode criticality in waste forms having highly enriched uranium, Ref. 5. The methodology is described in further detail in Ref. 6, and involves the following steps:

- 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.
- Determination of the sequence of the expected degradation processes, for those waste packages that are dripped on sufficiently to experience barrier breach and degradation of contents. Such sequences will generally be some variant of the following:
 - breach of the waste package due to aqueous corrosion, permitting wetting of all interior surfaces,
 - breach of the stainless steel canisters containing the HLW filler glass and the Pu ceramic waste form,
 - dissolution of the HLW filler glass,
 - breach of the inner cans that actually contain the plutonium ceramic disks,
 - corrosion of the stainless steel of the canisters and cans, and
 - dissolution of the ceramic waste form.

The configurations used for criticality evaluations, which typify these processes, are described in Section 3.3.2.

- Tracing the progress of reactions using the geochemistry code EQ6 (Ref. 6) in order to estimate the concentrations remaining in solution and the composition of the precipitated solids. For this purpose, water is added continuously to the waste package and builds up in the waste package over a sequence of time steps. The duration of a time step modeled for the individual EQ6 time steps range from 0.01 seconds to 1000 days as determined automatically by the program. The modeled duration of a sequence, including the initial sequence, stays constant within the limits imposed internally by the program. The rate of water buildup during each time step is determined by the drip rate of water entering the waste package, which varies over a range with the maximum, $0.5 \text{ m}^3/\text{yr}$, as specified in the Controlled Design Assumptions (CDA) (Ref. 7, p. 10-19), and minimum of $0.0015 \text{ m}^3/\text{yr}$. This latter value is equivalent to an infiltration rate of $0.2 \text{ mm}/\text{yr}$ over the waste package horizontal cross section area and is in the range of the lowest infiltration rate used in recent hydrologic models, 0.05 to $.3 \text{ mm}/\text{yr}$ (Ref 15, Section 4.2). The reaction progress is also controlled by the flushing action (removal of water

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added during one EQ6 sequence), which is simulated by specifying smaller amounts of water and solutes for input to the next EQ6 sequence than were present at the end of the preceding sequence. The mass of water simulated as removed equals the mass of water added, adjusted for water identified by EQ6 calculations as entering, or being released from, solids (including mineral precipitates). Solute is removed from the WP in proportion to their concentrations in that mass of water simulated as removed.

The results of this analysis are used to define the configurations that are evaluated for criticality, particularly the following determinations:

- Concentrations of neutronically significant elements in solution, as a function of time (from the output of EQ6 sequences over times up to or greater than 100,000 years).
- The amount of fissile material released from the waste package as a function of time (which thereby reduces the chance of criticality within the waste package).
- Composition and amounts of solids (precipitated minerals or corrosion products, and unreacted fragments of waste package components).
- The amounts of fissile elements and neutron absorbers retained within the waste package as a function of time.

3.1.2 Methodology for Evaluating Criticality

The methodology for evaluating criticality follows that established in the previous study of immobilized plutonium degraded mode criticality (Ref. 4). The present application of the methodology is further described in the detailed criticality calculation document for this study (Ref. 11). The methodology for estimating the effective neutron multiplication factor, k_{eff} , for different degraded internal configurations of the waste package is described by the following steps:

- criticality geometry models, representing different degraded internal configurations of the waste package, are developed for the MCNP4B2LV computer code (Computer Software Configuration Item: 30033 V4B2LV) (Ref. 9);
- spreadsheet calculations are used to transform the output of the EQ6 geochemistry computer code (Ref. 8) to the input for MCNP4B2LV, which consists of the amount of chemical elements or isotopes, their total mass, their total volume, and density; and
- the MCNP4B2 computer code, appropriate for performing nuclear criticality analysis, is run, for the computational models developed above, to estimate the k_{eff} . It should be noted that this code has not been well validated for values of $k_{eff} < 0.5$ (which is the range of most of the results of this study). While the specific values may be in question, the fact that they are far from one is indisputable.

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The analysis described in the above steps is iterated for a range of parameters representing all credible configurations (determined by the geochemistry analysis described in Section 3.1.1, above) to identify the worst cases.

3.2 Criticality Evaluations Relating to Intact Configurations

3.2.1 Description of Intact Configuration

The intact configuration is described in Sections 2.2, 2.3, and 2.4 above, for the ceramic disk, canister containing 28 cans of 20 disks each, and the waste package containing 5 canisters.

3.2.2 Criticality Calculations for Intact Configurations

The k_{eff} of the intact configuration has been estimated under two conditions: (1) no water in the waste package, and (2) water in the void spaces within the canister and waste package. The values are $k_{eff} = 0.12$, and 0.11 , respectively (Ref 11, Table 6-5). The reason for such low values is the relatively large loading of the waste form with the neutron absorber materials, specifically gadolinium and hafnium; the former being particularly effective in the thermal region of the neutron spectrum.

3.3 Criticality Evaluations Relating to Degraded Configurations

3.3.1 Degradation Processes, Scenarios, and Chemical Descriptions of Final Configurations

This section provides a summary of the degradation analysis given in Ref. 6, Section 2. An internal criticality could be possible if the fissile material remained behind in the waste package, and the Gd and Hf neutron absorbers are flushed from the system. Uranium and plutonium are quite soluble in the alkaline, CO_2 -rich solutions produced when the HLW glass degrades; on the other hand, the gadolinium mineral $GdOHCO_3$ is soluble in the acid solution that may be produced when stainless steel degrades after the strongly alkaline period of HLW glass degradation. One general scenario that maximizes the amount of gadolinium release from the waste package involves early breach of the 304 stainless steel canisters containing the HLW, followed by fast degradation of the HLW glass and removal of the alkaline components during a period of relatively high drip rate. This scenario continues with breach of the 316 stainless steel, exposing the Pu-bearing ceramic disks; in this second stage, the pH of the ambient solutions is controlled to low values (5.25 to 6.0), in part by the degradation of the stainless steel. The duration of this

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period is prolonged, and the depth of the pH lowering is increased, by the conservative assumption of a low drip rate during this second stage.

The scenarios chosen for this study build upon two previous analyses of U, Pu, Gd and B loss from waste packages containing fissile waste forms co-disposed with HLW glass (Refs 4 and 5). These prior studies suggested that the greatest removal of Gd would occur at low drip rates which would produce lower pH values caused by more strongly concentrating chromic acid (produced by corroding stainless steel) and by prolonging the period during which the chromic acid remains in the waste package. There were no sets of cases aimed at testing sensitivity to Hf loss, because the geochemistry analysis had indicated that Hf was virtually insoluble and would not be flushed from the waste package, as is explained in the discussion following Tables 3.3.1-2 and 3.3.1-3.

Two basic types of scenarios were modeled. In the first type, all package materials degrade simultaneously, albeit at different rates, and the drip rate of J-13 water into the package is kept constant throughout the run. Only one EQ6 case of the first type is reported, and that for reference purposes only. This limitation is because the first type of scenario maintains a moderate to high pH (minimum value 6.33, and that for only a few thousand years), so that there is little opportunity for loss of gadolinium.

In the second type of scenario, the sequence of EQ6 runs is divided into two stages with different drip rates. The first stage models the early degradation process in which all of the glass degrades, much of the stainless steel package materials degrade, but little, or none, of the ceramic degrades. This is consistent with the fact that the glass has the highest degradation rate, followed by the stainless steel, while the ceramic has a very low degradation rate, and is also somewhat protected from the water by the glass and steel. During this stage the drip rate is assumed to be the high nominal value ($0.5 \text{ m}^3/\text{yr}$, Ref. 7, p. 10-19). The first stage lasts as long as the degrading glass or period of high pH; the stage is terminated when the pH reaches a plateau minimum of ~ 6 , at $\sim 3.8 \times 10^3$ years. During this period of high pH and high drip rate, nearly all the uranium from the HLW filler glass is dissolved and flushed from the waste package. At a lower drip rate the first stage would last somewhat longer because some of the glass degradation products would maintain an elevated pH until a major fraction of the silica could be flushed from the waste package by the dripping water.

The second stage chemistry is dominated by the degradation products of the ceramic waste form and possibly the corroding stainless steel (via the formation of chromic acid). The worst case, with respect to gadolinium solubility, is expected to be the low drip rate; however, this inverse relationship between gadolinium loss and drip rate is weakened by the fact that reducing drip rate also reduces the rate at which dissolved gadolinium can be flushed from the waste package. Accordingly, most of the cases used second stage drip rates of 0.015 or $0.0015 \text{ m}^3/\text{yr}$; the former value corresponds to the present low estimate of this parameter (Ref. 10), and the later corresponds to the lowest estimate of recent hydrologic models (Ref 15), as was mentioned in Section 3.1.1. The ceramic is assumed to be in contact with the degradation products of the steel and glass, particularly with all the components in solution. During this phase the pH may then drop to ~ 5.25 , as the stainless steel continues to corrode, and the rate of influx of J-13 (which is mildly alkaline) water is reduced. There follows a period of relatively low pH, which may persist for thousands to

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tens of thousands of years; in this period of low pH, the solubility of $GdOHCO_3$ is at its highest, and dissolved Gd concentrations can reach 10^{-3} to 10^{-2} molal. The pH gradually rises, due to several factors: the inherent alkalinity of the J-13 water; the alkalinity built into the ceramic waste form; and the buffering capacity of the clays that were formed in the system. Seven simulations of this second type were run; only four (scenarios 4, 5, 6, and 7) produced a significant loss of Gd (~10 to 15%) from the system.

