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**Preliminary Assessment of
the Controlled Release of
Radionuclides from Waste
Packages Containing
Borosilicate Waste Glass**

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June 1990

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Pacific Northwest Laboratory
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PRELIMINARY ASSESSMENT OF THE CONTROLLED
RELEASE OF RADIONUCLIDES FROM WASTE PACKAGES
CONTAINING BOROSILICATE WASTE GLASS

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SUMMARY

The purpose of this report is to provide a preliminary assessment of the release-rate for an engineered barriers subsystem (EBS) containing waste packages of defense high-level waste glass at geochemical and hydrological conditions similar to those at Yucca Mountain. The relationship between the proposed Waste Acceptance Preliminary Specifications (WAPS) test of glass-dissolution rate and compliance with the NRC's release-rate criterion is also evaluated. Calculations are reported for three hierarchical levels: EBS analysis, waste-package analysis, and waste-glass analysis. The following conclusions identify those factors that most acutely affect the magnitude of, or uncertainty in, release-rate performance.

ENGINEERED BARRIERS SYSTEM ANALYSIS

- The NRC's release rate criterion is for the engineered barrier system. Meaningful evaluation of data needs and priorities must be based, therefore, on a perspective of integrated repository performance. Attempts to establish regulatory compliance by examination of one process or parameter, such as glass dissolution rate, are misleading and technically indefensible.
- The performance of the EBS is the sum of the release-rate behavior of waste packages containing both spent fuel and defense glass; their relative importance is a function of the respective radionuclide inventories and number of waste packages for each waste form.
- Based on current plans and concepts for an EBS at Yucca Mountain site, the release rate performance of waste packages containing defense glass is a small component of the release-rate performance of the EBS.
- Vapor-phase hydration of defense glass is inconsequential compared with the rapid release of soluble radionuclides from the cladding/fuel gap in spent fuel.

WASTE PACKAGE ANALYSIS

- Solubility-limited mass transport, rather than waste-form dissolution rate, is expected to limit the release of most radionuclides from the waste package. The U.S. National Academy of Sciences

previously reached a similar conclusion (NAS 1983), as have other national repository programs (KBS 1983; NAGRA 1985).

- Data from the WAPS test is largely irrelevant, therefore, to the release-rate performance at either the waste-packages or EBS level of analysis.
- Radionuclide solubility limits are key to establishing predictive reliability and safety for geologic disposal; obtaining such data should be one priority for future tests that are intended to support the performance assessment of defense high-level waste glass.
- Transport parameters, such as extremely low diffusion coefficients in partially saturated tuff, may dominate the release of radionuclides from waste packages, even for highly soluble radionuclides.

WASTE GLASS ANALYSIS

- Glass is a metastable solid and will, in the presence of water or water vapor, alter to a more stable set of phases. These phases will impose solubility limits to the concentration of many radionuclides within the waste package.
- Mechanistically based models for predicting the long-term glass dissolution and release of soluble radionuclides as a function of environmental variables exist; empirical models cannot be defensibly extrapolated to the long periods relevant to repository performance.
- There is paucity of test data on the most current defense glass (SRL-202) suitable for modeling of long-term dissolution rate.
- The WAPS test was intended as a quality control test, not as a performance test suitable for repository licensing.
- An alternative WAPS test methodology could be designed that would satisfy the original intent as a quality control test, yet provide more relevant data for evaluating the long-term dissolution rate of the defense glass.
- Because environmental variables such as temperature and pore water chemistry will affect the dissolution behavior of glass, no single performance confirmation test is possible.

