MOL.19970324.0023

PREDECISIONAL DRAFT

WBS: 1.2.1.10
QA: N/A

Civilian Radioactive Waste Management System
Management & Operating Contractor

Status Report on Degraded Mode Criticality Analysis of Immobilized Plutonium Waste Forms in a Geologic Repository

A00000000-01717-5705-00013 REV 00

September 25, 1996

Prepared for:

U.S. Department of Energy
Office of Civilian Radioactive Management
1000 Independence Avenue S.W.
Washington, DC 20585

Prepared by:

TRW Environmental Safety Systems Inc.
2650 Park Tower Drive
Suite 800
Vienna, Virginia 22180

Under Contract Number
DE-AC01-91RW00134

PREDECISIONAL DRAFT

10

PREFACE

This report summarizes the work in progress in analyzing the degraded mode criticality of immobilized plutonium waste forms in a geologic repository environment. Only the can-in-canister glass and ceramic waste forms are evaluated. The principal focus of this report is in the development of degradation scenarios for criticality calculations, establishing the range of parameters that will be evaluated, and the environmental conditions of the repository that contribute to these evaluations. An analysis methodology to conduct these evaluations is presented; the waste form characteristics and waste package design for emplacement are discussed; and the physical and chemical processes that could lead to potential critical configurations are delineated.

Because the evaluations are still in progress, all the possible scenarios are not yet completely defined. The results of the scenario development will be used as input data sets for the time-dependent (kinetic) evaluations, followed by the k_{eff} calculations (using the MCNP code). Because the fundamental dissolution, thermodynamic and thermochemical data is still being developed for these waste forms, the bounding analysis will be conducted for ranges for the principal variables, and sensitivity analyses will be performed, where possible.

INTENTIONALLY LEFT BLANK

CONTENTS

CONTENTS (Continued)

FIGURES

TABLES

1. INTRODUCTION AND BACKGROUND

The Office of Fissile Materials Disposition (MD) has undertaken an evaluation of numerous waste forms containing plutonium for ultimate disposal in a geologic repository. It has been determined that one of the principal technical considerations for disposal of these waste forms is their long-term performance in a repository environment. This long-term performance consists of two elements: total system performance of the waste form and package (i.e., releases to the accessible environment) in the repository, and long-term criticality behavior of these waste forms and packages in the repository. This report addresses only the criticality issues; the total system performance assessment is the subject of a separate report (Ref. 1).

Criticality issues for the plutonium waste forms as packaged for disposal in a geologic repository fall into three broad categories: those associated with the as-fabricated (intact) waste packages; those associated with the degraded package and waste form in the near-field environment; and those associated with the flow and transport of the fissile material into the far-field with reconcentration (external criticality). Earlier studies (Ref. 2) have shown that the as-fabricated or intact criticality is well within the NRC promulgated requirements for criticality control. These analyses considered several different waste forms: MOX spent fuels (both BWR's and PWR's) and waste forms immobilized in glass and ceramic matrices produced by different processes. This report focuses on only the degraded mode criticality considerations for two specific waste form configurations: can-in-canister glass and can-in-canister ceramic. External criticality is not addressed in this report.

Degradation scenarios that span the range of potential criticality occurrences have been developed. These scenarios are used to screen plutonium disposition alternatives and to rank them with respect to criticality risk. The possibility for the occurrence of these scenarios has been ascertained from simple mass balance models using currently available data on a range of parameter values pertaining to the alteration of typical glass and ceramic waste forms, and the solubility of the principal isotopic species of interest.

Section 2 of the report describes the waste forms and the waste package. Section 3 gives assumptions concerning the physical conditions and configurations which can lead to criticality, and describes the analysis methodology. Section 4 describes the conceptual processes and events which can lead to potentially critical configurations. Section 5 gives the input data values to be used in the evaluation calculations. Sections 6 and 7 are provided in preliminary or outline form to indicate their expected content of the final report.

INTENTIONALLY LEFT BLANK

2. WASTE FORM & WASTE PACKAGE DESCRIPTIONS

2.1 GLASS WASTE FORM

2.1.1 Nominal Pu-Glass Description

The can-in-canister glass waste form nominally consists of plutonium dissolved in a Lanthanide Borosilicate (La-BS) glass with an equi-molar ratio of a neutron absorber (gadolinium). Based on the latest data, the La-BS glass appears to be the most suitable, but other alternatives are still being investigated, particularly the alkali-tin-silicate (ATS) glass which could be the preferred form for the adjunct melter option. The plutonium bearing glass is poured into cans which are, in turn, supported on a rack/basket, and embedded in a DHLW glass filler within a DWPF-type canister as shown in Figure 1. The compositions of the La-BS and DWPF glass are presented in Appendix A, Tables A-1 and A-2.

The primary unit of this waste form is a glass cylinder inside a stainless steel can with the outside dimensions as 12.035 cm dia x 57.535 cm long and 0.3175 cm thick. The interior volume of this can (5808 cm^3) is 85 percent filled with a La-BS glass doped with approximately 10 wt% Pu and 6.6 wt% Gd (1:1 mole ratio with the Pu), as described in Table A-1. The Gd serves as the neutron absorber which prevents criticality, even when the waste package is filled with water. The density of the doped glass is approximately 5.5 gm/cm^3, so that each can has approximately 2.56 kg of Pu.

Different glass waste forms are being investigated that provide high solubility of Pu and Gd within the glass, and high resistance to dissolution in water having chemical composition similar to that expected in a Yucca Mountain repository environment. The ranges of dissolution rates for these glasses are summarized, together with the range of dissolution rates for the most likely ceramic waste form, in Section 5.1, Table 5.1-1.

It is assumed that the dissolution of the glass waste form is congruent, which means that each component of the glass will be released from the solid form at a rate which is equal to the glass dissolution rate multiplied by the weight fraction of that component. It is further assumed that the individual ionic breakdown products (components) of the glass dissolution will go into solution as the glass is dissolved. However, those ions which are insoluble will immediately precipitate, generally at the point of dissolution. These low solubility components will generally be incorporated into the altered layer (which is similar to the initial glass, but without all the soluble components of the initial glass).

2.1.2 Additional Glass Waste Form Composition Considerations

Optimum Neutron Absorber

Gadolinium has been the nominal choice for neutron absorber because, of all the elements, it has the largest cross section (most efficient) for thermal neutrons. However, other elements have better features with respect to other requirements. Samarium is the cheapest and may be almost as efficient as Gd for the entire neutron spectrum most appropriate to the Pu criticality issue. Hafnium is the

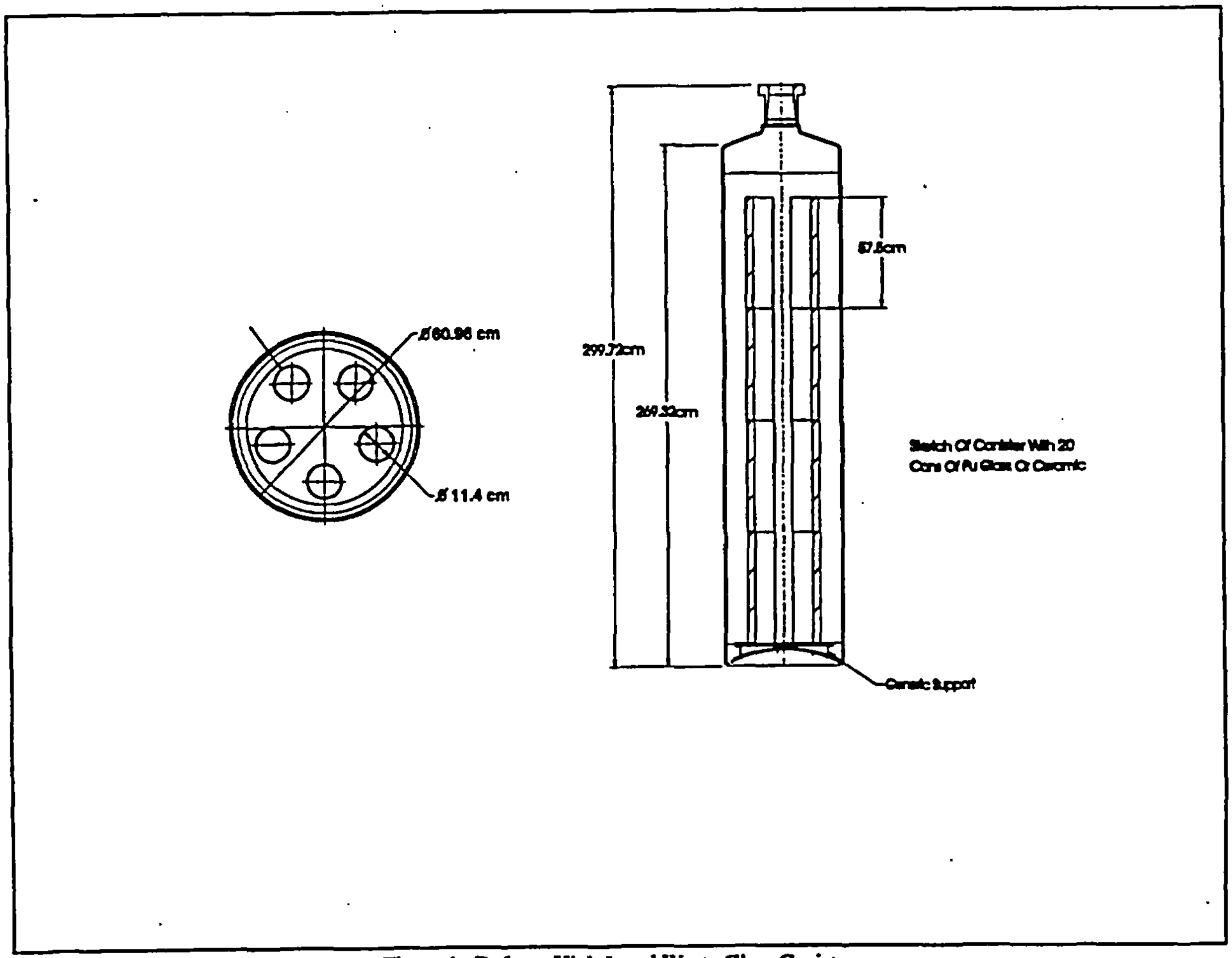

Figure 1. Defense High-Level Waste Glass Canister

least soluble (which is important in preventing removal of the neutron absorber over tens of thousands of years), but is also the most expensive.

Phase Separation Considerations for Pu and Gd

Tests on formulations of ATS and Loeffler glass showed that, while most of the plutonium dissolved in the glass, some sub-stoichiometric PuO_2 particles were present. This suggests that the solubility limit for Pu plus Gd was probably reached for this glass chemistry. It is expected that the La-BS glass; should be able to minimize such phase separation by slow processing or cooling.

If a Pu or Gd phase separation does occur, it is likely to cause non-congruent dissolution of the glass. Furthermore, inclusions could weaken the glass and make it more susceptible to both mechanical fracture and the chemical dissolution processes.

2.2 CERAMIC WASTE FORM DESCRIPTION

As with glass, the ceramic waste form is contained in cans, supported on a rack/basket, embedded in a DHLW filler glass, within a DWPF type canister, as shown in Figure 1. The size and number of the cans will be such that the amount of Pu per canister is the same as with the glass waste form. The precise size and content of the individual waste form units are being determined by some experimental optimization. For this analysis, the following parameters have been chosen, and closely approximate the glass waste form in can size.

2.2.1 Nominal Pu-ceramic Description

For the ceramic can-in-canister concept, each can is assumed to contain 5 ceramic cylinders. There are 20 cans per canister, just as for the glass waste form. The ceramic cylinders are assumed to be cold pressed and sintered, so there is no metal bellows or top & bottom plate.

Dimensions—Each disk (or cylinder) is assumed to be 11 cm diameter by 11 cm high; they are stacked 5 deep in each can. As with the glass can-in-can, the total can length is 57.535 cm, the can shell thickness is 0.3175 cm, and the can outer diameter is 12.035 cm.

Composition—The ultimate formulation of the ceramic has not yet been decided, but for calculation purposes it is assumed to be a variant of Synroc-C with the following mineral compositions (wt%): zirconolite (66%), pyrochlore (15%), hollandite (8%), and rutile (11%). The zirconolite incorporates 0.336 kg Gd per cylinder, and 0.512 kg Pu per cylinder. Therefore, each can contains just 2.56 kg of Pu and a 20 can canister has 51.2 kg of Pu, just as in the glass can-in-can alternative.

Mass—The total mass in each 11 cm high cylinder is 5.12 kg.

As with the glass waste form, it is assumed that any ceramic dissolution is congruent, which means that each component of the ceramic will be released from the initial solid waste form at a rate which is equal to the ceramic dissolution rate multiplied by the weight fraction of that component.

2.2.2 Future Decisions for Ceramic Waste Form Composition

Waste Form Dimensions

The waste form diameter will be as large as is practical within the constraints of the hot press process, but it is expected that it will be less than 9 cm. The length of the individual waste form cylinders is expected to remain approximately 11 cm.

Can Size

The can length will be adjusted to accommodate an integral number of waste form cylinders, or vice-versa, within the constraint of being close to an integral number of cans in the useable length of the DWPF size canister.

2.3 WASTE PACKAGE DESCRIPTION

The waste package for immobilized plutonium is the same for both glass and ceramic waste forms, since both waste forms will be fit into the same DWPF size canister. For this reason the waste package will be similar to the one planned for DHLW. The waste package can be loaded with 4 or 5 canisters. The cross section of a 4 canister package is given in Figure 2. The 5 canister package has the canisters arranged in a regular pentagon, similar to the 5 cans per layer cross section shown in Figure 1 (but more densely packed). To minimize the risk of criticality, it may be desirable to use an inhomogeneous loading strategy: with one plutonium canister surrounded by 3 or 4 DHLW canisters. The reduction in risk of criticality will be evaluated for such alternatives.

The waste package for the immobilized plutonium waste forms consists primarily of a corrosion allowance outer barrier and a corrosion-resistant inner barrier. The corrosion-allowance outer barrier will likely be Cu-Ni 5 cm thick or carbon steel 10 cm thick as is planned for the commercial SNF waste package. The former will minimize the availability of iron (which could significantly enhance the glass dissolution/alteration rate by forming Fe_2SiO_4), but the extent of the benefit is uncertain, and the latter is much cheaper. The inner barrier will be corrosion resistant, high nickel, Alloy 825 or Alloy 625, 2 cm thick. The performance, with respect to corrosion and penetration by water, of this two barrier system is discussed in Section 3.1, below.

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. The waste package size to accommodate these canisters is approximately 3.4 meters overall length. The waste package contains at least 4 of these canisters and therefore has an inner diameter of at least 150 cm. Alternatively, for more assured criticality control, the immobilized Pu canisters might be emplaced one to a waste package, with the other canisters being ordinary defense high level waste (DHLW).