Table 3.3.1-1 summarizes the conditions used and total Gd loss for 8 scenarios that span the range of possible environmental parameters; also shown are the minimum pH values achieved in the scenarios, the peak Gd concentration in solution, and the width of the peak (time between the half-maximum points). A typical time history of pH and Gd concentration in solution is shown

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Table 3.3.1-1. Key Parameters of Typical Degradation Scenarios
(from Ref. 6, Table 5.3-1)

#	Number of Stages	Corrosion Rates ⁽²⁾	J-13 Drip Rates (m ³ /yr)	Modeled Time (yr)	Min pH	Peak Gd conc. (kg/m ³)	Width of Gd peak (yr)	% Gd Loss
1	1	HLW: avg SS: avg Cer: avg	0.0015	1.07×10 ⁶	6.33	N/A	N/A	0.0432
2	2	HLW: high SS: high Cer: avg	0.5 & 0.0015	3.77×10 ³ & 6.49×10 ⁵	5.25	0.18	3640	1.86
3	2	HLW: high SS: high Cer: avg	0.5 & 0.015	3.77×10 ³ & 1.12×10 ⁵	5.49	0.019	2481	1.24
4	2	HLW: high SS: avg Cer: avg	0.5 & 0.0015	3.78×10 ³ & 1.46×10 ⁶	5.47	0.19	30000	14.8
5 ⁽¹⁾	2	HLW: high SS: high Cer: high	0.5 & 0.0015	3.77×10 ³ & 6.52×10 ⁵	5.32	2.50	2965	9.58
6 ⁽¹⁾	2	HLW: high SS: high Cer: high	0.5 & 0.0015	3.77×10 ³ & 6.50×10 ⁵	5.32	2.83	3285	13.2
7	2	HLW: high SS: avg Cer: high	0.5 & 0.015	3.78×10 ³ & 1.33×10 ⁵	5.87	0.036	25680	12.2
8	2	HLW: high SS: high Cer: very high	0.5 & 0.0015	3.77×10 ³ & 1.09×10 ⁶	6.13	N/A	N/A	0.0369

⁽¹⁾ Scenarios 5 and 6 are identical, except that 6 has a carbon dioxide partial pressure that is an order of magnitude smaller. This near duplication was intended to test the sensitivity to carbon dioxide partial pressure, which turned out to be small.

⁽²⁾ For HLW, the average rate=2×10⁻⁴ g/m²/day, and the high rate=2.8×10⁻² g/m²/day; for SS (stainless steel) the average rate=0.1 μm/yr, and the high rate=1 μm/yr, and for ceramic, the average rate=2×10⁻³ g/m²/day, the high rate=4×10⁻² g/m²/day, and the very high rate=4×10⁻¹ g/m²/day.

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in Figure 3.3.1-1, corresponding to Scenario #6 in Table 3.3.1-1, and covering the time period of greatest potential Gd loss. It should be noted that the width of the Gd peak given in Table 3.3.1-1 can be verified from Figure 3.3.1-1, as being from the rising half peak point at approximately 5000 years to the declining half-peak point at approximately 9000 years.

It should be noted that the values for the three designations for ceramic corrosion rate: average, high, and very high are given in Table 2.2.5-1, which is a copy of Table 5.1.1.6-1 of Ref. 6. The values in that reference were taken from Ref. 13, Table 6.2, and correspond to the metamict condition (most conservative, or highest, corrosion rate) under the range of environmental parameters. It can be seen from Table 3.3.1-1 that the percent gadolinium loss turns out to have very little dependence on ceramic corrosion rate for the scenarios represented in Table 3.3.1-1, since they all have the moderately high, metamict, corrosion rate. If the corrosion rate were much slower than the stainless steel corrosion rate, the majority of the Gd release from corroding ceramic could occur later than the pH minimum caused by the stainless steel corrosion. This would ensure that no Gd would be available for release at the time of peak Gd solubility, so very little Gd would be lost from the waste package. Such non-metamict corrosion rates were not evaluated in the present study because, as Table 3.3.1-1 shows, the Gd loss will be small for even the worst metamict conditions.

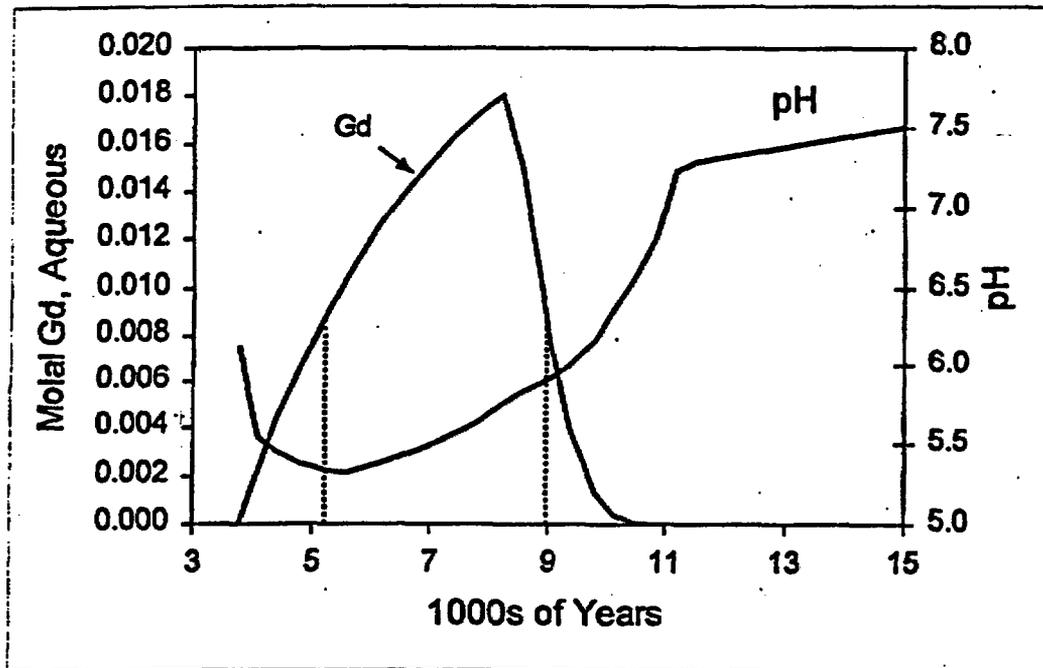


Figure 3.3.1-1. Gd concentration in solution and pH as a Function of Time (Scenario #6)

The results presented in Figure 3.3.1-1 show the inverse correlation between pH and Gd concentration in solution. The displacement between the time of minimum pH and the time of

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peak Gd concentration in solution, shown in Figure 3.3.1-1 indicates that the solubility of Gd depends on a balance of other species concentrations, as well as the pH, as explained later in this section and in Ref 6, Section 5.3.4.

The Gd loss is inferred from the amount of Gd remaining, as calculated by EQ6. It can also be computed by numerically integrating the product of the Gd concentration in solution, multiplied by the outflow from the waste package (approximated by the drip rate into the waste package). It will be noted that the Gd concentration in Figure 3.3.1-1 has a simple triangular peak over a limited range of time, and is nearly zero elsewhere. This suggests a simple approximation to illustrate the chemical and physical processes and to check the consistency of the EQ6 calculation of Gd loss (last column of Table 3.3.1-1). The numerical integral can be approximated by multiplying the drip rate by the average Gd concentration in solution and by the time period of interest. The latter product, the average Gd concentration in solution multiplied by the time period, can be approximated by product of the peak Gd concentration in solution multiplied by the width of the peak (since the Gd concentration is negligible for times outside of the peak). For scenario #6 this is $(0.0015 \times 2.83 \times 3285 = 13.9 \text{ kg})$; dividing by the initial 94 kg Gd gives a percent loss of 14.8%, which is close to the 13.2% from the EQ6 calculation, as given in Table 3.3.1-1. This consistency check also shows that the total Gd loss is really determined by the peak Gd concentration in solution over a relatively short fraction of the total time period being evaluated. For those scenarios that do not lead to a significant peak (e.g., scenarios 1 and 8), there will be no significant Gd loss at all. It should be noted that this discussion is for illustration only, the precise calculation of Gd loss is determined from the EQ6 output, and given in the last column of Table 3.3.1-1.