ACRONYMS

DHLW - defense high-level waste
DOE - U.S. Department of Energy
DWPF - Defense Waste Processing Facility
EBS - Engineering Barrier System
EPA - U.S. Environmental Protection Agency
GRD - Generic Requirements Document
MCC - Materials Characterization Center
NRC - Nuclear Regulatory Commission
OCRWM - Office of Civilian Radioactive Waste Management
PASS - Performance Assessment Scientific Support Program
PNL - Pacific Northwest Laboratory
PWR - pressurized water reactor
SRL - Savannah River Laboratory
WAPS - Waste Acceptance Preliminary Specifications

ABBREVIATIONS

Al - aluminum	O - oxygen
Am - americium	Pb - lead
B - boron	Pu - plutonium
Cs - cesium	Ra - radon
Cm - curium	s - second
Fe - iron	Si - silicon
H - hydrogen	Tc - technetium
K - potassium	Th - thorium
Na - sodium	U - uranium
Np - neptunium	

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1.0 INTRODUCTION

The U.S. Department of Energy (DOE) is presently evaluating the geologic formations located in the Nevada Research and Development Area, Yucca Mountain, Nevada, as a potential repository for the permanent disposal of high-level nuclear waste (HLW), including spent nuclear fuel from commercial reactors and reprocessed defense high-level waste (DHLW) in the form of borosilicate glass. Key processes and parameters affecting the safe and reliable performance of the repository must be known for both the far-field geologic subsystem and the near-field engineered barrier subsystem (EBS).

Figure 1.1, taken from the U.S. Department of Energy's Site Characterization Plan for the Yucca Mountain site (U.S. DOE 1988), shows the hierarchical relationship of process models and parameters that affect the release-rate performance of the near-field EBS. Three successive levels can be identified from this hierarchy: 1) the performance of the entire EBS (system level), 2) the performance of a waste package (waste package level), and 3) the waste form performance (waste form level). Information from any one level represents only a part of the overall data that is included in the preceding level.

Release rates from the EBS (system-level analysis) are, in the strict sense, the specific information that is relevant to demonstrating regulatory compliance with the U.S. Nuclear Regulatory Commission's 10 CFR Part 60.113. This regulatory framework is briefly described in Appendix A. The performance of the EBS will be a function of waste-package performance and the waste-package environment, as well as design, logistical, and natural factors that determine scenarios for radionuclide release (Figure 1.1). With respect to calculating EBS release rates, one key consideration is that two different high-level waste forms, commercial spent fuel and borosilicate glass, are likely to be disposed together in the same repository. Demonstration of regulatory compliance for EBS release, therefore, depends on factors such as the radionuclide inventories, number, and relative performance of waste packages containing these two different waste forms.

FIGURE 1.1. Structural Hierarchy of Models and Data Included in Performance Assessment of Radionuclide Release from the Engineered Barrier System (DOE 1988)

At the waste-package level, Figure 1.1 shows that the performance of an individual waste package is affected by many factors other than characteristics of the specific waste form. Waste-package geometry, container degradation, and waste-package environment all affect the release-rate performance of individual waste packages in addition to waste-form characteristics. In particular, the transport of radionuclides subsequent to release from the waste form is expected to control the rate of release of radionuclides from a waste package (Pigford and Chambré 1986).

Waste-form release is at the lowest level of the hierarchy for performance (Figure 1.1). The release of radionuclides from a waste form will be limited by one of two processes: the precipitation of radionuclide-bearing solids or the long-term dissolution rate of the waste form matrix. The magnitudes of these processes are sensitive to the composition of the groundwater.

The Performance Assessment Scientific Support (PASS) Program at the Pacific Northwest Laboratory (PNL)^(a) provides oversight support to the DOE at all levels of near-field and far-field assessments. The DOE has requested the staff within the PASS Program to assess the performance of borosilicate glass from the Defense Waste Processing Facility (DWPF) as a waste form in a geologic repository at each of these three levels. In addition, an evaluation of the relationship between proposed Waste Acceptance Preliminary Specifications (WAPS) tests on glass-dissolution rate and compliance with NRC's release-rate criterion was also requested.

1.1 ORGANIZATION

This report is organized in the same manner in which waste constituents are released to the environment. Thus, the focus starts at the waste form, in this case the DWPF glass, then moves to the packages containing glass, and finally to the ensemble of waste packages in the repository including spent fuel. Subsequent sections to the Introduction and a discussion of release modes (2.0), therefore, are "Glass Waste Form Performance Analysis (3.0),"

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"Glass Waste Package Performance Analyses (4.0)," and "Systems-Level Performance Analyses (5.0)." Section 6.0 discusses the impact of this performance assessment on the proposed WAPS, and Section 7.0 presents conclusions.