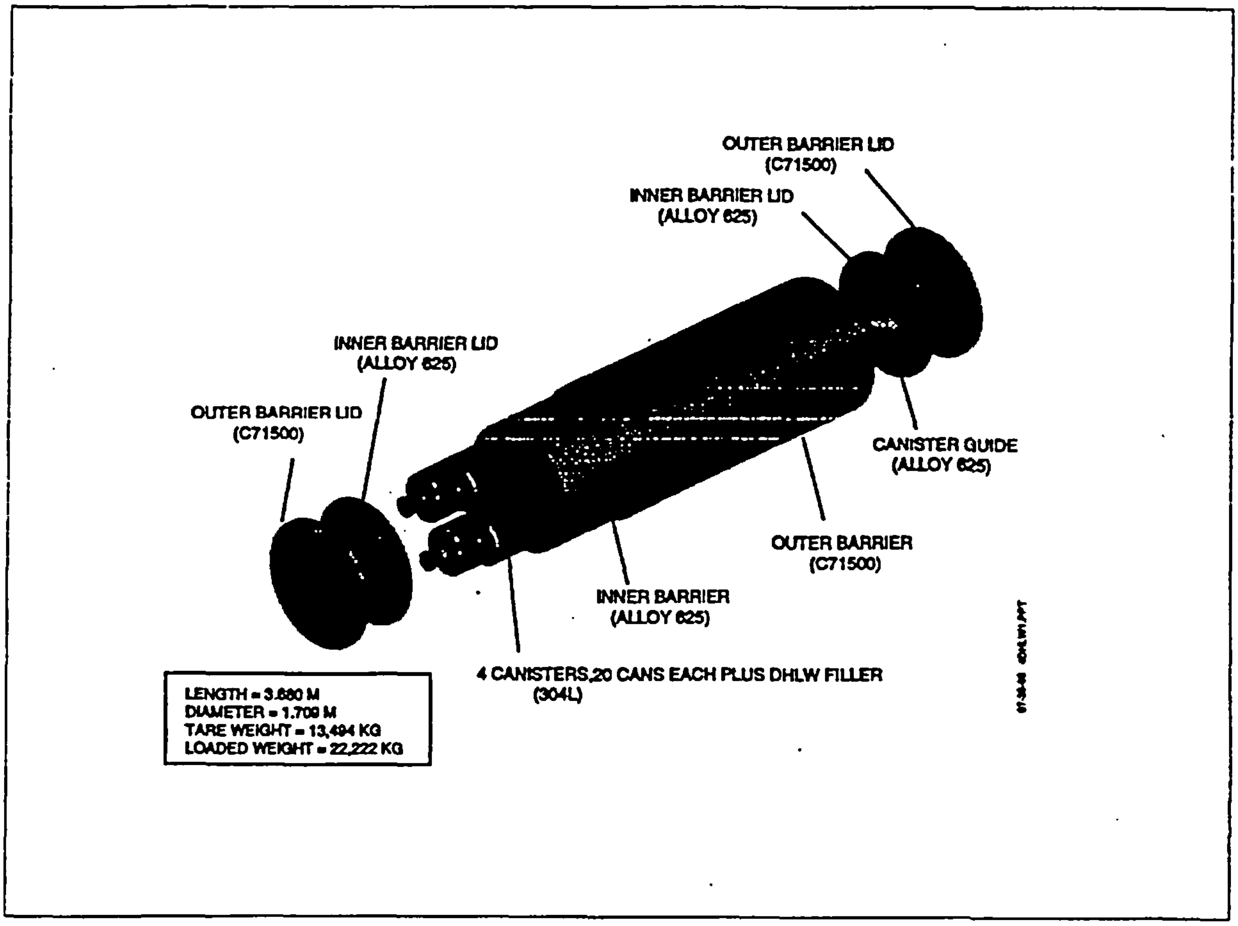

Figure 2. DHLW Waste Package

INTENTIONALLY LEFT BLANK

3. ASSUMPTIONS AND METHODOLOGY

The assumptions and methodology described here apply generally to both internal and external criticality and to both glass and ceramic waste forms. However, most of the illustrations are for internal scenarios and the glass waste form. This approach is necessary because the internal scenarios are the precursors to any external criticality, and because the glass waste form has more variations in resulting configurations. These distinctions are further explained with the discussion of specific scenarios (including processes following complete waste form degradation) in Section 4 and with the discussion of specific configurations (resulting from the specific scenarios, and including configurations with the possibility of near-field external criticality) in Section 6.

3.1 GENERAL REQUIREMENTS FOR CRITICALITY

The requirements identified in this section refer to the events and processes that must be present for a criticality event; however, they do not assure that a criticality will occur. The occurrence of criticality is determined/verified by calculation of k_{eff}.

3.1.1 Breach of Barriers

The barriers surrounding the Pu containing waste form must be breached before water can begin the dissolution process. These barriers are the inner and outer barriers of the waste package, the stainless steel canister, the filler glass, and the stainless steel can containing the actual waste form (glass or ceramic).

It is expected that each barrier will be first penetrated by pitting corrosion, but the rate of this corrosion is subject to some uncertainty. For this study the water penetration of the waste package barriers is assumed to occur at 3500 years because this is the time to first pit penetration averaged over all waste packages in the repository (TSPA 95, Ref. 3) using very conservative models of pit penetration for the corrosion-allowance material and the corrosion-resistant material. The conservative model used for Alloy 825/625 was similar to that used for stainless steel; out of the 3500 years mean first pit penetration time given in TSPA 95, 1000 to 2000 years were imputed to the inner barrier. Since the sum total of the can and canister thicknesses is equal to the waste package inner barrier thickness, it is reasonable to impute 1500 years as a mean first pit penetration time for the can and canister barriers. Making the further conservative assumption that the filler glass provides no protection, based on the fact that it will be highly fractured (by a factor of 30), the mean time for first water penetration to the waste form is 3500+1500 = 5000 years. All times to criticality given in this document are measured from the time of this first penetration.

3.1.2 Separation of Neutron Absorber from Fissile Material

For criticality to occur, nearly all the primary criticality control material, Gd, must be removed from the vicinity of the fissile material. Even if all this primary absorber is removed, there could still be enough of the secondary absorbers (particularly iron) to prevent criticality. For this reason, calculations of k_{eff} will include reasonably conservative estimates of the amounts of all insoluble neutron absorbers. There will be no credit taken for the boron in the filler borosilicate glass, because boron is very soluble and would be one of the first species removed from the waste package.

It is also possible to have a criticality by separating the fissile species (Pu and/or U) from the Gd once they are released (from either glass or ceramic) by congruent dissolution, while both remain in the waste package. The potential for such segregation is unknown at this time; however, preliminary EQ3/6 calculations suggest it may be possible to have selective precipitation (adsorption) of a significant fraction of the plutonium or uranium oxide on a metal surface, while virtually all Gd goes into the clay which has resulted from the filler glass dissolution. The criticality potential of such selective precipitation is limited by two considerations: (1) The precipitated layer of fissile oxide on a metal surface will be very thin (unfavorable criticality geometry); (2) Any layer of fissile oxide on a metal surface will be likely to re-dissolve with exposure water with higher oxygen content.

Both Pu and Gd can precipitate as oxides or hydroxides. Other phases are possible, depending on the water chemistry. Preliminary EQ3/6 modeling indicates that Gd will most likely precipitate as the hydroxycarbonate, phosphate, and/or fluoride. These preliminary EQ3/6 studies also indicate that the largest amounts of the 3 species of primary interest will be associated with specific minerals as follows: Pu in PuO_2; U in $Na_4UO_2(CO_3)_3$ or soddyite $[(UO_2)_5Si_2O_9 \cdot 6H_2O]$; and Gd in $GdOHCO_3$ or $GdPO_4 \cdot H_2O$

3.1.3 Sufficient Moderator

There are two possible moderators for criticality of ^{239}Pu or ^{235}U: water and silica. Preliminary evaluations of the configurations which can arise from the fissile material of a single waste package, have indicated that water has the dominant moderating effect. For this reason all the configurations likely to become critical must have a mechanism for retaining water in the package, or absorbed into highly saturated clay (which is one possible configuration of the altered glass waste form as explained in Section 4.1, below) or similar mineral.

For the scenarios described here, the moderating effects of both water and silica are considered. External to the waste package, with a large fissile volume, it might be possible to have a silica-moderated criticality. However, such a criticality would generally require a larger critical mass and a lower concentration of neutron absorbers, so it is expected to be much less likely than the water moderated, or internal, criticality, as explained in the discussion of specific scenarios in Sections 4 and 6, below.

3.1.4 Sufficient k_{eff}

Configurations which have above threshold values for the separation between absorber and fissile material and amount of moderator, are evaluated with respect to criticality by calculating k_{eff}. The physical requirement for criticality is $k_{eff} < 1.0$. However, the present NRC licensing requirement applicable to repository criticality is that the k_{eff} be < 1.0 minus a 5 percent safety margin and a further decrement for uncertainty and bias. For commercial SNF, this translates into $k_{eff} < 0.91$ including error/uncertainty arising from the Monte Carlo calculation of k_{eff}. However, for immobilized weapons grade Pu, there is no uncertainty associated with burnup credit, so the limit is more likely to be $k_{eff}<0.93$. There is some possibility that the NRC will remove the 5 percent safety margin requirement for long term disposal; at such time the results of this analysis may have to be updated.

3.2 ANALYSIS STRATEGY/METHODOLOGY

The following are the principal components of the strategy to achieve the objective of this evaluation: (1) Generate scenarios from the possible environmental input parameters and the possible waste package and waste form performance parameters with respect to various environmentally initiated degradation processes; this modeling predicts pH increase and decrease accompanied by a large increase in total dissolved species in a closed system; (2) Verification of solubilities of solids containing fissile isotopes and those with neutron absorbers at pH values predicted in (1), but with dilute water (unaltered J13); these calculations also confirm what solids are most stable; (3) Screen configurations of fissile and absorber material resulting from these processes according to threshold values relating to separation of absorber and fissile and relating to the amount of moderator; (4) Use MCNP to compute k_{eff} for those configurations for which the screening offers some possibility of criticality.

The first component of this strategy, generation of scenarios and resulting configurations is accomplished by the solution of a set of mass balance equations, which are described in Section 3.2.1, below. The solubility inputs for these calculations are found from experimental data and from theoretical calculations of chemical equilibria using the program EQ3/6, as described in Section 3.2.2, below.

The analysis considers internal criticality only within one waste package at a time. It also considers the possibility of external criticality in the near field, but with fissile mass no more than is available from a single waste package. The reason for this limitation is that the Pu bearing waste packages can always be placed sufficiently far apart that neutronic coupling between fissile material in, or from, different packages is virtually impossible.

3.2.1 Mass Balance Calculations

The configurations of waste package contents are determined by the use of a simple mass balance computer code for the simultaneous evaluation of the dissolution of the waste form and separation of fissile material from the neutron absorbers. The waste form is assumed to dissolve congruently, which means that each component goes into solution at a rate which is proportional to its initial percentage in the waste form. As the waste form is dissolved, the species go into solution, but any excess concentrations (above the solubility limit) are immediately precipitated. In the case of the glass waste form, these species will typically be incorporated directly into the altered phase which is formed from the immediate precipitation of most of the non-soluble components of the glass.

The intention is ultimately to model the potential for separation of neutron absorber from fissile material in the waste package. However, the present simple model bookkeeping lumps all the dissolution products remaining in the waste package (at any given time) together into what is called the dissolution product mixture. This dissolution product mixture also includes a relatively small fraction which is actually in solution and thereby available for removal from the waste package by water transport. Except for the relatively small fraction which is actually in solution, the dissolution product mixture serves as a surrogate for the several precipitated phases, and is considered to be available for inclusion in these precipitated phases as part of the sample configurations described in Section 6, below. The amount of each dissolution product species actually in solution is approximated by the solubility limit of that species. This approximation is accurate to within 10 percent, since, for the waste forms used in this study, the dissolution rate is more than 10 times faster than the removal rate.

The mass balance equations model the following processes: (1) Decay of ^{239}Pu to ^{235}U; (2) Dissolution of the waste form, permitting the species to go into solution; (3) Removal of the solution containing (at various concentrations) the species of interest. The governing mass balance equations are listed below. In the following equations, the waste form is designated as glass, but the equations can be applied equally to the ceramic waste form. The dissolution product mixture remaining in the waste package is designated by dpm. The quantities max U, max Pu, and max Gd are the solubility limit maximums which approximate the amounts actually in solution as described in the previous paragraph.

d(U in dpm)/(dt) = + (U frctn in glass)x(glass dsltn rate) + (Pu in dpm)/24100

- (volumetric flow rate)x(max U)

d(U in glass)/(dt) = + (Pu in glass)/24100 - (U frctn in glass)x(glass dsltn rate)

d(Pu in dpm)/(dt) = +(Pu frctn in glass)x(glass dsltn rate) - (Pu in dpm)/24100

- (volumetric flow rate)x(max Pu)

d(Pu in glass)/(dt) = -(Pu in glass)/24100 - (Pu frctn in glass)x(glass dsltn rate)

d(Gd in dpm)/(dt) = (Gd frctn in glass)x(glass dsltn rate)

- (volumetric flow rate)x(max Gd),

d(Gd in glass)/(dt) = - (Gd frctn in glass)x(glass dsltn rate)

The computer code to implement these differential equations in finite difference algorithms is given in Appendix B. In the present approximation the dissolution rate is adjusted for the decreasing surface area as the initial waste form is degraded.

It should be noted that when these differential equations are converted to difference equations for numerical solution, they cannot be solved simultaneously, so the order of solution becomes important. The order indicated here is correct for the following reasons:

- Solution change is computed before glass change for each of the three species; this is because the incremental amount of a species going into solution depends on the amount of the species initially present in the glass, but not vice-versa.
- Uranium change (for both glass and solution) is computed before plutonium change; this is because the uranium change depends on the plutonium concentration, but not vice-versa.

The initial quantity of ^{235}U is taken to be zero, and the initial quantity of ^{239}Pu is taken to be 93 percent of the total weapons grade plutonium.

In this pre-decisional draft, the mass balance has been limited to the three species of greatest neutronic activity. The iron released by the corrosion of the stainless steel canister and waste form cans will provide some neutron absorption, so its neglect is conservative. The final draft may include some explicit bookkeeping of iron using the formula for corrosion penetration depth $=0.075t^{0.75}$ microns, where the time, t, is measured in years. The mass of iron released is then obtained by taking the product of the penetration depth multiplied by the exposed stainless steel surface area and multiplying by the density of iron per unit volume of stainless steel.

3.2.2 Chemistry Calculations (EQ3/6) in Support of Mass Balance

The following types of EQ3/6 analyses are used in support of the scenario generation mass balance calculations: (1) A succession of quasi-equilibrium states tracing the degradation/dissolution of the waste form; (2) Verification of solubilities by equilibrium calculations with a limited number of species determined to be present in significant quantity, and with the pH determined, by the state tracing of the type 1 calculations; and (3) Examination of the alternative mineral/precipitate phases determined to co-exist in significant quantities from the state tracing calculations.

In addition to the fissile material and the largest cross-section absorbers, this methodology will be used to calculate the concentrations of other neutronically active materials. The stainless steel is expected to corrode primarily by pitting which might initially affect 1 percent of the canister surface (and volume). There will be approximately 2000 kg of Fe in a waste package of 4 canisters. If the 1 percent which is pitted is released, and assumed to be mostly iron, there will be 20 kg of Fe released. Some cases examined in Section 6 below show that the amount of this released iron which could deposit in the altered glass could be between 2 and 5 kg. As a first approximation, this range of mass can also be taken to represent the small concentration of other neutron absorbers in the steel (e.g. manganese).

For the ceramic waste form, the degraded form before complete dissolution is likely to be a collection of rubble at the bottom of the package, embedded in an altered glass, or clay, which is the filler glass. The ceramic rubble is expected to still contain the neutron absorber in nearly the same ratio to fisssile isotopes, as initially, so this configuration of ceramic rubble is not expected to become critical.

3.3 REPOSITORY ENVIRONMENT AND OTHER PARAMETERS

It is assumed that the geologic repository is an unsaturated site, in an arid climate, exposed to an oxidizing atmosphere. The available repository environmental parameters from the site characterization efforts at Yucca Mountain are used. The principal parameters are given in Appendix A. Values of parameters of repository environment and waste form performance used to generate the specific scenarios of this document are given in Section 5, below.

INTENTIONALLY LEFT BLANK

4. SCENARIO CONCEPTS FOR WASTE FORM DEGRADATION AND SUBSEQUENT PROCESSES

A systematic view of the processes which can lead to potentially critical configurations for Pu immobilized in glass is given in Figure 3. The individual processes are represented by boxes, which also represent yes/no points with respect to the outcomes of the processes. The processes and outcomes are arranged in horizontal layers by process type, with a brief identification of each type at the left side of the chart. This horizontal layering roughly corresponds to the flow of time from top to bottom of the chart. Each box is numbered, to serve as reference for the individual scenarios described below. The paths leading to the bottom of the chart represent scenarios which have the potential for criticality, while paths leading to the right of the chart represent scenarios which can not produce any criticality. It should be noted that boxes 12, 14, and 16, deal with the possibility of unmoderated criticality. These possibilities have not yet been analyzed; it is expected that the probability of collecting the necessary critical mass will be very small, and the risk of unmoderated criticality will be much smaller than the risk of moderated criticality.

The system perspective of Figure 3 is used to assure that all credible possibilities have been considered and to identify the most likely of these to be characterized by the sequence of physical and chemical processes. These perspectives are shown in Figures 4 and 5 for the physical and chemical processes, respectively. The details of these processes are described below.