The largest loss of Gd from the waste package in Table 3.3.1-1 is only slightly greater than 13% (scenarios #4 and #6). This low loss is small compared with the two previous studies that examined the chromic acid mechanism (Refs 4 and 5), and found some conditions under which all of the Gd was lost from the waste package. The first study of the subject (Ref. 4, for immobilized plutonium waste forms) was an evaluation of a similar waste form, but used only a heuristic functional dependence of Gd solubility on pH. The second study (Ref. 5, for highly enriched research reactor SNF) used analytic tools similar to those used in the present study, but the waste package was somewhat different, and the waste form was quite different. The following paragraphs explain, in more detail, why the present waste package is more robust with respect to limiting acidification, and why it will always retain nearly all the Gd.

- The U-Al alloy waste form used in Ref. 5 was itself a producer of acid during oxidation; in contrast, the Pu-ceramic is somewhat alkaline. Since the ceramic waste form is degrading during the entire period of interest, it is capable of neutralizing some of the acid produced by the corroding stainless steel.
- Alloy 22 is used for the inner barrier of the present waste package design, instead of the Alloy 625 used in previous studies. The latter was assumed to have a sufficiently high corrosion rate (albeit a much smaller rate than the stainless steel components of the waste package) that it could contribute a significant amount of chromic acid. Of course, the increment of chromic acid from Alloy 625 was small compared to that from the canisters inside the waste package, and was not enough to maintain an acid condition after the canisters had completely corroded. Nevertheless, it was enough to cause a significant solubility of Gd.

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- For those scenarios with long corrosion times of the stainless steel there will generally be alkaline precipitates from earlier degradation of the ceramic and the HLW filler glass. These precipitates, principally the calcium containing minerals, calcite and dolomite, will slowly be re-dissolving and producing an alkalinity that counters the acidification tendency of the corroding stainless steel, so the gadolinium will remain virtually insoluble. Furthermore, the EQ6 results that show the peak Gd concentration occurring after the minimum pH (Figure 3.3.1-1) indicate that the dissolving process of these minerals has a limiting effect on the Gd solubility, beyond the action of the pH. Only after the calcite and dolomite have been completely re-dissolved and the calcium ions flushed from the waste package (which may take upwards of 20,000 years), will the gadolinium become sufficiently soluble to be flushed from the waste package. The difference between the research reactor SNF (Ref 5) and the present ceramic waste form with respect to this mechanism, is that the ceramic waste form contains nearly 10% calcium (Table 2.2.3-1) while the research reactor SNF contains none. Both waste forms are co-disposed with HLW glass, which contributes approximately as much calcium as does the ceramic waste form. Therefore, although this buffering effect will be present in both cases, it will be approximately twice as large for the ceramic waste form.

The following observations can be made from the results given in Table 3.3.1-1:

- The results are not particularly sensitive to the second stage drip rate; the higher drip rate generally means a lower chromic acid concentration (higher minimum pH), which, in turn, means a lower peak Gd concentration in solution. However, this factor is balanced by the fact that the higher drip rate will remove what Gd is in solution at a faster rate. Hence, comparing scenarios 2 and 3 in Table 3.3.1-1 shows the former to have nearly a ten times higher peak Gd concentration in solution, but it has approximately the same Gd loss because of the 10 times lower drip rate.
- A slower corrosion rate for the stainless steel will prolong the acidic period, and hence will enlarge the width of the Gd concentration in solution peak. This behavior can be seen by comparing scenario 7 with scenario 3 (for the low drip rate) and scenario 4 with scenario 6 (for the high drip rate). The slower stainless steel corrosion rate will also make the pH minimum occur later. The time of pH minimum is not given in Table 3.3.1-1, but Ref. 6, Table 5.3-2 shows that the two scenarios with average stainless steel corrosion rate (4 and 7) have the pH minimum occurring at just under 60,000 years. The rest of the scenarios have the minimum occurring at less than 6,000 years. As would be expected, the time of peak Gd concentration in solution shows a similar behavior, but a wider variation across scenarios. For scenarios 4 and 7, the times of peak Gd concentration are under 60,000 years, respectively; for the rest of the scenarios with high stainless steel corrosion rates, the times of peak Gd concentration range from less than 4,000 years to over 13,000 years.
- A higher ceramic corrosion rate will sharpen the Gd concentration in solution peak (higher peak and narrower width), but have little effect on the overall Gd loss. This can be seen by comparing scenarios 4 and 7, which have different ceramic corrosion rates but similar total Gd loss. These two scenarios also have differing drip rates, but that has little effect on the width of the Gd concentration peak, as can be seen by comparing scenarios 2 and 3. In this regard, it should be noted that the principal effect of a high ceramic corrosion rate is to convert most of the Gd from the ceramic into GdOHCO_3 , from which it can be re-dissolved if, and when, the pH is decreased below 5.9. The duration of the pH decrease is determined by a balance

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between the acidification produced by the corroding steel and the alkalinity produced by the corroding ceramic. The balance is further complicated by the fact that even after all the ceramic has corroded, the alkalinity can still be maintained by the calcite and dolomite minerals that were produced from the calcium in the ceramic and the glass. The pH decrease, and Gd concentration in solution peak, will generally occur immediately after all the calcium in calcite and dolomite has been re-dissolved and flushed from the waste package, provided that there is still stainless steel left to degrade and produce the acidification.

Scenarios #2 and #6 are used to illustrate the time history of the most neutronically significant elements in the waste package solids (both initial component fragments and precipitates of degradation products). These scenarios are typical of the high and average stainless steel corrosion rates, respectively. The amounts of principal elements remaining as solids (which approximate the total amounts in the WP, except as noted) are shown as a function of time for these two scenarios in Tables 3.3.1-2 and 3.3.1-3, respectively. These tables also show the effect of the decay of the remaining ^{239}Pu to ^{235}U (4th and 5th columns), under the conservative assumption that this decay begins at time zero, or the time of waste package breach. Since the decay of ^{239}Pu has already begun by the time of emplacement, this evaluation overstates the ^{239}Pu compared with its daughter product, ^{235}U . Since the latter is generally less reactive by comparison with the former, this approximation is conservative. Furthermore, U is more soluble than Pu, and would be flushed from the waste package more quickly. Therefore, understating the ^{235}U (which is the result of delaying the initiation of ^{239}Pu decay) will overstate the total fissile material, a further conservatism. It should be noted, however, that this latter conservatism is not of much significance for the parameter ranges considered here, because even the fastest ceramic degradation rates are much slower than the glass degradation rate so that there will be very little fissile material released from the ceramic during the brief period of glass degradation (which is the only time of high pH to enable high solubility of U).

Although only those lines of the table corresponding to times of 11,500 years and 30,000 to 31,000 years are used in the criticality evaluations, the other time history information presented in these tables does provide useful insights into the geochemical processes, as described below.

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**Table 3.3.1-2. Total WP Kilograms of the Principal Elements Remaining as Solids⁽⁶⁾ Scenario
#2 (From Ref. 6, Table 5.3.2-2)**

Time ⁽²⁾	U ⁽¹⁾	Hf (Zr) ⁽³⁾	²³⁹ Pu raw ⁽⁴⁾	²³⁹ Pu decayed ⁽⁵⁾	²³⁵ U gen ⁽⁵⁾	Fe	Ni	Mn	Na	Al	Si	Gd
0.0	427.4	126.7	144.2	144.2	0.0	2561.1	360.7	177.1	653.2	176.5	1679.4	93.6
0.1	412.8	126.7	144.2	143.8	0.4	2559.5	360.4	177.1	588.9	176.6	1647.3	93.6
0.3	385.5	126.7	144.2	143.0	1.2	2552.0	359.3	176.9	468.3	176.7	1587.2	93.6
1.0	287.8	126.7	144.2	140.1	4.0	2527.6	355.7	176.3	35.9	176.8	1371.2	93.6
3.8	285.3	126.7	144.2	129.5	14.4	2520.5	338.6	176.1	3.9	176.8	1683.1	93.6
7.8	285.3	126.7	144.2	115.5	28.2	2520.8	256.3	176.1	3.8	176.9	1683.5	92.7
11.5	285.3	126.7	144.2	103.9	39.6	2520.8	257.6	176.1	3.6	176.9	1683.6	91.8
30.2	285.3	126.7	144.2	61.2	81.6	2520.1	259.8	176.1	2.8	176.8	1683.1	91.7
62.1	285.4	126.7	144.2	24.7	117.5	2520.2	259.8	176.1	3.3	176.8	1683.3	91.7
100.3	285.4	126.7	144.2	8.4	133.6	2520.3	259.8	176.1	3.6	176.8	1683.5	91.7
204.1	285.6	126.8	144.3	0.4	141.5	2520.9	259.8	176.1	4.2	176.9	1684.5	91.8
302.0	285.7	126.9	144.4	0.0	142.0	2520.4	259.8	176.1	4.4	176.9	1684.7	91.8
400.3	285.9	126.9	144.4	0.0	142.0	2520.6	259.7	176.1	4.5	176.8	1685.2	91.8
503.8	285.8	126.9	144.5	0.0	142.1	2520.5	259.7	176.1	4.6	176.8	1685.7	91.9
601.8	285.8	126.9	144.5	0.0	142.1	2520.7	259.7	176.1	4.6	176.8	1686.2	91.9
645.6	285.8	126.9	144.5	0.0	142.1	2520.6	259.7	176.1	4.6	176.9	1686.5	91.9

⁽¹⁾ Depleted uranium from the ceramic matrix (Table 2.2.3-1) plus the HLW filler glass (Table 2.2.4-1); all but 5 kg of the U from the filler glass is lost by 1000 years.