One of the vital roles for performance assessment is to guide data collection and model development. The final conclusions from the three separate levels of analysis are therefore presented in a "top-down" order so that the relative importance of factors is clearly indicated. A "top-down" sensitivity analysis is required to determine those areas that most acutely affect the magnitude or uncertainty in the overall system performance. Furthermore, the NRC's criterion for near-field radionuclide release is specific to the performance of the integrated, multi-barrier EBS, and not to any individual barrier material or subprocess.

1.2 FUTURE WORK

Future work will include a geochemical modeling study to assess how the gradients in the EBS affect the composition of the near-field pore water. Changes in the groundwater composition as a result of the thermal gradient will be factored into the behavior of the waste form, waste form packages, and system-level analyses.

2.0 RELEASE MODES

A schematic design for a waste package containing borosilicate glass (O'Connell and Drach 1986) is shown in Figure 2.1. A canister containing the high-level waste glass is overpacked with a container designed to ensure compliance with regulatory containment criteria. This waste package is emplaced within an excavated opening (shown vertically here), leaving a small "air gap" between the emplaced container and the host rock. If the containment barriers are breached, there are three general modes anticipated for radionuclide release from this engineered barrier system: "dry", "wet-drip", and "wet-continuous" (Figure 2.2; Apted, Liebetrau, and Engel 1989). Under partially saturated conditions, the last mode of release should be referred to as "moist-continuous" release mode.

2.1 DRY/GAS ADVECTION TRANSPORT

The purpose of the air gap is to cause water to flow around, rather than through, the emplacement borehole. Therefore, the anticipated condition for the majority (~90%) of the waste packages is for the packages to remain dry. With an intact air gap, no liquid water would contact the waste form even in the event of containment barrier failure. Under such "dry" conditions, gaseous transport is the only available pathway for release. Because volatile radionuclides (e.g., ^{14}C and ^{129}I) will have been removed from high-level waste during the processing and fabrication of borosilicate glass, this release scenario is not treated in this study.

2.2 WET-DRIP/CONVECTIVE MASS TRANSPORT

For some emplacement holes, there is a possibility that local variations in rock permeability will divert water flow into fractures that intersect the emplacement hole (O'Connell and Drach 1986). If this occurs, water may drip onto the waste package. Upon breaching the container and canister, dripping water could contact the glass waste form. However, the amount of water that could flow into a container is expected to be limited. The volumetric flow of water into a container would be equal to the product of water flux (in meters per year) and cross-sectional area (in square meters) normal to the assumed

FIGURE 2.1. Schematic Diagram of DHLW Waste Package for Vertical Emplacement in Tuff (from O'Connell and Drach 1986)

downward flux. This constitutes what is termed the "wet-drip" condition. It should be noted that the calculated release rate will go to zero as the flux of water goes to zero.

It is assumed that there is a hole near the top of the waste package, allowing the void space between the top of the glass monolith and the

FIGURE 2.2. Schematic Representation of Three Radionuclide Release Modes for Waste Packages Located in Partially Saturated Rock (O'Connell and Drach 1986)

container to fill. After the interior volume is filled, the inflow of new water is balanced by the outflow of an equal amount of water containing dissolved radionuclides (so-called "bathtub"). The concentration of dissolved radionuclides in the egressing water may be solubility limited, in which case the maximum steady-state release of a given radionuclide equals the product of the volumetric inflow and the solubility-limited concentration for that nuclide. For highly soluble nuclides, the release rate will be a complex function of the contact time, contact-surface area, and dissolution rate of the waste form. Details of the "wet-drip" scenario have been presented elsewhere (O'Connell and Drach 1986; USDOE 1988) and this scenario is not further treated here.