4.1 PHYSICAL SCENARIOS FOR GLASS WASTE FORM DEGRADATION

The physical processes involved in the degradation of glass waste forms and subsequent material movements are shown in Figure 4. In this chart time flow is generally from the top down. All scenarios begin with infiltration of water incident on the waste package followed by water penetration of the barriers, water penetration of the stainless steel canister containing the waste cans, water penetrating the filler glass, water penetrating the can directly containing the waste form, and water contacting the surfaces of the waste form beginning the waste form alteration process. This wetting of the interior surfaces immediately following the breach of the surrounding barrier is a conservative assumption, because the fractures defining many of these surfaces will have such narrow apertures that fresh water cannot access them sufficiently fast to maintain the dissolution rate.

These processes are indicated by the first five blocks on Figure 4. Following these initial degradation processes the waste package and its contents can be represented by the sketch in Figure 6. The short line segments in the filler glass represent fractures which can provide rapid penetration paths to the interior of the waste form.

Following these initial degradation steps, any wetted surfaces of the glass will continue to degrade. The scenarios then proceed along three parallel paths, as shown in Figure 4. These scenarios are characterized by differing locations of holes in the waste package and resulting differing flow regimes within the waste package. Glass degradation proceeds through two alteration layers: (1) a thin inner "gel" layer containing insoluble species from the degraded glass waste from, and (2) an outer, "altered," layer containing precipitated clays and similar minerals. The altered layer may serve as a focus for re-precipitation, particularly at the bottom of the package.

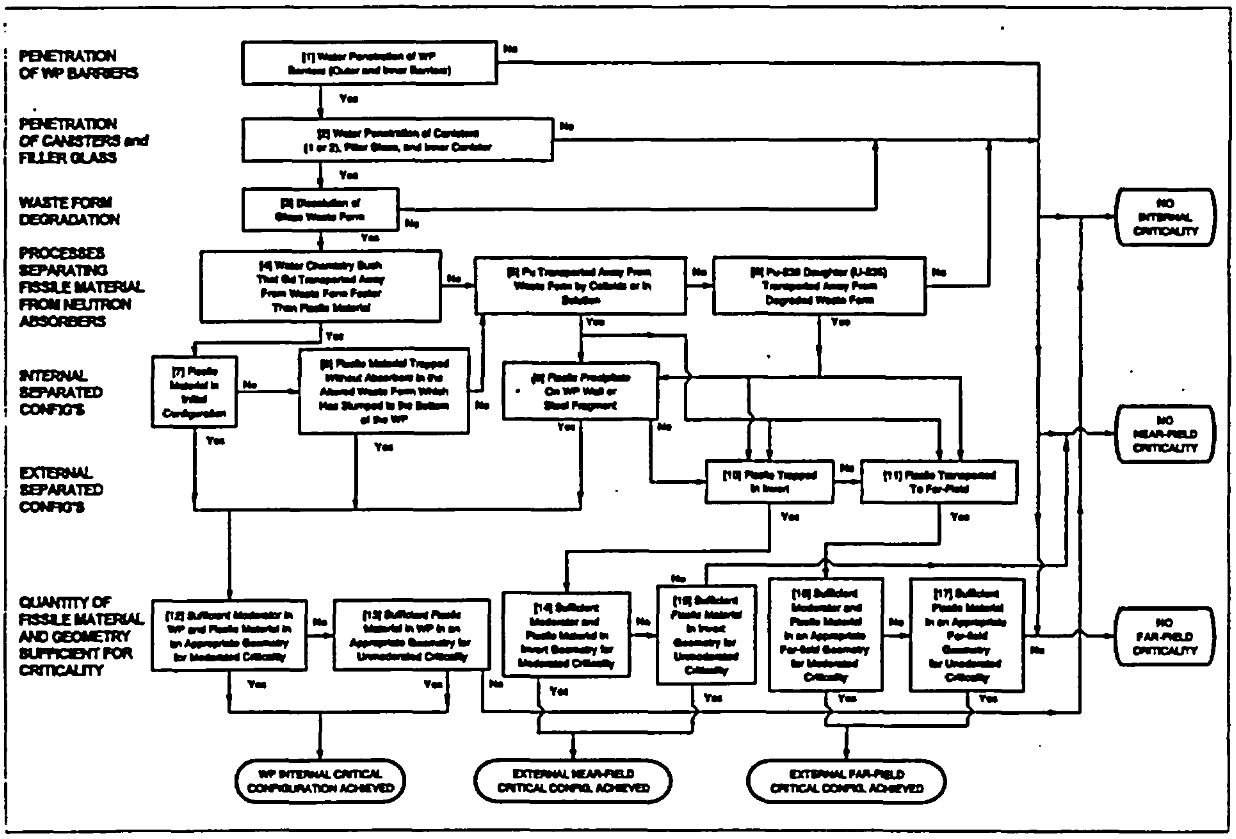

Figure 3. System Perspective of Event/Process Sequences for the Degradation of Pu Immobilized in Glass and Subsequent Material Movements

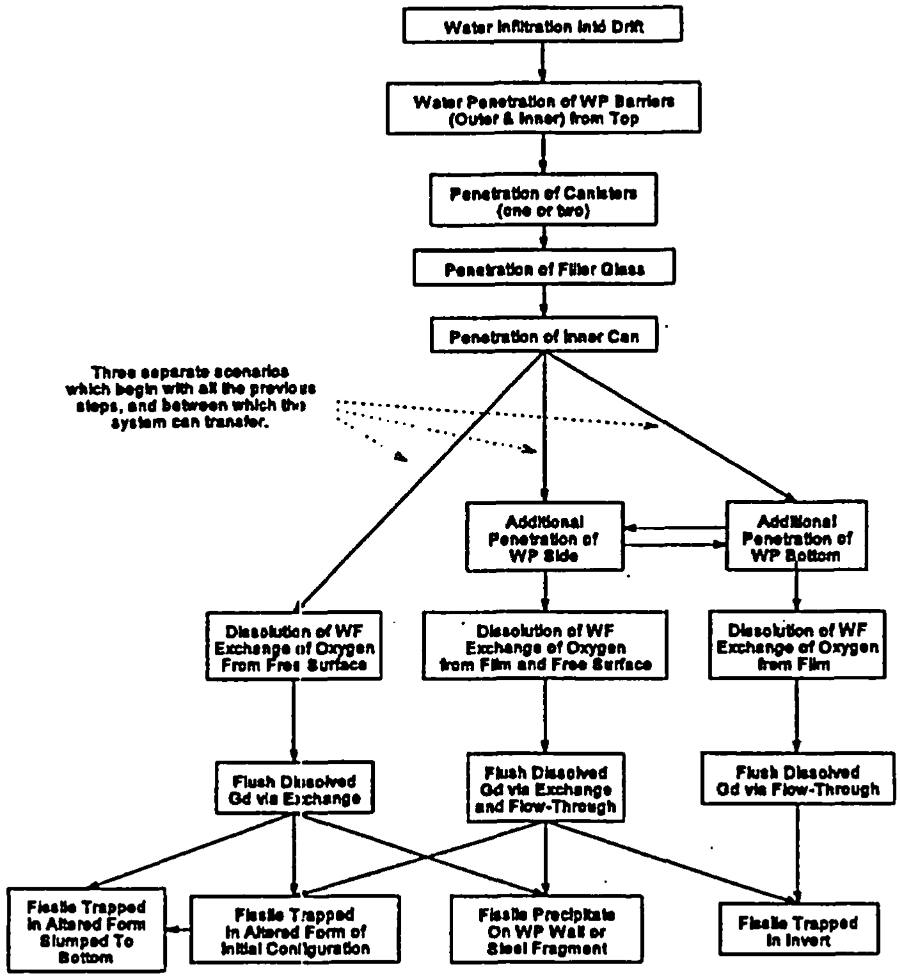

Figure 4. Physical Perpective of Event/Process Sequences for the Degradation of Pu Immobilized in Glass andSubsequent Material Movements

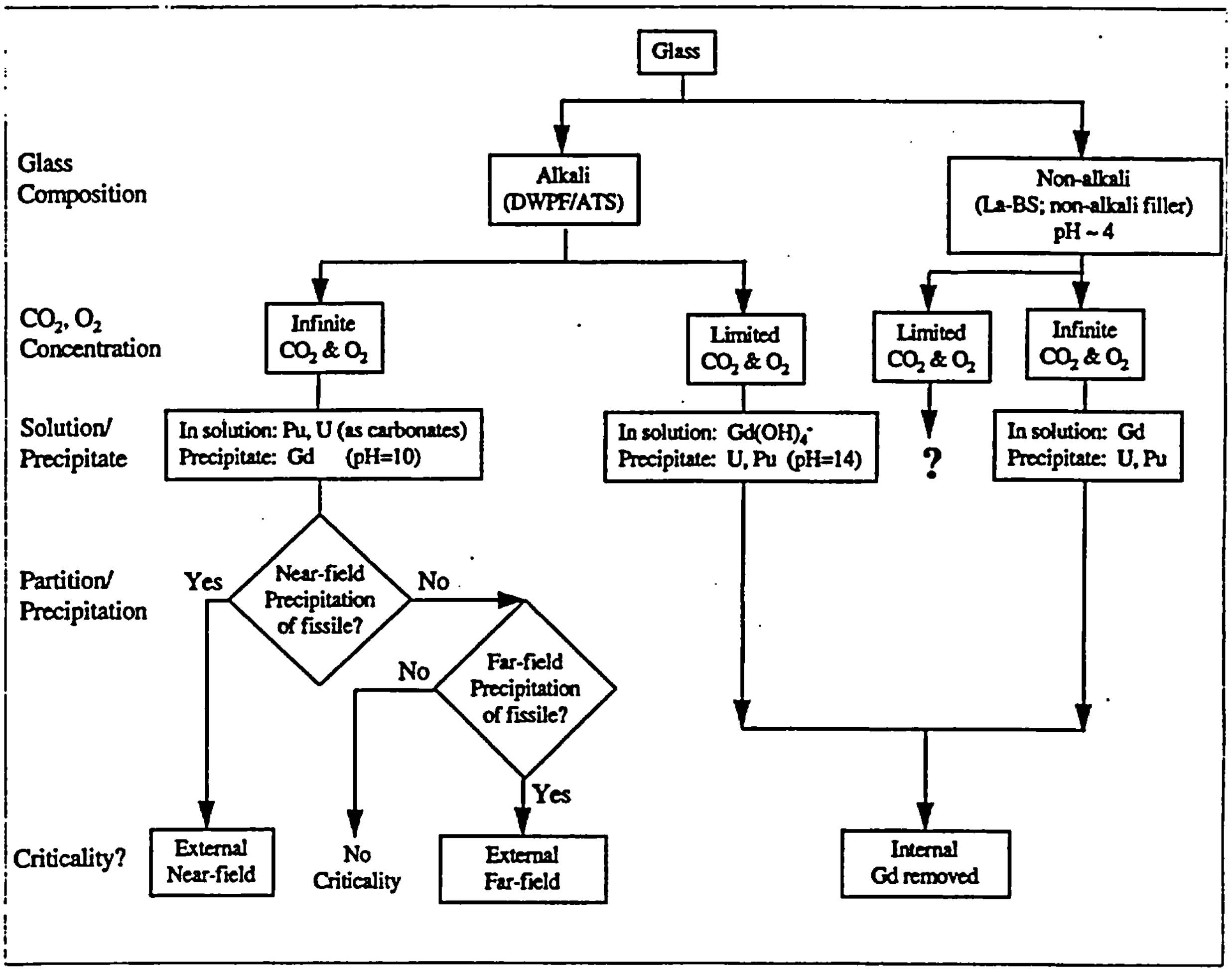

Figure 5. Chemistry Perspective of Process Sequences for the Degradation of Pu Immobilized in Glass and Subsequent Material Movements

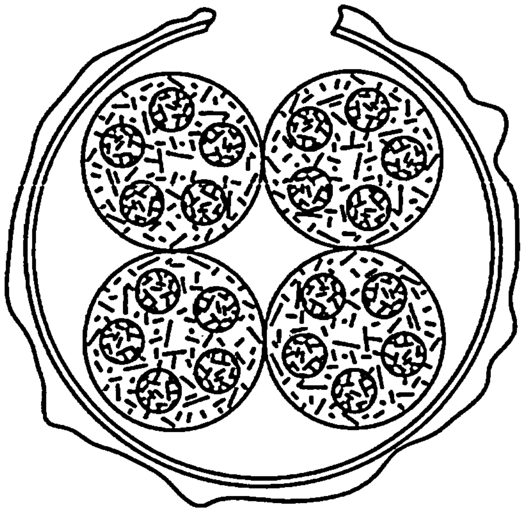

Figure 6. Degraded Barriers, Degraded Canisters, Glass Fractures

The following explanations will be helpful in understanding the physical processes represented by Figure 4.

The three boxes having text starting with, "Dissolution of WF," deal with the method of exchange which transfers oxygen and carbon dioxide from the air to the degrading surface of the waste form. These exchange methods are of two types:

- Exchange of oxygen and carbon dioxide from the free surface, which results when the water is standing to some depth in the waste package. The free surface (upper) of the water is the only boundary through which oxygen and carbon dioxide can pass, and these gases are transported to the dissolving surface by circulation, which is driven by the buoyant convection of the water heated by the still radioactive waste form.

- Exchange of oxygen and carbon dioxide from a film surface, which results when the water is flowing through the waste package and reacts with the waste form as a thin film. The dissolved gases are transferred from the outer film surface to the waste form surface by diffusion. Although the circulation exchange from the free surface is a more efficient process, the diffusion through the film can be very effective because of the short distance involved.

The three boxes having text starting with, "Flush dissolved Gd," deal with the method of removing Gd from the waste package. These removal mechanisms are of two types:

- Flow-through flushing in which the removal rate of a species is the product of the flow rate multiplied by the maximum concentration of the species in solution (solubility limit). This mechanism assumes that there is sufficient penetration in the lower portion of the waste package that the water flows through the package. It further assumes that all the water flowing through the waste package is sufficiently mixed that it carries the maximum concentration of each species dissolved from the waste form.

- Exchange flushing of dissolved material occurs when the lower portion of the package is not penetrated, so that most of the package is filled with water, and a major fraction of the water incident on the waste package will flow around the package only picking up dissolved species by physical mixing across the free surface boundary. In this situation the removal rate of all the species is reduced (in comparison with the flow-through flushing) by an exchange factor representing this mixing.

The three scenarios in Figure 4 lead to four final configurations, indicated by the four boxes at the bottom. These four configurations are described as follows:

- Fissile material trapped in the altered form with the altered form in its initial geometry; it is expected that this final configuration can be reached only from the breached-top-only scenario because it requires very slow removal rates. This configuration can only arise if the canisters and cans retain their structural integrity, while degrading sufficiently to permit extensive water infiltration.

- Fissile material trapped in the altered form with the altered form slumped to the bottom of the waste package in an ellipsoidal geometry. It is expected that this configuration can be reached from any scenario, except the bottom breach.

- Fissile material precipitated on a metal surface (waste package wall or stainless steel canister fragment) with a very thin slab or disk geometry. It is expected that this configuration can be reached from any scenario, except the bottom breach. There is experimental evidence for more precipitation of analogs of plutonium than precipitation of gadolinium on metal test vessel walls in PCT dissolution tests. Typically, the concentration of Gd in the acid solution which leaches from the vessel walls will be up to 2 times larger than the concentration in the solution within the vessel. In contrast, the concentration of an analog of plutonium, like cerium, will be 10 times larger in the acid wall leach than in the solution within the vessel. As discussed in Section 3.1.2, the criticality potential of such selective precipitation is limited by low thickness and potential for re-dissolution.

- Fissile material trapped in the invert. A possible mechanism leading to UO_2 precipitation in the invert could be a reduction in the amount of dissolved oxygen, and this less oxidizing environment would cause the uranium to reduce from the hexavalent to the quadrivalent state, and consequently precipitate. In contrast, the Pu will simply precipitate as soon as it can, so there is more likelihood of precipitation of Pu in the waste package before it can reach the invert. Another factor enhancing the rapid precipitation of Pu in the invert is the fact that the colloidal concentration of Pu is likely to be much greater than the Pu which is truly in solution. Pu colloids would likely be filtered out of the water by crushed rock in the invert, or by narrow fractures in the rock below. Yet another possible mechanism for concentration of fissile material in the invert is adsorption onto any Fe_2O_3 which could come from the corrosion/oxidation of iron containing metal in the waste package barrier or from the corrosion of iron containing waste package basked metal.