⁽²⁾ Time in thousands of years.

⁽³⁾ Zr used as surrogate for Hf, because of lack of thermodynamic data (explained further in Ref. 6, particularly Assumption 3.16).

⁽⁴⁾ As calculated by EQ6, which currently has no provision for radioactive decay.

⁽⁵⁾ All Pu taken as ²³⁹Pu and decayed to produce ²³⁵U (see assumption 3.17).

⁽⁶⁾ Insoluble degradation products plus fragments of initial materials

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**Table 3.3.1-3. Total WP Kilograms of Principal Elements Remaining as Solids⁽⁷⁾, Scenario #6
(From Ref. 6, Table 5.3.3-2)**

Time ⁽²⁾	U ⁽¹⁾	Hf (Zr) ⁽³⁾	²³⁹ Pu raw ⁽⁴⁾	²³⁹ Pu decayed ⁽⁵⁾	²³⁵ U gen ⁽⁵⁾	Fe	Ni	Mn	Na	Al	Si	Gd ⁽⁶⁾
0.0	427.4	126.7	144.2	144.2	0.0	2561.1	360.7	177.1	653.2	176.5	1679.4	93.6
0.1	412.8	126.7	144.2	143.8	0.4	2559.5	360.4	177.1	588.9	176.6	1647.3	93.6
0.3	385.5	126.7	144.2	143.0	1.2	2552.0	359.3	176.9	468.3	176.7	1587.2	93.6
1.0	287.8	126.7	144.2	140.1	4.0	2527.6	355.7	176.3	35.9	176.8	1371.2	93.6
3.8	285.3	126.7	144.2	129.5	14.4	2520.5	338.6	176.1	3.9	176.8	1683.1	93.6
7.8	285.3	126.7	144.2	115.4	28.3	2520.5	292.4	176.1	2.4	176.8	1683.1	74.6
11.5	285.4	126.7	144.2	104.0	39.5	2520.9	300.4	176.1	1.8	176.9	1683.4	81.3
30.9	285.3	126.7	144.2	60.0	82.8	2520.7	300.4	176.1	1.9	176.9	1683.6	81.2
63.1	285.3	126.7	144.2	24.0	118.2	2520.5	300.4	176.1	2.9	176.8	1683.4	81.2
101.3	285.3	126.7	144.2	8.1	133.8	2520.3	300.4	176.1	3.8	176.8	1683.6	81.2
205.1	285.3	126.7	144.2	0.4	141.4	2520.5	300.4	176.1	5.3	176.8	1684.2	81.2
303.4	285.3	126.7	144.2	0.0	141.8	2520.9	300.4	176.1	6.4	176.9	1685.0	81.2
401.6	285.3	126.7	144.2	0.0	141.8	2520.6	300.4	176.1	7.0	176.9	1685.4	81.2
603.2	285.3	126.7	144.2	0.0	141.8	2520.8	300.4	176.1	7.7	176.9	1686.4	81.2
647.0	285.3	126.7	144.2	0.0	141.8	2520.6	300.4	176.1	7.7	176.8	1686.6	81.2

⁽¹⁾ Depleted uranium from the ceramic matrix (Table 2.2.3-1) plus the HLW filler glass (Table 2.2.4-1); all but 5 kg of the U from the filler glass is lost by 1000 years.

⁽²⁾ Thousands of years.

⁽³⁾ Zr used as surrogate for Hf, because of lack of thermodynamic data (explained further in Ref. 6, particularly Assumption 3.16).

⁽⁴⁾ As calculated by EQ6, which has no capability to handle nuclear transformations.

⁽⁵⁾ All Pu is taken as ²³⁹Pu and decayed to produce ²³⁵U (Ref. 6, particularly assumption 3.17).

⁽⁶⁾ At 7.85×10^3 years, ~6.7 kg Gd is in solution, but the drip rate is so low that very little is flushed from the WP. By the next time step given in the table, 11.5×10^3 years, most of this Gd has re-precipitated, increasing the total Gd solids by a corresponding amount. The table also shows that iron (Fe) in solid form takes a similar, but much smaller, jump between these two time points, for similar reasons.

⁽⁷⁾ Insoluble degradation products plus fragments of initial materials.

These calculations show that nearly all the initial ²³⁹Pu (or its daughter product ²³⁵U) is retained in the WP. The tables also show that nearly all the Fe, Mn, Al and Si in the packages will be retained, and from 72% to 100% of the Ni will be retained. A few principal minerals will dominate the bulk volume in the degraded waste package, and will account for all the retention of Pu (and daughter U), Fe, Mn, Al, Si and Ni. The calculations predict that smectite clay (an Fe-rich nontronite) will overwhelmingly constitute the bulk of the volume, followed by hematite, pyrolusite and Ni₂SiO₄. The original Na will be almost completely lost over the course of ~10⁵ years. The uranium is mostly contained in soddyite ((UO₂)₂(SiO₄)·2H₂O) (Ref 6).

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A further observation of interest is that the EQ6 calculations predict no loss of Hf at all. The insolubility of Hf is well recognized; the fact that Zr has been used as a surrogate, because of insufficient experimental data on Hf, should not diminish the significance of this result. The chemical similarity of Hf and Zr is well known from the fact that they always occur together in natural minerals. Direct experimental evidence on the solubility of Hf is now being developed; in the meantime, it should be noted that these results on Hf insolubility are for information purposes only; none of the general criticality conclusions of this document depend on this interpretation.

In addition to the above general observations, the following time dependencies in Tables 3.3.1-2 and 3.3.1-3 are of interest:

- Depleted uranium from the HLW filler glass (included in the second column of each table, which also includes the depleted uranium from the ceramic matrix, and which has no relation to the ^{235}U in the 6th column) decreases sharply during the first thousand years. This is because of the high U solubility, caused by the high pH (greater than 9.0), which, in turn, is caused by the HLW filler glass degradation during this time period (Ref 6, Figure 5.3.2-2). This high solubility of U permits rapid flushing, particularly because of the high drip rate during this time period. After this time period the pH has dropped sufficiently that the U solubility is too low to permit any significant amount to be flushed from the waste package. Consequently, the U in solids remains constant after 1000 years. It should be noted that nearly all the U left after this initial period of high pH is the U from the ceramic matrix, which has not degraded significantly by this time, as quantified in footnote 1 of both Table 3.3.1-2 and Table 3.3.1-3.
- Although the solubility of Pu is also largest during the 1000 years of high pH, the solubility of Pu is always too small to permit significant flushing. Hence the values in the 4th column do not change significantly over time.
- In this conservative approximation of assuming ^{239}Pu decay to ^{235}U starting at the time of waste package breach, only a small amount of ^{239}Pu has decayed during the first thousand years when the U solubility is high enough to support a significant amount of flushing. Hence, the small amount of Uranium solids given in the 6th column of each table does represent a small additional margin of conservatism. In future refinements of this analysis the Pu to U decay will be simulated in the EQ6 calculation directly, which will ensure that appropriate amounts of Pu decaying into U are removed from the waste package to ensure proper mass balance.

3.3.2 Physical Description of Degraded Configurations (Geometry)

The chemical configuration descriptions developed in the Section 3.3.1 are combined with the physical and geometric descriptions developed in this section to provide the input for the criticality evaluations presented in Section 3.3.3. Further information on these physical descriptions and criticality evaluations is provided in the degraded mode criticality calculation document, Ref. 12.

For this criticality analysis the degraded configurations are divided into two types:

- Intermediate-level degraded configurations in which the ceramic waste form disks remain largely intact while all the other components have been degraded and/or fragmented (and the

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- soluble degradation products have been removed from the waste package), and
- Fully collapsed configurations, in which the ceramic waste form disks are also physically degraded and/or fragmented with all the fragments and insoluble degradation products mixed into a homogeneous layer at the bottom of the horizontal waste package.

These configurations are described in the following sections.

3.3.2.1 Intermediate-Level Degradation Configurations

Three conservative configurations are analyzed for intermediate-level degradation. These configurations are discussed in the following sub-sections. Since the waste form is intact, these calculations are independent of time. For all three configurations the ceramic disks have the intact composition given in Table 2.2.3-1. The first two configurations have a close packing arrangement of the tubes of disks, and the third is closely related to the second. The close packing arrangement has been shown to be conservative by calculations showing the k_{inf} (neutron multiplication factor for an infinite array of tubes) increasing with decreasing lattice spacing (Ref 11).

3.3.2.1.1 Square Geometry, Square Lattice Arrangement of Can Containing Tubes

The first of the intermediate-level degradation configurations consists of all 35 tubes of the plutonium ceramic in a waste package arranged in a nearly square lattice of the 35 tubes (a 6x6 array missing the top-right-hand corner tube). Each tube contains its initial load of 4 cans, and the array rests on the bottom of the waste package, with the package voidspace (interstices between the tubes and the package volume outside of the nearly square array) filled with water of several different densities. This arrangement is shown in Figure 3.3.2.1-1. Also shown are the inner and outer waste package barriers and the reflecting layer of water outside the waste package. This reflecting layer represents the most conservative configuration since the drift would have to be filled with water. It should be noted that the removal of the glass and steel (and their degradation products) from the waste package is a conservative simplification, since these materials are likely to be more neutron absorbing, and less neutron moderating, than the water. Although the conservatism is not proved, the simplification is acceptable for this study because the resulting k_{eff} turns out to be very low.

It is not expected that this square lattice would actually be achieved, but it does represent something close to a worst case arrangement of intact tubes of cans, or even of intact disks without the cans, since it puts the disks into very close proximity. The disks could be in closer proximity if the lattice were hexagonal close packed, instead of square (or rectangular), but the

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04/14/98 15:51:44
 Degraded Mode Criticality
 Analysis of Plutonium
 Immobilized in Ceramic
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 (1.000000, .000000, .000000)
 (.000000, 2.000000, .000000)
 origin:
 (-.40, 1.41, .80)
 constant = (234.95, 234.95)

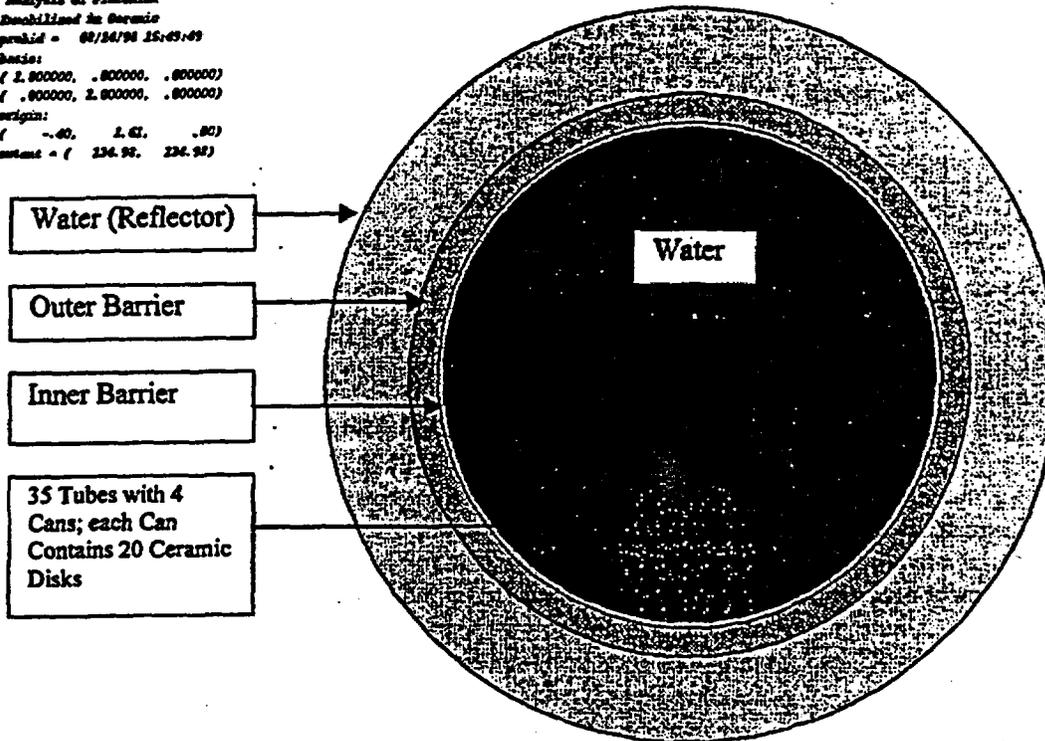


Figure 3.3.2.1-1. Cross-section of a Horizontally Emplaced Waste Package Showing a Square Lattice Arrangement of Tubes in a "Square" Geometry

hexagonal close packing would be unnecessarily conservative, since it would be impossible for the tubes to fall into such an arrangement. It should be noted that the rectangular close packing is metastable with respect to gravity, but the hexagonal close packing is unstable with respect to gravity. The following are further conservatisms of this configuration:

- There is an absence of degradation products of the other waste package components, since some of these degradation products are neutron absorbers (e.g., iron or manganese).
- The curvature of the waste package bottom would produce a slight vertical displacement of adjacent stacks of tubes; this would lead to a larger separation between tubes in adjacent stacks.

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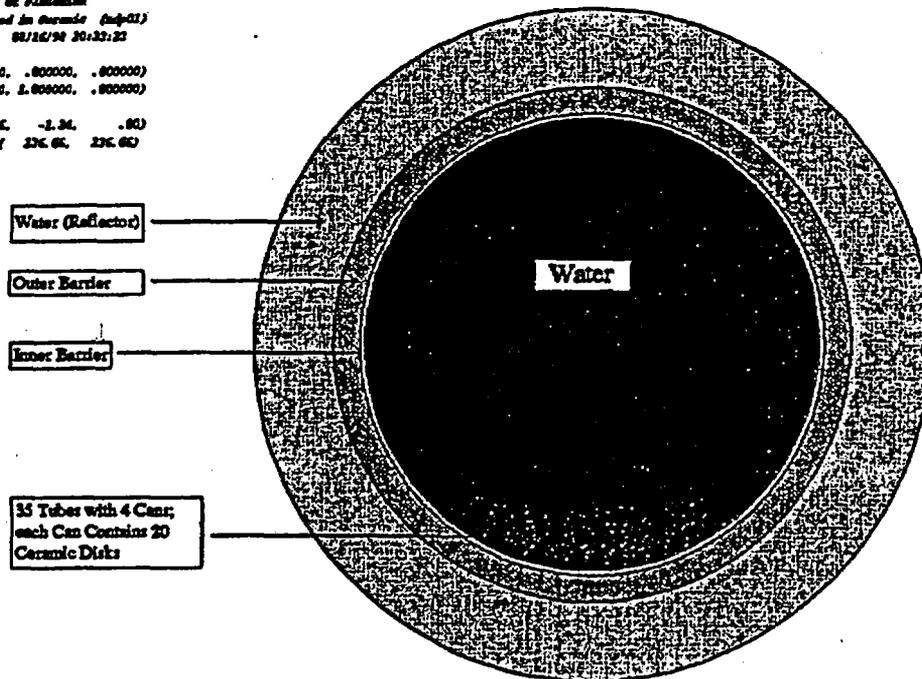
3.3.2.1.2 Pseudo-Cylindrical Segment Geometry, Locally Square Lattice Arrangement of Tubes

A later stage of intermediate-level degradation is represented by the configuration shown in Figure 3.3.2.1-2. As depicted in this figure, the thirty-five intact tubes (each containing four non-degraded cans of the Pu-bearing ceramic disks) create a "pseudo-cylindrical segment" geometry with tubes stacked at the bottom of the waste package. As with the configuration of Section 3.3.2.1.1, the tube stack lattice has a vertical and horizontal pitch equal to the can outer diameter. This configuration is formed by stacking the tubes vertically, with the bottommost tube of each stack resting on the waste package inner barrier. As with the configuration of Section 3.3.2.1.1, the removal of the glass and steel (and their degradation products) from the waste package is a conservative simplification, since these materials would be more neutron absorbing, and less neutron moderating, than the water. The simplification can be used because the resulting k_{eff} turns out to be very low.

The configuration of the 35 settled tubes shown in Figure 3.3.2.1-2 has three curved layers of tubes with 14, 12, and 9 tubes in the bottom layer, middle layer, and the top layer, respectively. Because of the variation in the vertical position of the inner barrier surface, tubes will be somewhat offset from one stack to the next, so the separation between tubes in adjacent stacks will be somewhat greater than in the completely square lattice of the previous subsection. This

```

02/16/98 20:35:22
Degraded Node Criticality
Analysis of Plutonium
Immobilized in Ceramic (44-01)
problem - 02/16/98 20:35:22
basis:
( 2.000000, .000000, .000000)
( .000000, 2.000000, .000000)
origin:
( -2.34, -2.34, .00)
extent = ( 236.65, 236.65)
    
```



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Figure 3.3.2.1-2. Cross-section of a Horizontally Emplaced Waste Package Showing a Stacking of 35 Tubes in a Pseudo-Cylindrical Segment Geometry

pseudo-cylindrical segment is less conservative than the square array of the previous sub-section, because the flatter arrangement will result in considerably more neutron leakage. However, it is a much more likely configuration because it represents a much more stable state with respect to gravity.