4.1.1 Breached-Top-Only Scenario, Circulation Flushing Only

Basis—In this scenario only the top of the waste package is breached, and the bottom remains unbreached for some long period of time, so that the package remains filled with water (to provide moderation for the criticality) while the waste form slowly degrades. Simple flow calculations show that this slow circulation flushing can be supported by infiltration rate between 1 mm/yr and 10 mm/yr. This scenario is possible because of the strong temperature dependence which is expected for the corrosion rate of Alloy 825 or 625 (provided by expert elicitation). The implication of this strong temperature dependence is that there may be some significant probability of penetration of the inner barrier while the waste package surface temperature remains above 70°C, but after 10,000 years the waste package will have cooled sufficiently that the waste package surface temperature will have dropped below 50°C, and the corrosion rate becomes very slow. Calculations with typical parameter values in this model indicate that following initial penetration of the top, penetration of the bottom could take up to 1 million years.

Alteration of Waste Form Process—As long as the waste form retains enough decay heat there will be circulation of the water within the waste package with cycle times less than a day. Therefore, the dissolving surfaces will be contacted by the water containing sufficient oxygen to maintain the dissolution process (which includes the oxidation of any uranium decay product of the Pu) of the glass waste form. Maintenance of this oxygen in solution may be partly supported by capturing oxygen at the free air-water interface. Oxygen supply (or some other electron acceptor) is important for converting quadrivalent uranium to hexavalent form, which makes it much more soluble.

Flush/removal Process—The rate of removal of fissile material and neutron absorbers is primarily determined by the flow rate incident upon the waste package, the internal circulation of the water within the waste package, the water chemistry (including pH, thermodynamic equilibrium constants, and dissolution rate parameters) which determine the glass alteration rate and solubility of the neutron absorber material, and the exchange of internal and external flows through the holes in the top of the waste package.

Final Configuration: Wall Precipitation—Fissile material and the neutron absorbers may be dissolved and re-precipitated on the waste package walls as thin mineral deposits. A criticality might occur if much of the fissile material re-precipitates inside the waste package while nearly all the neutron absorber remains in solution long enough to be flushed out. Whether such a separation occurs will depend on the basic chemistry and thermodynamic parameters for the fissile and neutron absorbing materials, particularly as expressed in the ratio of solubilities of the neutron absorbers to the solubility of the fissile material. The absolute values of these solubilities are important for determining how much Pu might be left in the waste package when the separation occurs. These solubilities are estimated by abstraction from EQ3/6 calculation results, as described in Section 4.3. As discussed in Sections 3.1.2, and 4.1, the criticality potential of such selective precipitation is limited by low thickness and potential for re-dissolution.

The quantity of Pu likely to be precipitated may be increased by any pure PuO_2 inclusions in the original waste form glass, as is discussed in Section 2.1.2, above.
This configuration is reached by the sequence 1-2-3-4-5-9-12 in Figure 3.

Final Configuration: Altered Waste Form in the Initial Geometry—This configuration is expected to have such low probability as to be insignificant. It is discussed briefly here, for the sake of completeness. Furthermore, preliminary calculations of k_{eff} have shown this configuration to be the most reactive with respect to criticality, so it may be considered as the worst case.

In this configuration most of the completely altered waste form retains its initial geometry. If it is to be critical nearly all the gadolinium would have to be dissolved and eventually flushed out of the waste package; preliminary EQ3/6 calculations have indicated that, at $pH<4.5$ Gd will have significantly higher solubility than U or Pu, but that the solubility is still so low that the Gd cannot be removed from the package in less than 300,000 years.

This configuration is reached by the sequence 1-2-3-4-7-12 in Figure 3. If this configuration exists at all, it is expected to be unique to the very low flushing rate of the breached top only scenario.

Final Configuration: Altered Waste Form in Collapsed (Ellipsoidal) Geometry—Fissile material and the neutron absorbers may be dissolved and re-precipitated as part of a pile of altered glass at the bottom of the waste package. This configuration is reached by the sequence 1-2-3-4-7-8-12 in Figure 3. The collapsed mass at the bottom of the waste package would be expected to have something like an ellipsoidal shape. The material will be a clay-like mass of silica/silicate and water with some concentration of the fissile and neutron absorber oxides. Because the package is filled with water, the water concentration in the collapsed mass could be as high as 60 percent, with the remaining 40 percent being silica and other species (the composition of which will be determined by EQ3/6 calculations).

As a final generalization on the contents of the collapsed altered form, It should be noted that as glass reacts, plutonium tends to precipitate as PuO_2 or an hydroxide phase and is retained in the smectite clay phase, likely as colloids, or on metal surfaces. Gadolinium also appears to associate itself with the clay phase. The degree of Pu and Gd segregation outside of the clay phase is unknown.

4.1.2 Breached-Top-and-Side Scenario, Both Flow-Through and Circulation Flushing

Basis—For this scenario the waste package will fill only partly, because the water can flow out the holes in the side. Such outflowing holes will establish a water level within the waste package, and it is likely that some of the waste form canisters will be above and some canisters will be below the water level. Although the holes in the top may be the most likely (because they are the most strongly gravity driven), holes in the side are the next most likely, because the outside will receive most of the film of water from dripping on to the top of the package, while the inside is exposed to a rising and lowering the level of water (resulting from variations in the infiltration rate, e.g. seasonal cycling) trapped inside the package. Intermittent wetting and drying is known to be the most stressing aqueous corrosion condition. Whether the intermittent drying actually occurs will depend on the dryout time is long enough and the humidity is low enough to fully dry the temporarily exposed surface.

In this scenario, the exchange between the solution inside the waste package and the outside dripping flow will be more rapid than for the breached-top-only scenario, because there is larger surface area for penetration by the fresh infiltrating water. The consequence is that there will be more rapid removal of solubility limited species, as is explained further below.

Alteration of Waste Form—The waste forms (canisters) which are below the water level will be altered at a rate similar to that in the breached-top-only scenario. The waste forms above the water level are altered by a film of water which is continuously moving and continuously re-supplied with oxygen, so the alteration process may be faster than for the breached-top-only scenario.

Flush/removal—The waste forms which are below the water level in the waste package will be flushed by circulation and exchange at a rate similar to that for the breached-top-only scenario. The waste forms above the water level will be flushed by a film of water which is continuously moving so the removal process will be much faster than for the breached-top-only scenario. Those waste forms above the water level cannot contribute to any criticality so the possibility of criticality in the initial geometry becomes remote. However, the accelerated alteration of the waste forms above the water level will increase the probability of achieving one of the other potentially critical final configurations (altered collapsed, precipitated on wall of metal surface, precipitated/trapped in the invert).

Final Configuration: Altered Waste Form Collapsed Geometry—As with the collapsed geometry configuration discussed in Section 4.1.1, above, this configuration is reached by the sequence 1-2-3-4-7-8-12 in Figure 3. This is the most likely configuration resulting from the general scenario of this section; it is characterized by the glass waste forms collapsed, or re-precipitated at the bottom of the waste package. Such a configuration would be expected to have an ellipsoidal shape, 20 percent water (less than the breached-top-only scenario because the package can be only partly filled with water since there are holes in the side of the package), 80 percent silica/silicate.

Final Configuration: Precipitation of Fissile Material on Metal Surface (Thin Slab Geometry)—As with the metal surface precipitation geometry configuration discussed in Section 4.1.1, above, this configuration is reached by the sequence 1-2-3-4-5-9-12 in Figure 3. Since the exchange with the outside fluid is much faster than the breached-top-only scenario, it is possible that much of the glass silica can be removed from the waste package, leaving a significant amount of uranium precipitating on the package wall, more in the form of a metal or oxide deposit, rather than embedded in silicates. The likelihood of this alternative is determined by the chemical/thermodynamic parameters which reflect partitioning among degraded/precipitated phases. Hence this possibility will be tested by EQ3/6 calculations, wherever possible. In addition, as shown above, the pitting corrosion of the waste package inner barrier may supply a significant amount of iron, as in the breached-top-only scenario. The resulting geometric configuration could be a thin slab, 50 percent water; it is possible that the chemistry calculations will indicate relatively low silicate concentration in this slab (since the silica from the glass may have been removed by the moderately rapid flushing).

Final Configuration: Fissile Material Trapped in the Invert (Near-field External Criticality)—This configuration is reached by both the sequences 1-2-3-4-5-10-14 or 1-2-3-4-5-6-10-14 in Figure 3. The external criticality for the breached-top-and-side scenario will be somewhat more likely than for the breached-top-only scenario, since the removal of fissile material is significantly faster. However, the near-field criticality will still be dominated by the breached bottom scenario, and will therefore be described below.

4.1.3 Breached-top-and-bottom Scenario, Flushing by Flow-Through

Basis—This scenario would have a volumetric flow through the waste package at rates up to a maximum of 40 liters per year (corresponding to an infiltration rate=10 mm/yr). This is estimated by multiplying the 0.001 meters per year infiltration rate by the inside cross-section area of the package along the axis, 4 sq meters. This volumetric flow could be increased by groundwater focusing due to fractures or other means of permeability enhancement, which could produce up to 4000 liters per year from a focusing factor of 100. No concentration factor is used in this study because a very conservative assumption has already been made with regard to effectiveness of water in removing waste form dissolution products: all the water flowing through the waste package will contact the dissolving surfaces, or will mix completely with water that has such contact. This assumption is realistic for a waste package partly filled with water, but it is very conservative for this much more rapid flushing by flow-through.

Alteration of Waste Form—In this scenario all the waste forms are altered by a film of water which is continuously moving and continuously re-supplied with oxygen. In general, this film will move faster and have more dissolved oxygen than either of the other (first two) scenarios. The metal corrosion rate is proportional to the dissolved oxygen concentration over some range of this concentration so this parameter may be important for determining the rate penetration of the steel canister and can. The glass dissolution rate is relatively independent of oxygen concentration in the solution.

Flush/Removal—The water film is also the primary flushing agent; since it is continuously moving, the removal process will be much faster than for the breached-top-only scenario. This is because the other two scenarios will have most, or much, of the water flowing by the waste package without contacting the waste forms.

Final Configuration: Altered Waste Form in Collapsed (Ellipsoidal) Geometry—Internal criticality is less likely with a breached top and bottom because any dissolved fissile species would be more likely to be flushed out of the waste package. Ordinarily, the absence of a distinct pool of water (such as is contained for the other two scenarios) will preclude the possibility of criticality. However, criticality in this configuration is a possibility if the altered form slumps to the waste package bottom as a moist clay. Since the clay can act as a sponge, it may retain a considerable water concentration, even though water continues to flow out of the waste package through the holes in the bottom. If this configuration did occur, it would resemble the internal criticality configurations for the previous two degradation scenario alternatives. Because of its expected low probability, this configuration is not reached by any of the scenarios in either Figure 3 or Figure 4

Final Configuration: Fissile Trapped in Invert (External Criticality, Near-Field)—If the breached bottom scenario ends with the fissile material flowing out of the waste package in solution, and if the uranium is re-concentrated by precipitating out of the resulting groundwater stream, a criticality could occur. A precipitation of fissile material could occur in the form of silicates or alkali silicates as the fissile bearing solution flows out of the waste package and encounters a less moist environment and leaves an evaporative type deposit. EQ3/6 analysis thus far indicates that the most likely minerals are soddyite, schoepite, haiweeite, or uranophane; however, further analysis could identify others. This configuration is reached by either of the sequences 1-2-3-4-5-6-10-14 or 1-2-3-4-5-6-10-14 in Figure 3.

If sufficient fissile material and very little neutron absorber were to precipitate in the invert, it would be likely to have a lower water concentration than the internal criticality configurations because of a lack of natural confinement for water, and lack of a clay formation to act as a sponge for water. For this reason this configuration is expected to have a very low probability, and has been assigned a low priority with respect to immediate analysis. It will, however, be evaluated in the near future.

Corrosion of the barrier steel could inhibit criticality in the near-field (invert) because significant amounts of low solubility Fe would precipitate in the same places as would be likely for U precipitation (if any). On the other hand, the presence of iron in solution could increase the precipitation of uranium, leaving the iron and uranium separated, which is the opposite of co-precipitation. Still another possibility is that the iron be present as Fe++ (possible if the oxygen concentration is very low), which has a strong reducing capability, thereby facilitating the co-precipitation of Pu. Preliminary EQ3/6 calculations indicate that this will be unlikely.

4.2 PHYSICAL SCENARIOS FOR CERAMIC WASTE FORM DEGRADATION

The data on the performance of ceramic waste forms is very limited. An R&D program is currently underway at LLNL to develop the physical characteristics and chemical constituents of the ceramic waste form to meet the requirements for production, Pu loading, and long term criticality. However, some information of interest exists in the literature on those ceramics which are candidates for nuclear waste immobilization. This information is summarized below, and serves as the basis of the degradation scenarios developed thus far.

Ceramic materials, especially oxides, are resistant to corrosive attack under a wide range of chemical environments. Plutonium can be accommodated in zirconolite, pyrochlore, monazite, and zircon. Recent emphasis has been placed on Synroc-C materials which are a mixture of zirconolite, hollandite, and rutile. Pyrochlore may also be present. Plutonium releases from zirconolite are about 1×10^{-5} g/m^2-d at 70-90°C in deionized water at pH 7. However, zirconolite and other ceramics are susceptible to metamictization as a result of radiation damage. This damage can result in complete amorphization, microcracking, swelling, and decrepitation. The presence of pyrochlore and large grain size appears to enhance this process in Synroc-C. Leach rates can be enhanced by about 10-15 times due only to metamictization with essentially no change in surface area. However, if microcracking, swelling (up to about 6 volume percent) and decrepitation occur, the surface area can be enhanced by 15,000 times the original geometric surface area. These processes can be reduced by reducing the grain size and pyrochlore content. Zircon and monazite are also affected by radiation damage. The dissolution of natural zircon in bicarbonate solution at 87°C increased as a result of alpha damage amorphization by 100 times from 10^{-3} to 10^{-1} weight percent. Natural monazite suffers radiation damage as well, with leach rate increases of up to ten times. However, natural monazite is almost always found in the crystalline state because of its low temperature of recovery from radiation damage.

Metamict radiation damage transformation could occur on the order of a few thousand years following ceramic waste form fabrication; this damage is primarily from atoms significantly displaced by recoiling nuclei from the ^{239}Pu alpha decay to ^{235}U. It should be noted that a similar radiation damage also occurs in glass, but is less significant in enhancing dissolution rate, because glass does not have a regular crystal structure to begin with, and the interior is already fractured from the initial fabrication process. The likelihood and extent of the metamict transformation from radiation damage in Synroc-C are proportional to the amount of pyrochlore contained in the ceramic and the fraction of the ceramic which contains large grains. The expected refinements in the ceramic technology may reduce the amount of pyrochlore and large grains to the point where the metamict transformation is insignificant.

Synroc-C ceramics dissolution products tend to form a very thin altered layer (much thinner than for glass dissolution). The composition of this thin layer has not been completely characterized with respect to the individual components, and this composition is likely to vary with water chemistry.

The layer is probably depleted in CaO, leaving primarily Ti and Zr oxides. The Ti oxide layer is believed to be primarily responsible for the low dissolution rates characteristic of the Synroc-C family of ceramics. Since the ceramic waste form dissolution goes through only this thin altered phase, there will be no analog for the two final glass waste form configurations which contain primarily glass altered form. Otherwise, the ceramic scenarios resemble those for the glass waste forms, except that the dissolution rate is expected to be much smaller, and its dependence on dissolved components (such as silica or H^+) might be quite different.

The ceramic scenarios are based on the use of gadolinium as the long-term criticality control material. Recent test data by Jostens, et. al. (Ref. 4) suggest that the Gd within the ceramic (Synroc-C) has a combined dissolution rate and/or solubility about one order of magnitude higher than the rest of the ceramic matrix and Pu, so it may be appropriate to use a less soluble material such as hafnium as the principal criticality control neutron absorber. However, hafnium is much more expensive than gadolinium, and Gd is a more efficient neutron absorber (particularly at thermal energies) so until more data are available, Gd remains the nominal choice. It is expected, however, that there will be some evaluation of the possibility of utilizing the Hf which is present in natural Zr (approximately 2 to 4.5 percent), thereby reducing the cost of Zr required for the zirconolite which is the major component of Synroc-C.