3.3.2.1.3 Pseudo-Cylindrical Segment Geometry, Square Lattice Arrangement of Ceramic Disks

The third and final intermediate-level degradation configuration is similar to those discussed above, but with the stainless steel can material removed. It is assumed that the ceramic disks preserve the same spacing as in the previous configuration (Section 3.3.2.1.2). This configuration may be expected to be more reactive than the previous configuration, due to the absence of the iron (a moderately effective neutron absorber) in the stainless steel. The iron oxide corrosion product of the stainless steel is insoluble, and it would be accurate to include it in the criticality calculation, both for its neutron absorbing effect and its moderator displacement effect. However, the iron oxide is omitted, in keeping with the conservative simplification that has removed all degradation products from the other intermediate-level configurations.

3.3.2.2 Fully Collapsed Configuration

The fully collapsed configuration is depicted in Figure 3.3.2.2-1. In this configuration all of the waste package components are either degraded or fragmented, and the products are homogenized. The sludge in the cylindrical segment at the bottom of the waste package contains a mixture of degradation products (including fissile and neutron absorbing materials) and non-degraded fragments of waste package components. The space above the cylindrical segment is filled with water. The moles of the principal elements, and isotopes, present in the sludge are listed in Table 3.3.2.2-1 for the compositions that have been used for criticality evaluation (taken from Ref 12, Table 5-2). These compositions are given in moles per liter of waste package void volume (3737.9 liters calculated in Ref 18, spreadsheet masses5.xls) to preserve consistency with the geochemistry calculations of Ref 6, and the MCNP calculations of Ref 12. The consistency between the mole data in Table 3.3.2.2-1 and the kilogram data in Tables 3.3.1-2 and 3.3.1-3 can be verified by dividing the kilograms by the atomic weight (to convert to kg moles), dividing by 3737.9 (to convert to per liter), and multiplying by 1000 (to convert from kilograms to grams).

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09/16/98 11:27:27
Degraded State Criticality
Analysis of Plutonium
Immobilized in Ceramic (SGP1)
problem = 09/16/98 11:36:17
basis:
(1.000000, .000000, .000000)
(.000000, 1.000000, .000000)
origin:
(.00, .00, .00)
current = (100.00, 100.00)

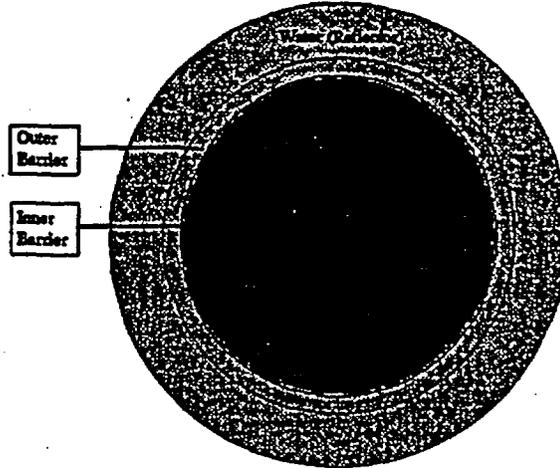


Figure 3.3.2.2-1. A Cross-sectional View of a Horizontally Emplaced Waste Package for the Full Degradation Configuration

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Table 3.3.2.2-1. Principal Elements or Isotopes in the Sludge Estimated by the EQ6 Code

Element or Isotope	Moles Remaining (per liter of WP void volume)		
	1.86% Gd Loss ⁽¹⁾	13.2% Gd Loss ⁽²⁾	All Gd Removed ⁽³⁾
	At 30,200 Years	At 30,860 Years	At 30,200 Years
O-16 ⁽⁶⁾	66.097	66.738	66.097
Ti	1.534	1.642	1.534
U-238	0.320	0.320	0.320
Pu-239	0.068 (0.116) ⁽⁴⁾	0.067 (0.116) ⁽⁴⁾	0.068
Hf	0.190	0.190	0.190
Ca	0.911	0.478	0.911
Gd	0.156	0.138	0
Al-27	1.753	1.754	1.909
U-235 ⁽⁵⁾	0.094 (0.046) ⁽⁴⁾	0.095 (0.046) ⁽⁴⁾	0.094
Fe	12.072	12.075	12.072
Na-23	0.033	0.022	0.033
Ni	1.184	1.369	1.184
Si	16.032	16.036	16.032
Mn-25	0.858	0.858	0.858

⁽¹⁾ Developed from values in the eighth line of Table 3.3.1-2.

⁽²⁾ Developed from values in the eighth line of Table 3.3.1-3.

⁽³⁾ Developed from the 1.86% Gd loss column, with the remaining Gd₂O₃ replaced by Al₂O₃ to preserve a realistic sludge solids volume, since there was no consistent geochemical analysis (EQ6) that could produce a removal of all the gadolinium. This replacement has no direct effect on criticality, since aluminum has a very low neutron cross section.

⁽⁴⁾ Changed to reflect the major isotopic differences between the 7th and 8th lines in both Tables 3.3.1-2 and 3.3.1-3.

⁽⁵⁾ Includes 0.0007 moles from the ceramic depleted uranium (at 0.2% enrichment), but neglecting the less than 0.00002 moles from the less than 5 kg of HLW filler glass uranium (at 0.5% enrichment) remaining.

⁽⁶⁾ Oxygen in sludge solids. The oxygen in water is accounted separately.

3.3.3 Criticality Evaluations of Degraded Configurations

3.3.3.1 Criticality Evaluation Results for the Intermediate-Level Degradation Configurations

The k_{eff} estimates, and their corresponding standard deviations for the intermediate-level degradation configurations, which were described in Section 3.3.2.1, are provided in Tables 3.3.3.1-1 and 3.3.3.1-2. As explained in Section 3.3.2.1, filling the waste package with water is a simplification of the actual configuration, which would have the clay degradation product of the HLW glass partly filling the space not occupied by the ceramic. Varying the water density between 0.01 g/cm³ and 1.0 g/cm³ provides a simplified model of the sensitivity of k_{eff} to the

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concentration of water in such clay. The results show some initial increase in k_{eff} with increasing water density, and that beyond some density, the k_{eff} decreases with increasing water density. The initial increase is due to some small amount of moderation to enhance fission. Increasing moderation beyond some optimum simply provides more thermal neutrons to be absorbed by the gadolinium (which has a much higher thermal absorption cross section than the fission cross section of the uranium or plutonium). The limited number of cases, in these tables, does not provide sufficient resolution of the effects of water density to determine the precise location of the maximum k_{eff} .

Table 3.3.3.1-1. k_{eff} Estimates for Intermediate-Level Degradation Configuration: Square Arrangement⁽¹⁾

Water Density (g/cm ³)	k_{eff}	Standard Deviation
0.01	0.338	0.00051
0.1	0.368	0.00053
1.0	0.364	0.00061

⁽¹⁾ 6x6 square array missing the top right-hand corner element; geometry shown in Figure 3.3.2.1-1

The pseudo-cylindrical segment configuration is generally expected to have a lower k_{eff} than a square geometry having the same number of tubes because the neutron leakage will be greater due to the higher aspect ratio geometry. This expectation is justified by comparing the k_{eff} values for the pseudo-cylinder segment geometry cases in Table 3.3.3.1-2 with the square geometry cases in Table 3.3.3.1-1. The only case in which the cylindrical segment geometry had a higher k_{eff} is the case having the cans degraded, and the waste package filled with water at a density of 1.0 g/cm³ (case 6 of Table 3.3.3.1-2 compared with case 3 of Table 3.3.3.1-1). This is because the configuration with more neutron leakage will have its k_{eff} increased by a material change that results in more fission by thermal neutrons (which will occur if the moderator displacing, and neutron absorbing, iron is removed). This fact also explains why the cases in Table 3.3.3.1-2 all show increased k_{eff} with increasing water. It should be recognized that this explanation is only qualitative; the variations in k_{eff} are the result of several factors, and the magnitude of the changes is so small that the balance among them must be very close.

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Table 3.3.3.1-2. k_{eff} Estimates for Intermediate-Level Degradation Configuration: Pseudo-Cylindrical Segment Geometry⁽¹⁾

Condition of Stainless Steel Cans	Water Density (g/cm ³)	k_{eff}	Standard Deviation
Present	0.01	0.288	0.00051
Present	0.1	0.328	0.00065
Present	1.0	0.348	0.00075
Removed	0.01	0.309	0.00057
Removed	0.1	0.343	0.00069
Removed	1.0	0.379	0.00078

⁽¹⁾ Geometry shown in Figure 3.3.2.1-2.

3.3.3.2 Criticality Evaluation Results for the Fully Degraded Configurations

The selection of worst case scenarios and times for criticality evaluation is based primarily on the following two considerations: (1) The decay of ²³⁹Pu to ²³⁵U decreases the k_{eff} with time because the former is generally more reactive than the latter. (2) The possible loss of Gd from the WP may increase the k_{eff} with time. For the Scenario #6 in Table 3.3.1-1, the Gd loss reaches 13.2% after 11,500 years and remains nearly constant thereafter, so the k_{eff} should be largest at this time. On the other hand, in Scenario #4 of Table 3.3.1-1 the Gd loss reaches a plateau of 14.8%, but not until 60,000 years (Ref 18, files Cerd2W0_00151.allpost and Cerd2W0_00151.lastpost). It is, therefore, necessary to test the relative sensitivity of k_{eff} to variation in time (which implies a variation in the ratio of ²³⁹Pu to ²³⁵U) compared with the variation in Gd loss. For this purpose the timestep near 11,000 years was compared with the timestep near 31,000 years, and Scenario #2 (1.86% maximum Gd loss) was compared with Scenario #6 (13.2% maximum Gd loss). The results are shown in Table 3.3.2-1. The first six lines of this table are based on Scenario #2, in which the maximum Gd loss is 1.86% of the initial loading. The second set of 6 lines is for Scenario #6, in which the maximum Gd loss is 13.2% of the initial loading. The sludge compositions for these two sets of cases are given in the second and third columns of Table 3.3.2.2-1, respectively.

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Table 3.3.3.2-1. k_{eff} Estimates for the Full Degradation Configurations with Partial Gd Loss⁽¹⁾

Case #	Time after the initial breach of the Waste Package (years)	% Gd Loss	Water Content of the Homogenized Sludge (vol%)	k_{eff}	Standard Deviation
1	11500	1.86	0	0.353	0.00073
2	11500	1.86	9 ⁽²⁾	0.366	0.00074
3	11500	1.86	23 ⁽²⁾	0.355	0.00080
4	30200	1.86	0	0.322	0.00060
5	30200	1.86	9 ⁽²⁾	0.320	0.00057
6	30200	1.86	23 ⁽²⁾	0.295	0.00053
7	11500	13.2	0	0.364	0.00071
8	11500	13.2	10 ⁽²⁾	0.380	0.00059
9	11500	13.2	30 ⁽²⁾	0.354	0.00063
10	30860	13.2	0	0.332	0.00069
11	30860	13.2	10 ⁽²⁾	0.327	0.00067
12	30860	13.2	30 ⁽²⁾	0.285	0.00050

⁽¹⁾ Geometry shown in Figure 3.3.2.2-1.

^{(2), (3)} These values do not match between the two different Gd loss cases (1.86% and 13.2%) because they were developed from different dilution strategies. However, both sets cover sufficient range to demonstrate the decrease in k_{eff} with increasing water content.

In Table 3.3.3.2-1 it is seen that the difference in k_{eff} for the corresponding members of the set (1,2,3) with the set (4,5,6), is between 0.03 and 0.06, while the difference between set (1,2,3) and the corresponding members of set (7,8,9) is between 0.010 to 0.001. Since the former is greater than the latter, it is concluded that the sensitivity to time (surrogate for the ²³⁹Pu-²³⁵U split) is greater than the sensitivity to Gd loss. A similar comparison of the differences between sets (7,8,9) and (10,11,12) with the differences between sets (4,5,6) and (10,11,12) supports the same conclusion. This greater sensitivity to time differences than to Gd loss differences suggests that Scenario #6 is more conservative than scenario #4, even though the Gd loss in the latter is 10% greater than the Gd loss in the former, because the former reaches its largest Gd loss at 11,500 years, while the later only reaches it at 60,000 years.

Another result of interest in Table 3.3.3.2-1 is that the k_{eff} for the later time (lower ratio of ²³⁹Pu to ²³⁵U) is monotonic decreasing as the water content of the sludge is increased, while the earlier time indicates a peaking at some intermediate water concentration (although the precise location is not identified by this coarse analysis). The slight peaking of the higher ²³⁹Pu cases is caused by the 35% higher thermal fission cross section of ²³⁹Pu compared with ²³⁵U, which enables it to better compete for the additional thermal neutrons which result from the initial increase in sludge water content. As the water content increases further, the Gd and fissile material are spread out, and other factors become dominant, particularly the greater effectiveness of Gd with decrease in its self-shielding. Consequently, the k_{eff} decreases with further water content.

It should be further noted that the times near 30,000 years in Tables 3.3.1-2 and 3.3.1-3 differ slightly (30,200 years and 30,860, respectively) because of a slight difference in the way the EQ6 flow-through procedure happened to work out for these two scenarios.

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Table 3.3.3.2-2 shows the results for a set of hypothetical configurations in which all the Gd is lost. The EQ6 analyses of this study have shown that such configurations are not possible, but it is of some interest to evaluate them as a set of non-mechanistic worst cases for comparison purposes only.

Table 3.3.3.2-2. k_{eff} Estimates for the Hypothetical Full Degradation Configurations with no Gd Present (for comparison purposes only, since complete removal is non-physical)⁽¹⁾

Water Content of the Homogenized Sludge (vol%)	k_{eff}	Standard Deviation
0	0.581	0.00112
23	0.824	0.00136
41	0.918	0.00137
60	0.946	0.00117

⁽¹⁾ Geometry shown in Figure 3.3.2.2-1.

These results show an increase in k_{eff} with increasing water content of the homogenized sludge. This is because the removal of all Gd leaves only the Hf as neutron absorber. The thermal neutron cross section of Hf is much less than that of ²³⁹Pu or ²³⁵U, so it will not out-compete the fissile elements for thermal neutrons.

The results presented in Table 3.3.3.2-2 indicate that for water content greater than 60% the configuration could be critical. Since none of the degradation scenarios showed any possibility of a complete Gd loss, such possibility of criticality was not investigated further at this time. The following observations are, however, of interest:

- It was shown in Ref. 4, Section 7.5, that a few kilograms of Gd are generally sufficient to prevent criticality. Therefore, if there were a mechanism for removing most of the Gd, there would most likely be enough left to prevent criticality.
- There is no experimental information on the long-term maximum sustainable homogeneous water concentration. However, water concentrations higher than 60% are possible in clay (Ref 5, Section 6.5), but it is questionable whether heavy precipitates, such as the minerals produced by these calculations, could remain suspended in such large water concentrations for long periods of time.
- If a mechanism for large Gd loss were discovered, it would be possible to prevent criticality by increasing the Hf content, although Hf is a much less efficient absorber of thermal neutrons than is Gd. It has been found (Ref 4, Section 7.5.5) that for a similar mass of ²³⁹Pu and ²³⁵U, to that used here 28 kg of Hf to equal .5 kg of Gd (56 to 1). Based on the analysis in Ref 4 it would take approximately 50% more Hf than is already planned for the ceramic to prevent criticality in the complete absence of Gd.

4. FINDINGS AND CONCLUSIONS

4.1 Findings

4.1.1 Maximum Loss of Neutron Absorber

In each of the cases most of the primary neutron absorber, gadolinium, is retained in the waste package because it is just as insoluble as uranium or plutonium. This result is in contrast with previous analyses that showed a higher solubility of gadolinium due to pH values below 6.0, which could be caused by chromate ion produced by the corrosion of stainless steel. For the present ceramic waste form, the geochemistry analysis with EQ6 shows that during the time of simultaneous degradation of the ceramic and the stainless steel there will generally be alkaline precipitates from earlier degradation of the ceramic and the HLW filler glass. These precipitates, principally the calcium containing minerals calcite and dolomite, will be slowly re-dissolving and flushing from the waste package. During this re-dissolution process the steady state concentration of calcium ions produces enough alkalinity to counter the acidification tendency of the corroding stainless steel. Therefore, the pH remains nearly neutral, and the gadolinium remains nearly insoluble. As a consequence the maximum removal of gadolinium is only 13.2% for Scenario #6 or 14.8% for Scenario #4, with the former taking 11,500 years and the latter requiring 60,000 years (Section 3.3.1).

Since the differing parameters of these two scenarios cover the likely range of corrosion rates for stainless steel and the ceramic waste form, it is concluded that there will be no set of corrosion rates (for ceramic and stainless steel) found to produce a significantly larger Gd loss.

It was also shown that there is virtually no loss of hafnium in upwards of several hundred thousand years (Section 3.3.1). The criticality prevention capability of this neutron absorber becomes important only if all the Gd is lost (Section 3.3.3.2).