As with the glass waste form scenarios, the ceramic waste form scenarios begin with water incident on the waste package followed by breach of the waste package barriers and the canister containing the waste form to permit the water to attack the ceramic surfaces (beginning at least 5000 years after emplacement). EQ3/6 analysis of the glass waste form has indicated that the dissolution of the filler glass surrounding the ceramic cans inside the DWPF type canisters within the waste packages will control the pH early in time, the first few thousand years, at a value which may be as high as 9 or 10, depending on rates of reaction of filler glass and Cr alloys. Under these conditions, the Pu dissolving from the Synroc-C would remain in solution owing to the formation of carbonate complexes. The solubility of the neutron poison materials under these conditions is likely to be low. However, the amount of Pu in solution is still very low and little Pu would be lost by flushing the system during this period of time.

After the first few thousand years, the DWPF filler glass in the canisters will be converted mostly to clay phases or silicates and the pH will begin to decrease toward neutrality, i.e., the pH would approach that of the original J-13 water as the high pH water is flushed out. The pH may be lowered further to about 4 to 4.5 over many thousands of years by the buildup of oxidation products of chromium, molybdenum and niobium (chromic, dichromic, molybdic and niobic acids) from these elements present in the nickel-base inner barrier materials. (If only limited oxidation of these metals to form metal oxides, not acids, occurs, the pH will remain slightly, to moderately, alkaline.) Under the acidic conditions, Pu is not soluble and PuO_2 or other stable precipitates will form. The Gd, hafnium and other rare earth elements, are also likely to be insoluble under these conditions. In fact, the EQ3/6 analysis of the glass waste form has indicated that, although the low pH (below 4.5) may raise the solubility of Gd above that of U or Pu, it is still small enough to assure that enough Gd will remain in the waste package to prevent internal criticality for at least 500,000 years.

However, over this period of time, Pu will be converted to uranium, and uranium may be soluble under acidic (low pH) conditions as was indicated by the EQ3/6 calculations for glass, and is corroborated by preliminary EQ3/6 calculations for ceramic. Over time, the bulk ceramic material will degrade by a combination of grain boundary dissolution and metamictization as a result of radiation damage. However, due to the low solubility of the ceramic grains, the amount of fissile material in solution will likely be small. Thus the ceramic scenarios which could lead to criticality then have to have nearly complete dissolution of the waste form matrix.

Thus, from these studies, two cases for geochemical and criticality analyses of Synroc-C can be deduced. The first considers that the ceramic material is in a metamict state with no increase in surface area. The release rate of plutonium can be assumed to increase 10-15 times. The fissile material is assumed to precipitate on the available surfaces as a thin film. It is further assumed that the pH is lowered to less than 5 and remains there so that some fissile and a larger fraction of neutron absorber material are flushed from waste package because of the increased solubility of the neutron absorber. The second case is for a complete decrepitation where the release rate is enhanced and the surface area is also enhanced by a factor of 15,000 times. In this latter case, it is assumed that the ceramic rubble will be distributed onto a bed of clays and silicates. The two final configurations are then identified for criticality analysis as follows:

- Precipitation/adsorption on metal surfaces, for which criticality could occur under either of the following conditions:
    - Most of the neutron absorber is removed from the waste package
    - Fissile material precipitates on the metal surface before most of it can flow out of the waste package. As with the glass precipitates on metal surfaces, this is expected to be only a very thin layer.
- Precipitation/adsorption in the invert, for which criticality could occur under either of the following conditions:
    - Most of the fissile material (nearly all uranium) is transported from the waste package by water, with the fissile material being either in solution or as a colloid. It then precipitates, or is adsorbed, from the solution on fracture walls, or precipitates in the interstitial space, in the invert below the waste package.
    - Neutron absorbers (gadolinium or iron) transported from the waste package in solution, are subject to much less precipitation or adsorption in the invert, than the fissile material.

In subsequent studies, scenarios will be refined when the results of the EQ3/6 kinetic-thermodynamic code are available and the differences from the glass waste form scenarios are better understood. This refinement process will also consider the faster dissolution rates which are expected for the non-crystalline (metamict) forms which the ceramic can develop. These are either partial radiation damage or the metamict form caused by more complete radiation damage.

The EQ3/6 calculations which form the basis of this preliminary discussion are summarized in Appendix C, Table C-4.

4.3 CHEMICAL SCENARIOS FOR GLASS WASTE FORM DEGRADATION

The scenario perspectives shown in Figure 5 identify the chemical parameters which determine the possible separations of the fissile material from the neutron absorbers. The alternatives shown in this chart serve as planning guidelines for the EQ3/6 calculations which have already been performed and for those which will provide additional solubilities and other solution parameters. These parameters are used in the mass balance equations to determine which species are removed from the waste package as a function of time; they are also used to determine the partitioning among different precipitating species.

4.3.1 Unlimited CO_2 and O_2 with Alkali Glass Composition

This appears to be the most likely condition, because the nominal DWPF filler glass has a significant alkali concentration and because preliminary analysis (Ref. 5) shows the exchange of O_2 and CO_2 between the solution and the air to be sufficiently rapid by comparison with the rate of consumption of the species in the reactions.

Preliminary EQ3/6 calculations indicate that the pH will initially rise to between 9 and somewhat over 10. This rise is primarily from the highly soluble alkali ions dissolving from the glass; the maximum depends on relative rates of glass and metal dissolution. This phenomenon, together with the formation of soluble Pu and U carbonate complexes, appears to enhance the solubility of both Pu and U greatly. For the La-BS glass the U peak solubility is 1,000 ppm. For comparison purposes, it may be noted that this enhanced solubility may be as high as 200,000 ppm for the Loeffler glass, which has a higher pH than La-BS glass because of the large concentration of barium in the Loeffler glass case. This behavior would tend to prevent criticality internal to the waste package, since Pu and U would be removed much faster than Gd.

Since this high pH solubility is also contingent on the availability of CO_2 to form carbonate, any reduction of dissolved CO_2 would decrease the concentration of carbonate (because of the CO_2 - carbonate equilibrium balance), which, in turn, would lead to a decrease in the solubility of Pu. Such a reduction in CO_2 concentration could result from contact with minerals which would scrub the CO_2 from solution.

After tens of thousands of years this initial behavior could be reversed by the buildup of oxidation products of Cr, Nb, and Mo (from the stainless steel of the cans and canister or from the alloy 825 or 625 of the waste package inner barrier). These oxidations may produce abundant acid (chromic or dichromic, molybdic, niobic) and are capable of reducing the pH to the range 4 to 4.5, even in the presence of the alkali resulting from the dissolution of glass. Flushing out of the high pH solution before complete oxidation may permit even lower pH values.

If the system is flushed, but the pH remains in the range 4 to 5, Gd, as well as U and Pu, remain highly insoluble. On the other hand, if the Cr and other metals do not oxidize to chromates, molybdates, and niobates, as may be the case owing to the great insolubility of their oxides, the pH will remain high, 9 to 10. (For example, Cr_2O_3, the mineral eskolaite, is known to occur as pebbles in a river in Guyana.)

Any persistent low pH is likely to cause the Gd to dissolve and to precipitate the Pu and U.

The EQ3/6 calculations which form the basis of this preliminary discussion are summarized in Appendix C. In Table C-1, the relevant cases have suffix 50 (with filler glass fracture factor of 100), 50c (with filler glass fracture factor of 30), and 56b (suppression of Cr oxidation). Table C-2 gives a summary of the limited component equilibrium runs to determine low pH solubilities; because these are strict equilibrium calculations it is not possible to associate a time for their applicability, so they are linked to the time of occurrence of the low pH (typically 4.5).

4.3.2 Limited CO_2 and O_2 with Alkali Glass Composition

This situation could arise if the waste package is nearly filled with water so that there is only a small water-air interface through which to exchange these gases. Preliminary EQ3/6 calculations indicate an initial pH increase similar to the previous case, but without the CO_2 to support the formation of carbonates, and the absence of O_2 due to its early depletion by oxidation of metals and lack of a replenishment, the Pu and U will be highly insoluble. Without the presence of O_2 to continue the oxidation of Cr, there will be no reversal of the pH, which will continue to increase to 14, at which point Gd will become very soluble, in the form of $Gd(OH)_4^-$.

The greater solubility of Gd would result in the separation of the neutron absorbers from the fissile material. However, the nearly full condition would also imply a very slow exchange rate or removal rate for the dissolved species, such that build up of fissile materials could be delayed by tens of thousands of years.

The EQ3/6 calculations which form the basis of this preliminary discussion are summarized in Appendix C, Table C-1, cases with suffix 54.

4.3.3 Unlimited CO_2 and O_2 with No Alkali in the Glass

This case is similar to that described in Section 4.3.1, above, except that the waste form glass would have to be the nominal La-borosilicate (not the ATS glass), and the filler would be some non-alkali glass instead of the nominal DWPF glass. Preliminary EQ3/6 calculations indicate that the pH would eventually decrease to close to 4, lowering the maximum solubility of U and Pu by 3 orders of magnitude, to less than 1 ppm, but increasing the maximum solubility of Gd to nearly 10 ppm. This assumes oxidation of Cr to chromic acid.

4.3.4 Limited CO_2 and O_2 with No Alkali in the Glass

Preliminary EQ3/6 calculations indicate that these conditions will not lead to high solubilities for the species of interest. This inference will be verified by further EQ3/6 calculations.

4.4 CHEMICAL SCENARIOS FOR CERAMIC WASTE FORM DEGRADATION

Evaluation of general ceramic degradation concepts has been discussed in Section 4.2, above. EQ3/6 calculations for specific configurations will provide the necessary information for the final report. Since the long-term potential for extensive ceramic fracturing is presently unknown, a broad range of 4 orders of magnitude will be represented in the sensitivity studies. The preliminary EQ3/6 calculations which serve as part of the basis for the discussion of Section 4.2 are summarized in Table C-4.

INTENTIONALLY LEFT BLANK

5. INPUT DATA VALUES

The tables in this section provide a possible range of input parameter values. This range is based on data available in the literature and the results of some experimental efforts currently underway. Because specific data for plutonium loaded glass and ceramic matrices under repository environmental conditions is not available, this range represents a basis for sensitivity analysis. The dissolution rates are applicable to the either glass or ceramic waste forms, as indicated. The other parameters are applicable to both the glass and ceramic waste forms.

A more detailed description of all the environmental parameters is given in Appendix A.

5.1 DISSOLUTION RATES

The waste form glass dissolution rates are based on limited PCT testing performed by Bates, primarily on ATS glass (Ref. 13). Preliminary test results on Loeffler glass, which is representative of three possible glass dissolution stages, the tests indicate that the glass remains in the stage with the slowest dissolution rate for at least a year, which leads to the low end of the range of dissolution rates in Table 5.1-1. The Pu and Gd appear to remain in the reacted (altered) glass layer, without apparent segregation. Only a thin clay layer is expected to form. However, the layer may thicken with time.

Table 5.1-1. Dissolution Rates

Material	Max ($g/m^2/day$)	Min ($g/m^2/day$)
DWPF glass (filler)*	3.7×10^{-3} (at 66°C)	1.5×10^{-4} (at 26°C)
ATS **	0.01	8×10^{-6}
Ceramic (Synroc-C)†	10^{-4}	10^{-7}

* From formula developed by Bourcier and reported in TSPA-95, evaluated at pH=7. Review of experimental data by M.J. Plodinec has suggested a range of 0.1 to 0.0001 (Scenarios for the Evaluation of the Criticality Potential of High Actinide Glasses, WSRC-RP-95-1016 Rev 0). However, this reference suggests that the high end of this range may be too conservative because it is based on a 28 day test which included a significant amount of the high dissolution rate stage I (which typically lasts only 7 days).

** Inferred from Bates (Ref. 13); the range of values is expected to cover the La-BS glass, for which the actual experimental data should be available by 9/97.

† Jostens et. al., reviewed by R. Van Konynenburg

The actual dissolution rates, in mass per unit time, are determined by multiplying the appropriate dissolution rate per unit area, from the above table, by the waste form surface area. For this purpose, it should be noted that both ceramic and glass have their surface area enhanced by extensive internal fracturing. In glass this fracturing arises directly from differential stresses acquired during the cooling from the melt. In ceramic the fracturing arises over 1000 years from the differential radiation induced expansion, principally between the major crystal type, zirconolite, and the minor types pyrochlore and hollandite. The present ceramic optimization effort on behalf of this program will include the minimization of the amount of pyrochlore and/or minimizing the grain size to minimize this effect. The range of values used are given in Table 5.1-2.

Table 5.1-2. Surface Area Multiplication Factor for Internal Fracturing

Material type	Max	Min
DWPF glass (filler)	100	30
ATS, La-borosilicate	30	6
Ceramic (Synroc-C)	15,000*	1

*Represents extreme metamictization.

The outer glass surface area for each can is approximately 0.194 m^2 (a cylinder with length equal to 85 percent of the can inside length, and diameter equal to the inner diameter of the can). For the waste form sizes and waste package loading specified in this document, the external surface area is approximately 15.5 m^2 per waste package, so the total surface area exposed to dissolution is 1550 m^2.

It should be noted that need for the dissolving water to traverse the filler glass may have some retarding effect on the dissolution rate of the Pu glass. However, it is expected that the filler glass will dissolve at least 10 times faster than the Pu-glass so any such protection could only delay the Pu-glass dissolution by less than 10 percent. Furthermore, the internal fracturing of the DWPF glass permits rapid penetration by water. For these reasons, and for conservatism, the relatively minor delay due to the protection provided by filler glass is neglected.

5.2 SOLUBILITY

The solubility limits in Table 5.2-1 have been derived from a number of sources, as indicated in the notes. In particular, some of them have been inferred from the extrapolation of time dependent experimental data, as indicated in the notes.

5.3 ENVIRONMENTAL PARAMETERS

Table 5.3-1 is a summary of the range of the environmental parameters which are directly used in the EQ3/6 calculations and the mass balance calculations. These ranges are typical of those which would be expected in a nuclear repository containing 63,000 MTU of commercial SNF situated in an environment like Yucca Mountain. The numbers are consistent with those used in TSPA-95. Details are given in Appendix A, and in TSPA-95.

Table 5.2-1. Solubility

Species	Max (ppm, or g/m^3)	Min (ppm, or g/m^3)
Pu(1)	2.4(5)	2.4×10^{-3}
U(1)	2400(6)	2.4×10^{-3}
Gd(2)	16	0.01
Eu(3)	15(7)	.015
B	10^4	?
Fe(4)	450	4.5

1. TSPA95 and Shaw, et. al. private communication (LLNL)
2. Inferred from Bates' reports of experimental observations. It should be noted that recent, but limited, data from ASTO (Jostens, et.al.) indicates that Gd appears to dissolve about two orders of magnitude faster than Pu, although these rates are very low. This may be related to the locations of the Gd and Pu within the ceramic phases. This should be studied as part of the ceramic evaluation effort at ANL.
3. Shaw, et. al. private communication (LLNL)
4. Literature review
5. For $pH<5$, very low oxygen, and assuming that the precipitation of Pu is kinetically inhibited; a more representative maximum would be 0.024 ppm.
6. For very low silica only; a more representative maximum would be 2.4 ppm.
7. For $pH<5$ only, a more representative maximum would be 0.15 ppm.

Table 5.3-1. Environmental Parameters

Parameter	Max	Min
Temperature (°C)	66 (5,000 yrs)	26 (100,000 yrs)
Infiltration (mm/yr)	10	0.1
pH	7.4	6.9
Partial Pressure CO_2	$10^{-2.6}$ bar	$10^{-4.6}$ bar
Dissolved O_2 (mg/liter)	5.7	2 (?)
Silica (mg/liter)	64.3	57

INTENTIONALLY LEFT BLANK

6. REPRESENTATIVE WASTE FORM DEGRADATION CONFIGURATIONS

The final configurations described in this section are representative of the range of potential criticalities which can occur. At this time the scenario calculations have not been completed, so only the format of the configuration summary tables is given.

6.1 TYPICAL CONFIGURATIONS FROM GLASS WASTE FORM DEGRADATION

In Tables 6.1-1 and 6.1-2 the nominal configurations are potential plutonium criticalities, while the others are potential uranium criticalities, as indicated.

Table 6.1-1. Input Parameters which Generate the Scenarios Leading to the Final Configurations Presented in Table 6.1-2.