4.1.2 Criticality of the Intact Configuration

The completely intact configuration has no potential for criticality at all. The calculated $k_{eff} = 0.12$ for the nominal case, and $k_{eff} = 0.11$ when all of the voidspace in the waste package is filled with water. In most potentially critical configurations water would act as a moderator and increase the k_{eff} , but in this case thermalization of neutrons only facilitates their more efficient absorption by the gadolinium. (Section 3.2.2)

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4.1.3 Criticality of Degraded Configurations

The successive stages of degradation may be characterized by the following configurations, and by their resulting criticality:

1. Intermediate degradation, with all 5 canister shells corroded and the filler glass degraded to clay. This case has been approximated by replacing the clay with water. The cans containing the ceramic disks are largely intact so that their iron is available for neutron absorption, even though the cans have been penetrated by water. The cans are nominally still contained in 35 tubes (5 canisters x 7 tubes per canister), which are stacked in a nearly square geometry at the bottom of the waste package. For the waste package filled with water $k_{eff} = 0.34$, while the dry case has only $k_{eff} = 0.29$. A hexagonal close packaging arrangement would have been more conservative, but its occurrence would be incredible. (Section 3.3.2.1.1)
2. Intermediate degradation with the same chemistry as the previous configuration, but with all 35 tubes laying at the bottom of the waste package filling a cylindrical segment with a somewhat curved upper surface. These tubes are stacked in a square lattice close packing, similar to the previous configuration. This pseudo-cylindrical configuration gives $k_{eff} = 0.37$ when all of the space around and between the ceramic disks is filled with water having a density of 1 g/cm^3 , and a $k_{eff} = 0.31$ when this space is empty (approximated by the lowest density used for water, 0.01 g/cm^3). (Section 3.3.2.1.2)
3. Completely degraded: the insoluble degradation products of the waste form, the HLW filler glass, and the steel are assumed to form a homogeneous sludge, which is slumped to the bottom of the waste package, where it uniformly fills a cylindrical segment. The rest of the waste package is filled with water, which serves as a reflector. Under these circumstances a maximum of 13.2% of the neutron absorbing gadolinium will be dissolved and flushed from the waste package. This configuration gives $k_{eff} = 0.33$ when there is no water mixed in the sludge, and $k_{eff} = 0.28$ when the sludge has 30% water by volume. (Section 3.3.2.1.3)

The only change in the waste package contents that can result in a configuration that might have a k_{eff} near the regulatory limit of 0.95 is the complete, or nearly complete, loss of gadolinium. Previous studies had identified scenarios that could lead to complete loss of gadolinium. These previous studies were either more conservative (but less rigorous) or dealt with a less alkaline waste form. Even though the present study indicates that such large losses of Gd are not credible, the complete loss of gadolinium has been evaluated, for information purposes only, with the finding that criticality cannot occur unless the water content of the remaining sludge is greater than 60 vol%. (Section 3.3.3.2)

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4.2 Conclusions

No criticality is possible for this ceramic waste form, even with 5 Pu canisters per waste package, primarily because of the small amount of gadolinium lost. (Section 3.3.3)

The findings on gadolinium retention in the waste package are relatively insensitive to ceramic dissolution rate, except for the following two extreme conditions:

- A very low ceramic dissolution rate will prevent the release of any gadolinium from the waste package (not even the small amount, 13%, released under the conditions of finding #3 of 4.1.2, above), because there will be no gadolinium released from the waste form until after all the stainless steel has corroded and there is no longer any possibility of acidification.
- A very high initial drip rate, extending over several thousand years, coupled with a high corrosion rate of the ceramic waste form, could facilitate a significant removal of gadolinium from the waste package. Under such a condition all of the alkaline minerals could be flushed from the waste package before most of the stainless steel corroded. If this very high drip rate were followed by a period of very low drip rate, the pH drop could be of long enough duration to remove most of the gadolinium.

The second of these conditions is not credible. A high drip rate persisting over several thousand years would not be credible. Furthermore, the second condition would be prevented by the occurrence of the first. A very slowly degrading ceramic would preclude the early removal of all the alkaline minerals (since some of the alkaline minerals come from the ceramic itself) before most of the stainless steel had degraded. Therefore, the waste package solution could not become acidic, since all the stainless steel (with its acid producing potential) would be gone before much of the ceramic had degraded. (Section 3.3.1)

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5. REFERENCES

1. United States Department of Energy 1996. *Disposition of Surplus Highly Enriched Uranium Final Environmental Impact Statement*. Washington, D.C. TIC: 231278.
2. United States Department of Energy 1997. *Record of Decision for the Storage and Disposition of Weapons-Usable Fissile Materials Final Programmatic Environmental Impact Statement*. Washington, D.C. TIC: 239425.
3. Civilian Radioactive Waste Management System (CRWMS) Management & Operating Contractor (M&O) 1998. *Technical Document Preparation Plan for the Report on Intact & Degraded Criticality for Selected Plutonium Waste Forms in a Geologic Repository*. BBA000000-01717-4600-00011 REV 00. Las Vegas, NV. CRWMS M&O. ACC: MOL.19980911.0307
4. CRWMS M&O 1997. *Predecisional Document Degraded Mode Criticality Analysis of Immobilized Plutonium Waste Forms in a Geologic Repository*. A00000000-01717-5705-00014 REV01. Las Vegas, NV. CRWMS M&O. ACC: MOL.19980422.0911.
5. CRWMS M&O 1998. *Evaluation of Codisposal Viability for Aluminium-Clad DOE-Owned Spent Fuel: Phase II Degraded Codisposal Waste Package Internal Criticality*. BBA000000-01717-5705-00017 REV 01. Las Vegas, NV. CRWMS M&O. ACC: MOL.19980701.0782
6. CRWMS M&O 1998. *EQ6 Calculations for Chemical Degradation of Pu-Ceramic Waste Packages*. BBA000000-01717-0210-00018 REV 00. Las Vegas, NV. CRWMS M&O. ACC: MOL.19980918.0004.
7. CRWMS M&O 1998. *Controlled Design Assumptions Document*. B00000000-01717-4600-00032 REV 05. Las Vegas, NV. CRWMS M&O. ACC: MOL.19980804.0481.
8. Wolery, Thomas J., and Daveler, Stephanie 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. Lawrence Livermore National Laboratory. Livermore, CA. TIC: 205002.
9. Briesmeister, Judith F., Ed. 1997. *MCNP - A General Monte Carlo N-Particle Transport Code*. LA-12625M, Version 4B. Los Alamos National Laboratory. Los Alamos, NM. ACC: MOL.19980624.0328.
10. CRWMS M&O 1998. *Complete Draft VA UZ Abstraction/Test Document - B00000000-01717-2200-00201, Unsaturated-Zone Flow: Preliminary Draft Section 2.3 of TSPA-VA Document*. B00000000-01717-2200-00201. Las Vegas, NV. CRWMS M&O. ACC: MOL.19980428.0202

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11. CRWMS M&O 1998. *Criticality Evaluation of Plutonium Disposition Ceramic Waste Form: Intact Mode*. BBA000000-01717-0210-00012 REV 00. Las Vegas, NV. CRWMS M&O. ACC: MOL.19980811.0635.
12. CRWMS M&O 1998. *Criticality Evaluation of Plutonium Disposition Ceramic Waste Form: Degraded Mode*. BBA000000-01717-0210-00014 REV 01. Las Vegas, NV. CRWMS M&O. ACC: MOL.19980918.0003.
13. Lawrence Livermore National Laboratory 1998. *Plutonium Immobilization Project, Data for Yucca Mountain Total Systems Performance Assessment, Rev. 1*. PIP Milestone Report, Milestone 2.b.b. PIP 98-012. Livermore, CA. ACC: MOL.19980818.0349.
14. CRWMS M&O 1996. *DHLW Glass Waste Package Criticality Analysis (SCPB: N/A)*. BBAC000000-01717-0200-00001 REV 00. Attachment I, Table 3.3.8. Las Vegas, NV. CRWMS M&O. ACC: MOL.19960919.0237.
15. Not Used.
16. CRWMS M&O 1995. *Total System Performance Assessment – 1995. An Evaluation of the Potential Yucca Mountain Repository*. B000000000-01717-2200-00136 REV 01. Las Vegas, NV. CRWMS M&O. ACC: MOL.19960724.0188.
17. CRWMS M&O 1996. *Report on Evaluation of Plutonium Waste Forms for Repository Disposal, Revision 1*. A-00000000-01717-5705-00009 REV 00A. Las Vegas, NV. CRWMS M&O. ACC: MOL.19961210.0066.
18. CRWMS M&O 1998. *Electronic Attachments for: BBA000000-01717-0210-00018 REV 00, EQ6 Calculations of Chemical Degradation of Pu-Ceramic Waste Packages*. Las Vegas, NV. CRWMS M&O. ACC: MOL.19980831.0169.