Final Configuration	U slblty (ppm)	Gd slblty (ppm)	dsltn rt ($g/m^2/dy$)	infl rate (mm/yr)
Initial Shape, nominal				
Initial Shape, U retained				
Slumped to bottom				
Slumped, retaining U in clay				
Wall precipitate, nominal				
Wall, U reduced by Fe				
Invert, nominal				
Invert, U reduced by organic				

Preliminary calculation results have suggested the following scenarios/configurations as representative of potential criticalities. Their descriptions are given here for illustrative purposes only. They may be significantly changed in the final report.

Initial Shape, Nominal—If the altered form retains its shape (most likely resulting from the waste form can retaining its structural integrity even though it has a significant fraction of its area degraded to permit the entry of water), and if the clay/alteration layer remains small, the resulting configuration could retain the original glass shape. For this configuration to present a criticality concern, it is necessary that the Gd removal process be complete before 75,000 years, because after that time there is no-longer enough undecayed Pu left to form a critical mass. It is assumed that the uranium formed by the decay of Pu will be removed at a much higher rate than the Pu. [This is the result of the much higher assumed solubility of uranium than of plutonium, or gadolinium.]

Table 6.1-2. Key Parameters Describing Final Configurations

Final configuration	Gd, kg	U, kg	Pu, kg	Fe, kg
Initial Shape, nominal				
Initial Shape, U retained				
Slumped to bottom				
Slumped, retaining U in clay				
Wall precipitate, nominal				
Wall, U reduced by Fe				
Invert, nominal				
Invert, U reduced by organic				

Initial Shape, U Retained—Similar to the nominal case, above, but with the assumption of an anoxic aqueous environment (or a pH<5.5) so that the uranium (decay product of ^{239}Pu) may have a lower solubility than Gd. Both these enabling conditions are unlikely at Yucca Mountain.

Slumped to Bottom—If the altered layer does not retain the initial shape of the glass (most likely from failure of the structural integrity of the can and canister), the resulting mass will slump (collapse) to the bottom of the waste package. In the nominal case, the U will be removed at a much more rapid rate than the Gd, just as in the Initial Shape, nominal configuration described above.

Slumped, Retaining U in Clay—This is similar to the previous configuration, except that there is either an anoxic environment, such as for the Initial Shape, U retained case above, or there exists some mechanism for immediately reducing any oxidized uranium as the clay is formed.

Wall Precipitate, Nominal—This configuration has Pu precipitating on the waste package or some other metal wall, while the Gd precipitates on the degrading glass itself (largely as part of the alteration layer). It might arise when both Pu and Gd have very low solubility, but the Gd solubility is the lower. Under such conditions, the Gd would tend to precipitate very close to where its source solid (in this case Pu glass) had degraded, hence the altered layer. The more soluble Pu, which is in solution dominantly as a Pu(VI) complex, may remain in solution long enough to contact a metal surface where it may be released and precipitated as Pu(IV) solid, e.g. PuO_2. This configuration may have a higher iron concentration than those listed above, because of the intimacy with the source of iron. This configuration, and the one following, will have a much lower silica concentration than any of the others because they are no longer directly connected with the waste form. It should be noted, however, that the wall precipitate configuration could occur in combination with the slumped configuration, particularly if the steel is sufficiently reactive with uranium to sustain an iron-glass reaction. Such a wall-glass combination would have a silica concentration intermediate between the glass and wall values. As mentioned in previous sections, the criticality potential of such selective precipitation is limited by low thickness and potential for re-dissolution.

Wall Deposition, U Reduced by Fe--This configuration could result if the hexavalent uranium in solution is reduced by oxidizing the iron in the stainless steel of the canisters, although such oxidation would likely be limited to surfaces which have potentially reducing constituents.

Invert, Nominal—The most likely configuration to result from waste package effluent flowing through the invert is removal/precipitation/adsorption of slightly soluble species onto the extensive surface area of the invert material (which will probably be crushed tuff). We will eventually have to evaluate the selectiveness of such a removal process with respect to the principle species of interest: U, Pu, Gd.

Invert, U Reduced—This configuration is a variation of the above case, in which there is some reducing agent acting on the hexavalent uranium in solution. It is more likely than the Invert, nominal case, above because it would take several tens of thousands of years for the Pu glass to degrade to a significant degree, and by that time most of the Pu has decayed into U.

6.2 TYPICAL CONFIGURATIONS FROM CERAMIC WASTE FORM DEGRADATION

The configurations resulting from ceramic waste form degradation have not yet been analyzed to the same extent as those from the glass waste form degradation, because the relatively slow dissolution rate pushes out the earliest time to criticality, and requires very low uranium solubility (somewhat unlikely) so that the uranium which is released in very small increments from the ceramic waste form can be retained in the waste package until enough has accumulated for a critical mass and enough of the gadolinium has been removed to permit the criticality. A typical set of input parameters which could result in criticality are the following:

- Ceramic dissolution rate 1×10^{-5} g/m^2/day
- U solubility=0.1 ppm
- Gd solubility=0.103 ppm
- Pu solubility=0.1 ppm.

The resulting earliest time to criticality is =753,000 years and the remaining fissile material (which by this time is virtually all uranium) =52.2 kg. It should be noted that the dissolution rate is just 10 percent lower than the value used for this example, there can be no criticality. This is an important conclusion because the dissolution rate value used here is considered to be so high as to be unlikely, unless the ceramic has been subjected to the metamict transformation (which may well be the case after such a long time period).

INTENTIONALLY LEFT BLANK

7. CRITICALITY CALCULATIONS (k_{eff})

The scenarios developed from the mass balance calculations, utilizing the range of input parameters and the solubility limits identified by the EQ3/6 calculations will be used to determine the specifications of final configurations, filling in the details of Section 6, particularly Tables 6.1-1 and 6.1-2. The Monte Carlo neutronics code, MCNP, will then be used to calculate k_{eff}, and evaluate the proposed Pu immobilization waste forms.

INTENTIONALLY LEFT BLANK

8. FINDINGS AND RECOMMENDATIONS

To be supplied

INTENTIONALLY LEFT BLANK

9. REFERENCES

1. *Total System Performance Assessment of a Geologic Repository Containing a Plutonium Waste Form Rev 00,* CRWMS (Civilian Radioactive Waste Management System) M&O (Management and Operating Contractor), August 15, 1996.

2. *Report on Evaluation of Plutonium Waste forms for Repository Disposal, Rev 01*, DI: A00000000-01717-5705-00009 Rev. 01, CRWMS (Civilian Radioactive Waste Management System) M&O (Management and Operating Contractor), March 29, 1996.

3. *Total System Performance Assessment - 1995: An Evaluation of the Potential Yucca Mountain Repository,* DI: B00000000-01717-2200-000136 Rev 01, CRWMS M&O.

4. *Experience Gained with the Synroc Demonstration Plant at ANSTO and its Relevance to Plutonium Imobilization,* Jostons, A., Ridal, A., Mercer, D.J., Vance, E.R., Australian Nuclear Science and Technology Organization, 1995.

5. *Second Waste Package Probabilistic Criticality Analysis: Generation and Evaluation of Internal Criticality Configurations,* DI#:BBA0000000-01717-2200-00005, Rev 00) CRWMS M&O, March 27, 1996

6. *Characteristics of Potential Repository Wastes,* DOE/RW-0184-R1, Vol 1, July, 1992.

7. Benson, L. V., and McKinley, P. W., 1985, *Chemical Composition of Ground Water in the Yucca Mountain Area, Nevada,* 1971-84, USGS Open File Report, USGS-OFR-85-484.

8. Ogard, A. E., and Kerrisk, J. F., 1984, *Groundwater Chemistry Along Flow Paths Between a Proposed Repository site and the Accessible Environment,* Los Alamos National Laboratory, LA-10188-MS.

9. Wilder, D. G., 1993, *Preliminary Near-Field Environment Report Volume II: Scientific Overview of Near-Field Environment and Phenomena,* Lawrence Livermore National Laboratory, UCRL-LR-107476 Vol 2.

10. Shaw, H. (LLNL) private communication

11. Van Konynenburg, R.A. (LLNL) private communication

12. McCoy, J.K. Nominal compositions for materials, CRWMS M&O IOC# LV.WP.JKM.09/96-223, September 17,1996

13. Bates, J.K., A.J.G. Ellison, J.W. Emery, J.C. Hoh, *Glass as a Waste Form for the Immobilization of Plutonium,* Mat. Res. Soc. Symp. Proc. 412, 57-64, (1996).

INTENTIONALLY LEFT BLANK

APPENDIX A
REPOSITORY ENVIRONMENT PARAMETERS

APPENDIX A
REPOSITORY ENVIRONMENT PARAMETERS

This appendix provides parameters of the waste form and the repository environment; these parameters are used as input for the detailed process codes such as EQ3/6.

Waste Form Composition—The following lanthanide-borosilicate glass composition has been provided by informal memo (Ref. 10). The 4th significant figure is for reference only, since the calculations in this study are only considered to 3 significant figure resolution, and since the final composition is still subject to some change.

Table A-1. La-BS Glass Waste Form Composition

Component	Wt%
SiO_2	25.80
B_2O_3	10.40
Al_2O_3	19.04
ZrO_2	1.15
La_2O_3	11.01
Nd_2O_3	11.37
SrO	2.22
PuO_2	11.39*
Gd_2O_3	7.61**

*Equivalent to 10 Wt% Pu

**Equivalent to 6.6% Wt% Gd, which is a 1:1 mole ratio to Pu.

It should be noted that this glass composition has been adjusted to eliminate the need for lead (Pb).

Filler Glass Composition—The DWPF filler glass has not been finally specified; however, the blend composition given in Ref. 6, Table 3.3.8, should be close to the final composition. This is repeated in Table A-2, below.

Table A-2. Projected Composition of Savanah River Site DWPF Glass

Component	wt%
Al_2O_3	3.98
B_2O_3	8.01
$BaSO_4$	0.27
CaO	0.97
$CaSO_4$	0.077
Cr_2O_3	0.12
CuO	0.44
Fe_2O_3	6.95
FeO	3.11
K_2O	3.86
Li_2O	4.40
MgO	1.35
MnO	2.03
Na_2O	8.73
Na_2SO_4	0.10
NaCl	0.19
NiO	0.89
SiO_2	50.20
ThO_2	0.19
TiO_2	0.90
U_3O_8	2.14
Group A(1)	0.14
Group B(2)	0.36

(1) Group A radionuclides of Tc, Se, Te, Rb, and Mo

(2) Group B radionuclides of Ag, Cd, Cr, Pd, Tl, La, Ce, Pr, Pm, Nd, Sm, Tb, Sn, Sb, Co, Zr, Nb, Eu, Np, Am, and Cm.

Waste Package Metal Composition—The compositions of the metals expected to be used for the waste package barriers and the canisters and waste form cans are given in the Table A-3, below. These values are from standard metals handbooks; the specific chain of authority for each is given in Reference 11.

Table A-3. Waste Package Metal Composition

Steel type/use	Nominal Composition, % by Mass						
	Si	Cr	Mn	Fe	Ni	Nb	Mo
A516/outer barrier	.275		1.03	98.7			
625/ inner barrier		21.5			65.9	3.65	9
304L/canister, cans		19		71	10		

Thermal History

Figure 4.2-8 from Ref. 6 provides thermal history at the waste package top surface up to 10,000 yrs. This can be idealized and extrapolated to 100,000 years as the following profile:

Table A-4. Thermal History

Time (yrs)	Temperature (°C)
5000	66.0
6000	59.5
7000	55.5
8000	53.0
9000	51.0
10000	50.0
15000	45.1
20000	40.6
30000	34.3
40000	31.4
50000	29.7
60000	28.6
80000	27.3
100000	26.5

For initial calculations, these values are used without any spatial temperature change into the invert material. If the temperature variation into the invert is needed, or more detail is needed in the thermal profile, thermohydrologic modeling calculations should be done to address the specific scenarios.

Water Compositions

Table A-5 lists three typical water compositions based on J-13 well samples. The table also gives an extreme concentrated solution which could arise from a 90 percent reduction due to evaporation.

Liquid Flux Scenarios

- No flux (diffusion only)
- Low flux: 0.1 mm/yr
- Medium flux: 1.0 mm/yr (base case)
- High flux: 10 mm/yr

It is suggested in TSPA-95 (Ref. 3) that the liquid flux might cycle through these scenarios with an approximately 100,000 year period, based on the larger period of the Milankovitch glacial cycle.

Transport processes investigated should cover a range of Peclet numbers from very low (diffusion dominated) to very high (advection dominated).

Crushed Tuff Invert Material Composition and Physical Properties

The Topopah Spring Tuff composition is summarized by the following table (Ref. 9).

Table A-5. Composition of Water Incident on the Waste Package

Water Scenario	Na$^+$ mg/l	K$^+$ mg/l	Ca^{2+} mg/l	Mg^{2+} mg/l	NO$_3^-$ mg/l	HCO$_3^-$ mg/l	Cl$^-$ mg/l	F$^-$ mg/l	SO^{2-} mg/l	SiO$_2$ mg/l	pH	O$_2$ mg/l
J-13A[i]	42	5.0	12	2.1	NA	124	7.1	2.4	17	57	7.2	5.7
J-13B[ii]	45	5.3	11.5	1.76	10.1	NA	6.4	2.1	18.1	64.3	6.9	5.7
J-13avg[iii]	45.8	5.04	13.0	2.01	8.78	128.9	7.14	2.18	18.4	61.1	7.41	NR
Evaporated	460	50	106	13.1	87.5	29.7	764	6.0	184	6.1	7.90	8.4

i. J-13A analysis from Ref. 7. Note that Li$^+$ and Sr^{2+}, which were measured at microg/l concentrations, have been left out of this report. NA stands for "not analyzed".

ii. J-13B analysis from Ref. 8. Note that Li, Fe, and Mn, which were measured at microg/l concentrations, have been left out of this report. NA stands for "not analyzed".

iii. J-13avg is set of values given in Table 3-2 of Ref. 9. NR stands for "not reported".

iv. The values in this line were generated by an EQ6 simulation of an evaporation of approximately 90% of the water. These values were used to generate the results reported in Table C-3 in Appendix C.

Table A-6. Topopah Spring Tuff Whole-rock Composition

Oxide	Abundance (wt%)
SiO_2	78.73
Al_2O_3	12.17
Fe_2O_3	0.996
CaO	0.474
MgO	0.123
TiO_2	0.101
Na_2O	4.08
K_2O	3.28
P_2O_5	0.02
MnO	0.052

The following physical parameters of the Topopah Spring Tuff are taken from Table 4.2-1 of Ref. 3.

Porosity	0.5
Residual saturation	0.01

APPENDIX B
PROGRAM TO TRACK WASTE PACKAGE DEGRADATION PARAMETERS

APPENDIX B
PROGRAM TO TRACK WASTE PACKAGE DEGRADATION PARAMETERS

```
/* pugd.c  Computes remaining Pu, Gd, U considering both glass dissolution and removal
and subsequent removal of these species from the waste package by flow through, and
by, the waste package.  The timestep is 1000 years.  To identify the time at which
criticality might occur, the program compares remaining Pu and Gd against the
regression of minimum Gd concentration required to avoid criticality for the collapsed
glass configuration (as determined by a series of MCNP calculations which identified a
series of fissile (Pu + 235U), Gd concentrations which would make keff = 1. The
regression line is given by gdf = 2.1*(-.107 + .109ff), where gdf and ff are the
fractions of Gd and fissile, respectively in the medium of interest (either glass or
solution).  Using the combination of Pu + 235U neglects the difference in fission
efficiency between these two fissile isotopes, but is adequate for the screening
objective of this program, since any potentially critical configuration will be
re-examined for the individual species, using MCNP.

Note that variables pertaining to solution count everything which has dissolved from
the waste form but still remains in the waste package.  In other words, solution is
what is truly in solution (maxpu or maxu or maxgd) plus what has precipitated (in the
altered layer or otherwise.  Only what is truly in solution is available for removal.
This is computed as the product of the volumetric flow-through or exchange flushing of
the waste package, multiplied by the maximum .
concentration of the species (solubility).  At the present time exchange flushing is
simply represented by a lower volumetric rate.  The program may be updated to
incorporate a specific exchange factor multiplying the basic infiltration rate.  This
exchange factor would be one for flow-through, and something between .1 and .001 for
exchange flushing.  However, this feature is not implemented in the present version.*/

#include <stdio.h>
#include <stdlib.h>
#include <math.h>
#include <string.h>
#define PI 3.14159


void main()
(int i,j,k,yr,
   maxyrs=1000, //Maximum time in 1000 yrs
   printyr=10;  //Interval for printout in 1000 yrs
float pusltn,pugls,usltn,ugls, gdsltn, gdgls,fsltn,
        fgls,fl,ftotal,gdtotal,pudecayg,pudecays,glsrate,glsrateg,
        sltnratet,tgls,totalwf,
        pu0=205,          //Initial Pu in 4 canister waste package
        gd0=134,          //Initial Gd at mole per mole ratio with Pu
        pkgarea=3.9,     //Horizontal cross sectional area inside waste
        pkg
        pkgvoid= 3,      //Void volume inside waste package
        puhalf=24.1,     //Half-life of Pu in 1000 yrs
        fracarea=100*15.5, //Surface area per waste pkg (80 cans x 100 fracture)
        totalwf0=10*pu0;//Assume Pu is 10% of waste form
```

```
float dsltnrate, inflrate, maxpu, maxgd, maxu;
char dummy[80],outs[10];
FILE *fin, *fout,*ferr;
fin=fopen("pugd.in","r");
fout=fopen("pugd.out","w");
ferr=fopen("junk.out","w");
fgets(dummy,79,fin);
while(fscanf(fin,"%f %f %f %f %f",//Read input parameters for this case
  &maxpu,&maxgd,&maxu,&dsltnrate,&inflrate)!=EOF)
  {fprintf(fout,"maxPu=%6.2f  maxU=%8.2f maxGd=%5.2f\n",maxpu,maxu,maxgd);
  pugls=pu0; //Initialize Pu amount in glass
  gdgls=gd0; //Initialize Gd amount in glass
  ugls=0;    //Initialize U amount in glass
  pusltn=0;  //Initialize Pu amount removed from glass and still in pkg
  usltn=0;   //Initialize U amount in solution (still in pkg)
  gdsltn=0;  //Initialize Gd amount removed from glass and still in pkg
  fgls=pugls;//Initialize fissile in glass
  fsltn=0;   //Initialize fissile in solution
  totalwf=totalwf0;//Initialize waste form mass
  ftotal=fgls+fsltn; //Initialize total fissile
  gdtotal=gdgls+gdsltn; //Initialize total Gd
  yr=0;            //Initialize time after start of waste form dissolution
  glsrateg=dsltnrate*fracarea* //Dissolution rate times initial surface area
           .001*               //Convert gm to kg
           365*1000;  //Convert days to 1000 years
  sltnratet=inflrate*pkgarea* //Volumetric flow incident on package
          .001*              //Convert mm/yr to meters/yr
          .001* //Prepare to multiply by concentration in ppm (gm=>kg)
          1000;             //Convert yrs to 1000 yrs
  tgls=30*pu0/glsrateg; //Pu glass lifetime, assuming 10%Pu
  fprintf(fout,"Dssltnn rate =%f  Infltrtn rate =%f  Glass life=%f\n",
          dsltnrate,inflrate,tgls);
  fprintf(fout,"%10s%10s%10s%10s%10s%10s%10s\n",
       "Time","Pu Gls","U Gls","Gd Gls",
       "Pu Sltn","U Sltn","Gd Sltn");
  while((yr<maxyrs)&&(ftotal>30)) //Iterate while there is sufficient fissile
    {pudecayg=(pugls>0?pugls/puhalf;pugls);//glass Pu=>U this 1000 yrs
    if((yr<tgls)&&(totalwf>0))//Compute total glass dissolution for this step
      glsrate=glsrateg*pow(1-(yr+.5)/tgls,2);//Adjust for reduced surface area
    else if ((yr>=tgls)&&(totalwf>0)) glsrate= totalwf;
    else glsrate=0;
    pudecays=(pusltn>0?pusltn/puhalf:0);//solution Pu=>U this 1000 yrs
    usltn+=pudecays //Increment solution U for solution Pu=>U
         +glsrate*ugls*(totalwf>0?1/totalwf:0)
                 //Increment sltn U from glassdssltn
      -(usltn>sltnratet*maxu?sltnratet*maxu:  //Flush only maxu
         (usltn>0?usltn:0));      //No decrement if none left
    if(totalwf>0)
      ugls+=pudecayg-glsrate*ugls/totalwf; //Decrement U in glass
```

```
   pusltn+=glsrate*pugls*(totalwf>0?1/totalwf:0)
          //increment sltn Pu from glass dsltn
        -pudecays//decrement solution Pu from solution Pu=>U
       -(pusltn>sltnratet*maxpu?sltnratet*maxpu: //Flush only maxpu
        (pusltn>0?pusltn:0));              //No decrement if none left
   if((pugls>0)&&(totalwf>0))
      pugls-=pudecayg+glsrate*pugls/totalwf; //Decrement Pu in glass
   else pugls=0;
   gdsltn+=glsrate*gdgls*(totalwf>0?1/totalwf:0)
       //Increment sltn Gd from glass dssltn
       -(gdsltn>sltnratet*maxgd?sltnratet*maxgd: //Flush only maxgd
       (gdsltn>0?gdsltn:0)); //No decrement if none left
   gdgls-=glsrate*gdgls*(totalwf>0?1/totalwf:0); //Decrement Gd in glass
   totalwf-=glsrate;  //Decrement glass for dissolution this step
   if (totalwf<0) totalwf=0;
   fsltn=usltn+pusltn; //Update fissile in solution
   fgls=ugls+pugls;    //Update fissile in glass
   ftotal=fgls+fsltn; //Update total fissile
   gdtotal=gdgls+gdsltn; //Update total Gd
   yr+=1;                        //Increment time (by 1000 yrs)
   if(gdgls<2.1*(-.107+.109*fgls/3.2))
      strcpy(outs,"Glass"); //Output that criticality is possible in glass
   else if (gdsltn<2.1*(-.107+.109*fsltn/3.2))
      strcpy(outs,"Solution");//Output criticality possible in solution
   else strcpy(outs,"  ");
   if(yr%printyr==0)
       fprintf(fout,"%10d%10.2f%10.2f%10.2f%10.2f%10.2f%10.2f%10s\n",
           yr,pugls,ugls,gdgls,pusltn,usltn,gdsltn,outs);}
 fprintf(fout,"%10d%10.2f%10.2f%10.2f%10.2f%10.2f%10.2f%10s\n\n",
           yr,pugls,ugls,gdgls,pusltn,usltn,gdsltn,outs);})
```

APPENDIX C
SUMMARY OF RESULTS OF PRELIMINARY EQ3/6 CALCULATIONS

APPENDIX C
SUMMARY OF RESULTS OF PRELIMINARY EQ3/6 CALCULATIONS

The tables in this appendix provide a summary of results from numerous calculations that are most relevant to nuclear criticality issues. The calculations were done with the EQ3/6 package of computer codes, which simulate reaction progress toward a final equilibrium state. The tables include only a small fraction of the results from individual runs. The output also reports the concentrations of all other aqueous species and the names and amounts of numerous solid phases predicted to form during the course of reaction.

Various assumptions had to be made to conduct these simulations. In view of the long time frame it was assumed in most computer runs that the eventual result would be the true equilibrium assemblage, not some metastable condition, as might persist even at the end of laboratory experiments lasting several years. Thus, quartz and PuO2, not chalcedony and Pu(OH)4, respectively, were assumed to be the stable phases. Another assumption was that once the metal barriers, i.e. the corrosion-allowance (Cu-Ni or carbon steel), the Alloy 625 corrosion-resistant barrier, and the 304L stainless steel containers for the glasses were breached at 5000 years there would be sufficient internal convection to keep the J-13 water circulating among the Alloy 625 internal surface, all of the exposed 304L, and the fractured DWPF and La-BS glasses. This was modeled as a closed system in view of the lack of a flow-through/flushing option within EQ6.

Because of the lack of Pitzer's coefficients for activity coefficients for many of the constituents, it has not been possible to model the final stages of reaction progress. The leaching of the DWPF glass has the potential to produce extremely high ionic strengths, well beyond the capability of the activity coefficient option that had to be used. Similarly, the assumption of approach to equilibrium results in a prediction of oxidation of the Cr in the metals to chromates; this, too, would increase the ionic strength dramatically and simultaneously produce acid conditions perhaps to a pH as low as 4.

In view of these limitations the final stages of reaction progress, as given by the computer runs, are not reported in the tables in this appendix. Some runs were made to evaluate solubilities at low pH and are included. The questions of how to handle continuing reaction after high ionic strength has been reached, and how to handle a flow-through scenario, have not yet been resolved.

Table C-1. Modeling Results, Element Specific, Glass Waste with Average J-13 Water

Run #	Time	Log Total Aqueous Molalities/ppm			Pu, U, and Gd Solids		Description	Comment
		Gd	Pu	U	Name	Log Mol/g†		
j13avwp50 pH 9.83	56 y	-6.03/ 1.35E-01	-4.72/ 4.31	-1.47/ 7.55E+03	GdOHCO3‡ PuO2 Rhabdophane	-2.10/1.24 -2.16/1.64 -3.97/0.02	LaBS glass, DWPF glass, 304L, & Alloy 625 reaction with J-13 water. SKB thermodynamic data added to data base. Glass fracture factor (FF) = 100. Cr allowed to oxidize fully to chromate. Fully saturated in air.	Limit of accurate calculations with available data, i.e. about ionic strength 1 as here.
j13avwp50c pH = 8.79	7.8 y	-7.13/ 0.012	-10.76/ 0.42E-05	-4.12/ 18.2	GdOHCO3 PuO2 Soddyite Rhabdophane	-4.21 -4.23 -3.21 -4.12	LaBS glass (FF=6), DWPF glass (FF=30), 304L, & Alloy 625 reaction with J-13 water. SKB thermodynamic data added to data base. Cr allowed to oxidize fully to chromate. Fully saturated in air.	Maximum pH. Slower rate of DWPF reaction compared to that of Cr alloys keeps this maximum lower than the j13avwp50 run.
j13avwp50c pH=8.15	101 y	-7.32/ 7.0E-03	-11.69/ 4.71E-07	-5.09/ 1.82	GdOHCO3 PuO2 Soddyite Rhabdophane	-3.09/-0.13 -3.13/0.18 -2.10/1.89 -4.26/0.01	Continuation	Ionic strength = 0.78, i.e. approximate limit of accurate calcula-tions.
j13avwp50c pH = 7.14	616 y	-5.37/ 5.27E-01	-12.26/ 1.03E-07	-7.44/ 6.83E-03	GdOHCO3 PuO2 Soddyite Rhabdophane LaF3-ss	-2.30/0.79 -2.35/1.08 -1.44/8.67 -3.70/0.03 -4.96/<0.01	Continuation	Approximate limit of applicability of results; ionic strength = 4.2
j13avwp54 pH = 5.18	436 y	-1.21/ 8.23E+03[1]	-10.12/ 1.57E-05	Not in-cluded in waste form for this run	PuO2 Rhabdophane	-1.22/14.4 -7.12/<0.01	LaBS glass, 304L, & Alloy 625. SKB thermodynamic data added to data base. FF = 100. Fully saturated in air.	Results resemble those expected in the absence of high alkali filler glass. Ionic strength 2.3 -- somewhat beyond range of accurate calculations
j13avwp54 pH = 4.95	872 y	-0.91/ 1.46E+04[1]	-9.92/ 2.19E-05	Not in-cluded	PuO2 Rhabdophane	-0.92/28.9 -7.22/9.45	Continuation	Ionic strength 4.7, ~ applicability limit.

Table C-1. Modeling Results, Element Specific, Glass Waste with Average J-13 Water (Continued)

Run #	Time	Log Total Aqueous Molalities/ppm			Pu, U, and Gd Solids		Description	Comment
		Gd	Pu	U	Name	Log Mol/g†		
j13avwp56b pH = 10.06	58 y	-5.80/ 2.30E-01	-3.77/ 38.61	-1.47/ 7.52E+03	GdOHCO3 PuO2 Rhabdophane	-4.51/0.05 -3.68/0.05 -3.42/0.06	LaBS glass, DWPF glass, 304L, & Alloy 625 reaction with J-13 water. SKB thermodynamic data added to data base. FF= 100. Cr not allowed to oxidize to chromate. Fully saturated in air.	No solid U species. Ionic strength = 1.24, ~ limit for accuracy. Note high U solubility
j13avwp56b pH = 10.15	104 y	-5.70/ 2.75E-01	-3.12/ 1.61E+02	-1.19/ 1.34E+04	Na4UO2-(CO3)3 GdOHCO3 Rhabdophane	-3.27/0.13 -4.24/0.01 -2.48/0.11	Continuation	No solid Pu species N.B. Solubility of Pu and U are high
j13avwp56b pH = 10.28	643 y	-5.56/ 3.41E-01	-2.24/ 1.10E+03	-2.20/ 1.17E+03	Na4UO2-(CO3)3 GdOHCO3 Rhabdophane	-0.87/32.0 -2.37/0.67 -2.10/0.06	Continuation	No solid Pu species. Log moles GdPO4•H2O = -3.34
j13avwp56b pH = 9.59	30,342 y	-6.26/ 7.63E-02	-5.31/ 1.07	-0.93/ 2.51E+04	PuO2 Na4UO2-(CO3)3 GdOHCO3 Rhabdophane	-0.73/44.43 -1.02/22.53 -0.67/34.0 -3.34/0.07	Continuation	33.94 moles of solvent water, out of initial 55.51, still present. This means 15.3 g of U in solution vs. 22.5 in solid. Ionic strength never got outside range that could be handled approximately.
j13avwp58 pH = 9.83	56 y	-6.04/ 1.34E-01	-4.73/ 4.25	-1.47/ 7.55E+03	GdOHCO3 PuO2 Rhabdophane	-2.10/1.24 -2.16/1.64	LaBS glass, DWPF glass, 304L, & Alloy 625 reaction with J-13 water. SKB thermodynamic data added to data base. Glass fracture factor (FF) = 100. Cr allowed to oxidize fully to chromate. Precipitation of quartz, tridymite, and coesits suppressed. Fully saturated in air.	Ionic strength 1.2, ~ limit for accuracy. No U solid

Table C-1. Modeling Results, Element Specific, Glass Waste with Average J-13 Water (Continued)

		Log Total Aqueous Molalities/ppm			Pu, U, and Gd Solids			
Run #	Time	Gd	Pu	U	Name	Log Mol/g†	Description	Comment
j13avwp58 pH = 10.06	234 y	-5.78/ 2.06E-01	-2.79/ 3.13E+02	-2.35/ 8.32E+02	GdOHCO3 Na4UO2-(CO3)3 PuO2 Rhabdophane	-1.48/5.20 -0.88/31.0 -1.56/6.58 -3.46/0.05	Continuation	N.B. High solubilities of Pu and U Ionic strength 4.0, ~ applicability limit.

[1] High values of dissolved Gd, but within limits for which calculations give acceptable results.

† Values are log gram-atoms of metal (or cation) and grams of metal, not the entire weight of the solid.

‡ Equilibrium constant taken to be equal to that for NdOHCO3.

In Table C-2, the set of computer runs from 80 through 87 were designed to obtain reasonable values for the solubility of Gd, Pu, and U at pH in the vicinity of 4.5, as earlier runs indicated might be possible. These earlier runs went beyond the range in which reliable results were possible with the existing data base. Runs 80 & 83 were with "fresh", i.e. unaltered, J-13 water. 81 with J-13 and added U, Pu, Gd, F, & PO4. 84 was J-13 initially nearly devoid of F & PO4. 85 & 86 used F & PO4 concentrations from the end of run 50. 87 used 0.1m NaF added to J-13. A large excess of the predicted products, PuO2, Soddyite, Rhabdophane solid solution, and lanthanide fluoride solid solution of the (compositions of solid solutions at the end of run 50) were input to runs 80, 81, & 86. Runs 83-85 & 87 used only pure Gd end-members which enhanced solubility. (No run 82.)

Care was taken to test complexation by using comparable to higher concentrations of potential complexing species. Runs at the high end of ionic strengths that can be modeled not yet made, only up to approximately 0.1 m using NaF, the use of which significantly enhanced the complexation and solubility of Pu and U, but not of Gd.

Table C-2. Modeling Results, Element Specific, Evaluation of Gd Solubility at Low pH

Run #	Zi*	Log Total Aqueous Molalities/ppm			Pu, U, and Gd Solids		Description	Comment
		Gd	Pu	U	Name	Log Mol/g†	See general desc above	
j13avwp80 pH = 4.53	1.9E-06	-7.95/ 1.75E-03	-9.03/ 2.30E-04	-5.61/ 5.80E-01	PuO2 Soddyite Rhabdophane LaF3-ss	A large excess of each (1.0 mole)		
j13avwp81 pH = 4.51	1.2E-06	-5.14/ 1.15	-9.03/ 2.31E-04	-5.61/ 5.78E-01	PuO2 Soddyite Rhabdophane LaF3-ss	A large excess of each (1.0 mole)		
j13avwp83 pH = 4.56	2.2E-05	-4.68/ 3.30	-8.94/ 2.77E-04	-5.51/ 7.33E-01	PuO2 Soddyite GdPO4•H2O GdF3•0.5-H2O	A large excess of each (1.0 mole)		
j13avwp84 pH = 4.61	4.8E-05	-4.32/ 7.54	-9.17/ 1.66E-04	-5.77/ 4.07E-01	PuO2 Soddyite GdPO4•H2O GdF3•0.5-H2O	A large excess of each (1.0 mole)		
j13avwp85 pH = 4.87	2.2E-05	-6.20/ 0.10	-7.73/ 4.57E-03	-4.36/ 10.41	PuO2 Soddyite GdPO4•H2O GdF3•0.5-H2O	A large excess of each (1.0 mole)		
j13avwp86 pH = 4.96	2.1E-05	-8.30/ 7.85E-04	-7.86/ 2.34E-03	-4.53/ 6.97	PuO2 Soddyite Rhabdophane LaF3-ss	A large excess of each (1.0 mole)		

Table C-2. Modeling Results, Element Specific, Evaluation of Gd Solubility at Low pH (Continued)

Run #	Zi*	Log Total Aqueous Molalities/ppm			Pu, U, and Gd Solids		Description	Comment
		Gd	Pu	U	Name	Log Mol/g†	See general desc above	
j13avwp87 pH = 4.67	1.5E-04	-5.39/ 0.63	-3.82/ 36.4	-3.52/ 71.0	PuO2 Soddyite GdF3•0.5-H2O	A large excess of each (1.0 mole)		The solution did come to saturation in GdPO4•H2O in a very long run. Gd solubility is limited by the fluoride. The solid phosphate used as input is being slowly converted to solid fluoride
j13avwp88 pH = 4.53	1.9E-06	-7.95/ 1.75E-03	-9.03/ 2.30E-05	-5.61/ 5.80E-01	Baddeleyite PuO2 Soddyite GdF3•0.5-H2O	A large excess of each (1.0 mole)	Purpose was to make a preliminary evaluation of the solubility of Hf, using Zr as chemical analog, should Hf be added to the waste as the oxide.	Zr solubility was 6.8E-10 molal, or 6.2E-05 ppm

*Zi is a measure of reaction progress (a measure of how much solid has reacted).

‡ Equilibrium constant taken to be equal to that for NdOHCO3.

† Values are log gram-atoms of metal (or cation) and grams of metal, not the entire weight of the solid.

Table C-3. Modeling Results, Element Specific, Glass Waste with Evaporated J-13 Water

		Log Total Aqueous Molalities/ppm			Pu, U, and Gd Solids			
Run #	**Time**	**Gd**	**Pu**	**U**	**Name**	**Log Mol/g†**	**Description**	**Comment**
j13evapwp3 pH =9.74	11 d	-6.14/ 1.10E-01	-5.48/ 7.67E-01	-1.78/ 3.75E+03	GdOHCO3‡ PuO2 Rhabdophane	-4.81/<0.01 -3.74/0.04 -3.72/0.03	LaBS glass (FF = 100), DWPF glass (FF = 100), 304L, & Alloy 625 reaction with J-13 water evaporated by a factor of 10 with a preceding EQ6 run. SKB thermodynamic data added to data base. Cr allowed to oxidize fully to chromate.	Results essentially the same as for non-evaporated water. Ionic strength 0.7, ~ limit for accuracy. No U solid
j13evapwp3 pH = 10.11	203 y	-5.73/ 2.30E-01	-2.78/ 3.25E+02	-2.15/ 1.33E+03	GdOHCO3 Na4UO2-(CO3)3 Rhabdophane	-3.94/0.02 -0.97/25.4 -2.87/0.21	Continuation	Maximum pH. No Pu solid. Ionic strength 3.80 ~ applicability limit.

† Values are log gram-atoms of metal (or cation) and grams of metal, not the entire weight of the solid.
‡ Equilibrium constant taken to be equal to that for NdOHCO3.

Table C-4. Modeling Results, Element Specific, Ceramic Waste with Average J-13 Water

Run #	Time	Log Total Aqueous Molalities/ppm			Pu, U, and Gd Solids		Description	Comment
		Gd	Pu	U	Name	Log Mol/g†		
j13avcer1 pH = 8.82	28 y	-9.30/ 7.78E-05	-9.84/ 3.43E-05	-3.18/ 1.54E+02	PuO2 Soddyite Rhabdophane	-5.48/<0.01 -2.69/0.49 -3.88/<0.01	Ceramic waste, modeled as a homogeneous special reactant (FF = 10), DWPF glass (FF = 30), 304L, and Alloy 625 reaction with J-13 water. SKB data base. Cr allowed to oxidize fully. Mid-range of reaction rate (1.0E-5.5 g/m**2/day)	Maximum pH. Course of reaction essentially the same as for glass, except for smaller amounts of Pu, U, and Gd (and other components of the glass, such as B) being added to the solution.
j13avcer1 pH = 7.44	542 y	-8.32/ 5.79E-04	-12.4/ 7.48E-08	-6.39/ 7.57E-02	PuO2 Soddyite Rhabdophane	-4.19/0.02 -1.35/10.6 -4.64/<0.01	Continuation	Ionic strength 4.75, ~ applicability limit.
j13avcer2 pH = 8.80	29 y	-9.27/ 8.29E-05	-9.89/ 3.07E-02	-3.22/ 1.38E+02	PuO2 Soddyite Rhabdophane	-5.24/<0.01 -2.69/0.49 -3.88/<0.01	Ceramic waste modeled as consisting of separate phases of zirconolite, pyrochlore, Zr-containing rutile, and Ba-hollandite. Used dissolution rate of 1.0E-5.5 g/m**2/day for zirconolite and pyrochlore, 10 times faster for Ba-hollandite, and 1/2 the rate for rutile. FF = 10 for all minerals, and 30 for DWPF. Reaction also with 304L, Alloy 625, and J-13 water.	Maximum pH. Course of reaction essentially the same as for glass, except for smaller amounts of Pu, U, and Gd (and other components of the glass, such as B) being added to the solution.
j13avcer2 pH = 7.08	715 y	-8.24/ 6.96E-04	-12.25/ 1.05E-07	-7.51/ 5.66E-03	PuO2 Soddyite Rhabdophane	-3.91/0.03 -1.40/9.48 -4.49/0.01	Continuation	Ionic strength 4.78, ~ applicability limit.

† Values are log gram-atoms of metal (or cation) and grams of metal, not the entire weight of the solid.

EXISTING 6.0 PPS TO BE REPLACED BY WBS 1.2.1.10 PPS

Participant PLUTONIUM DISP Prepared - 03/14/96:13:05:26	Repository Analysis for Plutonium Disposition PACS Participant Work Station (PPWS) Participant Planning Sheet (PSA03)	01-Apr-95 to 30-Apr-95 Page - 1 Inc. Dollars in Thousands

P&S Account No. - 6.1.1.1 1R

P&S Account Title - REPOSITORY ANALYSIS FOR PLUTONIUM DISPOSITION

WBS No. - 6.1.1.1

WBS Title - REPOSITORY ANALYSIS FOR PLUTONIUM DISPOSITION

BASELINE Start Date - 10/01/95

BASELINE Finish Date - 09/30/96

Element ID - 1R111

Fiscal Year Distribution

	Prior	FY1996	FY1997	FY1998	FY1999	FY2000	FY2001	FY2002	FY2003	FY2004	FY2005	Future	At Complete
Annual Budget	0	765	0	0	0	0	0	0	0	0	0	0	765

Statement of Work:

Conduct evaluations of fissile material disposition waste forms for disposal in a HLW repository.

Provide technical inputs to RW for their support of the Office of Fissile Materials Disposition.

Complete the Fissile Material Disposition Alternatives' Technical Summary analysis support effort started in FY95.

Modify/update technical reports for RW to support requests from MD.

Conduct long term criticality and performance analyses for the screened plutonium disposition forms.

Evaluate R&D experimental data, develop models, and conduct long term criticality analysis for the selected waste forms.

Conduct Total Systems Performance Analysis based on a TSPA 95 data set.

Support efforts associated with the Red Team Task.

Provide repository inputs to the MAUA effort.

Conduct long term criticality analyses for the PWR MOX spent fuel from Existing Reactors.

Support the Joint US/Russian study team through reviews of the documents.

- The QARD does not apply to the planning, performance, verification, and/or documentation of this work.

DELIVERABLES

Deliv ID	Description/Completion criteria	Due Date
PU61006210	REPORT ON CRITICALITY ANALYSIS Criteria - An MD approved report which contains long term criticality analysis for each of the approved immobilised waste forms. These waste forms will consist of a glass and ceramic form, and a MOX PWR SNF. The analysis should be based on development of degradation scenarios, based on	30-Aug-96

Participant PLUTONIUM DISP
Prepared - 03/15/96:09:44:09

Repository Analysis for Plutonium Disposition
PACS Participant Work Station (PPWS)
Participant Planning Sheet (PSA03)

01-Apr-95 to 30-Apr-95

Inc. Dollars in Thousands

P&S Account No. - 6.1.1.1 TR -REPOSITORY ANALYSIS FOR PLUTONIUM DISPOSITION

DELIVERABLES

Deliv ID	Description/Completion criteria	Due Date
PU61006210	Information/data available in literature and the R&D experimental work for these waste forms. Also, experimental data needs will be identified, and interfaces with the Immobilization Team established as part of this evaluation. The long term criticality analysis will consider relevant parameters such as plutonium concentrations, neutron absorbers; relative dissolution rates of the matrix, plutonium, and neutron absorbers, etc. Where possible, bounds of safe operation will be defined based on NRC requirements, and waste package designs modified to allow for these calculations. This report shall present the results of the analyses in such a manner as to facilitate comparison between the plutonium waste forms, and between the plutonium waste forms and commercial SNF and DHLW. This report will be provided to RW for their support of the Office of Fissile Materials Disposition and the Record of Decision on the Storage and Disposition of Weapons-Usable Fissile Materials scheduled for Fall of 1996..	
PU61006220	REPORT ON PERFORMANCE ASSESSMENT Criteria - An M&O approved report on the Total System Performance Assessment for the plutonium waste forms based on the approved data set from TSPA 95. New data available from the R&D experimental work will be incorporated in this analysis. This analysis is required to support the Office of Fissile Materials Disposition and the Record of Decision on the Storage and Disposition of Weapons-Usable Fissile Materials scheduled for Fall of 1996.	30-Aug-96

Participant PLUTONIUM DISP	Repository Analysis for Plutonium Disposition PACS Participant Work Station (PPWS) Participant Planning Sheet (PSA03)	01-Apr-95 to 30-Apr-95 Page - 3 Inc. Dollars In Thousands
Prepared - 03/15/96:09:44:09		

P&S Account No. - 6.1.1.1 TR -REPOSITORY ANALYSIS FOR PLUTONIUM DISPOSITION

Approvals

S.S.SAREEN	3/18/96	DL 3/29/96 Steve Braxton	4/2/96		
Preparer - print name	Date	Technical Reviewer - print name	Date	QA Reviewer - print name	Date
S. S. Sareen					
Preparer - Signature		Technical Reviewer - Signature		QA Reviewer - Signature	Date

YMP-223-R0
09/18/95

Participant - M&O
Database - PROPOSED
Prepared - 6-Aug-1996

Yucca Mountain Site Characterization Project
Planning and Control System (PACS)
Participant Planning Sheet (PSA04)

Contract - DE-AC01-91RW00134
Page 1 of 2
Inc. Dollars in Thousands

P&S Account - TR1A2
P&S Account Title - Repository Analysis for Plutonium Disposition
PWBS Element No. - 1.2.1.10
PWBS Element Title - Fissile Material Disposition

BASELINE Start 1-Oct-1995
BASELINE Finish 30-Sep-1996

QA - NA

FISCAL YEAR DISTRIBUTION

Annual Budget

Prior	FY 1996	FY 1997	FY 1998	FY 1999	FY 2000	FY 2001	FY 2002	FY 2003	FY 2004	FY 2005	Future	At Complete
	665											665

STATEMENT OF WORK

Conduct evaluations of Fissile Material disposition waste forms for disposal in a HLW repository.
Provide technical inputs to RW for their support of the Office of Fissile Material Disposition.
Complete the Fissile Material Disposition Alternatives' Technical Summary analysis support effort started in FY1995.
Modify/Update technical reports for RW to support requests from MD.
Develop long-term criticality scenarios, evaluate experimental data, develop models, and initiate analysis
Conduct Total Systems Performance Analysis based upon TSPA95 data set. Support efforts associated with the Red Team Task.
Provide repository inputs to the MAUA effort. Conduct long term criticality and performance analyses for the PWR MOX spent fuel from existing reactors.
Support the Joint US/Russian study team through reviews of the documents.
The QARD does not apply to the planning, performannce, verification and/or documentation of this work.

DELIVERABLES

Deliv ID	Description/Completion Criteria	Due Date
PU610D6210	Status Report on Degraded Mode Criticality Analysis of Immobilized Plutonium Waste Forms in a Geologic Repository (non-Q) Criteria: An M&O approved report which contains scenarios for long term criticality analyses for each of the approved immobilized waste forms. These waste forms will consist of a glass and ceramic form. The initial focus will be on development of degradation scenarios, based on available information/data in literature and from any R&D experimental work for these waste forms. Also, experimental data needs will be identified and interfaces with the Immobilization Team established as part of this evaluation. Long term criticality analyses will be initiatd and will consider relevant parameters such as plutonium concentrations; neutron absorbers; relative dissolution rates of the matrix, plutonium, and neutron absorbers, etc. Where possible, bounds of safe operations will be defined based upon NRC requirements, and waste package designs modified to allow for these calculations. This	30-Sep-96

CONCURRENCE

S.S. SAREEN 8/8/96
Preparer - print name / Date

Preparer - signature

for Steve Brocoum 8/2-/96
Technical Reviewer - print name / Date

Technical Reviewer - signature

QA Reviewer - print name / Date

QA Reviewer - signature

YMP-246-R0
09/18/95

Participant - M&O
Database - PROPOSED
Prepared - 6-Aug-1996

Yucca Mountain Site Characterization Project
Planning and Control System (PACS)
Participant Planning Sheet (PSA04)

Contract - DE-AC01-91RW00134

Page 2 Of 2

P&S Account - TR1A2

P&S Account Title - Repository Analysis for Plutonium Disposition

DELIVERABLES

Deliv ID	Description/Completion Criteria	Due Date
PU610D6 210	Status Report on Degraded Mode Criticality Analysis of Immobilized Plutonium Waste Forms in a Geologic Repository (continued) report shall present degradation scenarios and the status and preliminary results of the analyses. Where possible, the information shall be provided in such a manner as to facilitate comparison between plutonium waste forms, and between the plutonium waste forms and commercial SNF and DHLW. This report will be provided to RW for their support of the Office of Fissile Materials Disposition and the Record of Decision on the Storage and Disposition of Weapons-Usable Fissile Materials scheduled for Fall of 1996.	
PU610D6 220	Total System Performance Assessment of a Geologic Repository Containing Plutonium Waste Form (non-Q) Criteria: An M&O approved report on the Total System Performance Assessment for the plutonium waste forms based on the approved data set from TSPA95. New data available from the R&D experimental work will be incorporated in this analysis. This analysis is required to support the Office of Fissile Materials Disposition and the Record of Decision on the Storage and Disposition of Weapons-Usable Fissile Materials scheduled for fall of 1996.	30-Aug-96