2.3 MOIST-CONTINUOUS/DIFFUSIVE MASS TRANSPORT

If the waste package contacts the host rock under partially saturated conditions, either by physical displacements within the emplacement hole or by sedimentation within the air gap, a third, "moist-continuous" mode can exist

for radionuclide release (see Section 4.2). In this case, a continuous hydrologic pathway is formed between the waste form and the host rock for diffusive/convective transport of radionuclides. This pathway would also occur for saturated hydrologic conditions.

A number of mass-transfer models have been developed for diffusive and diffusive/convective transport of radionuclides from waste packages (Chambré et al. 1985; Pigford and Chambré 1988) and applied to prediction of long-term release performance of engineered barrier systems (Apted and Engel 1988; Garisto and Leneveu 1988; KBS 1983; Mangin et al. 1989; Apted, Liebetrau, and Engel 1989). In these models, both solubility and reaction-rate boundary conditions have been employed. Under the conditions of the moist-continuous mode of release, the release rate does not approach zero even if the water flux goes to zero; diffusive transport leads to a finite release rate. An analytical model for time-dependent release by diffusive transport has been implemented in the AREST code and previously applied in the analysis of spent fuel as a waste form (Apted, Liebetrau, and Engel 1989). The AREST code and this same mass-transfer model have been used here to calculate radionuclide release from a waste package containing DWPF glass.

3.0 GLASS WASTE FORM PERFORMANCE ANALYSIS

An assessment of the long-term performance of a glass waste form in a repository must rely on the use of an accurate model that has been validated against sound results from the testing of these waste forms in the laboratory. To be effective, a model for the performance of glass in a repository must apply to reactions for the glass under plausible repository scenarios. It should be possible with such a model to calculate the changes in solution concentration for each element, including key radionuclides, in the glass matrix as a function of time and to account for the mass of each mineral phase that precipitates as a result of the gradual dissolution of the glass waste form when contacted by water. Understanding the release from (dissolution of) the glass waste form allows one to calculate the release from the repository more effectively because movement of radionuclides is sensitive to the local chemistry, which dictates radionuclide chemistry.

In this section the interaction of water with the DWPF glass will be modeled to the degree that data are available (see Section 3.2). However, the evolution of the solution concentrations of individual radionuclides is not calculated here (see Sections 4.0 and 5.0); rather, only the overall dissolution of the glass matrix is calculated to provide information on possible phase precipitation that might be useful in explaining solution concentrations as a function of glass dissolution. Later, when more data are available, these calculations will serve as the basis for more refined calculations.

3.1 GLASS/WASTE INTERACTION

It is important in understanding the topics discussed in this section that the current state of empirical knowledge of the glass/water interaction be reviewed. When a waste glass is placed in water, ion exchange occurs between alkali ions (Na^+ , K^+ , etc.) in the glass and H^+ or H_3O^+ in aqueous solution (Grambow 1984; Pederson 1987). This event takes place within the first minutes to hours of contact with the aqueous solution. Simultaneous with this event, the glass matrix, a complex, random arrangement of the glass constituents, begins to break down. Those elements with high solubility in groundwater (B, Na, etc.) relative to a secondary phase containing that

element go into solution; those with low solubility (Al, Fe, etc.) remain at the glass surface. Later, some elements that first went into solution may reach concentrations that exceed the solubility for a solid phase containing that element. The solids that remain/precipitate directly on the surface of the glass constitute what has become known as the gel layer. Generally, this layer consists of an assemblage of amorphous to cryptocrystalline phases with no or poorly-defined x-ray diffraction patterns. Some of the phases that occur precipitate on the surface of the gel layer as well as interior to the gel layer. During most laboratory experiments and in nature (e.g., obsidians), the original (starting) surface of the glass becomes the surface of the gel layer, and any phases that reprecipitate from solution generally form on the surface of the gel layer (Grambow 1984).

There are, therefore, two zones that are important to the understanding of the glass/water interaction. Ion exchange reactions create a transition zone between unaffected glass and the gel layer (Grambow 1984). This zone is formed and remains basically the same thickness, but moves inward during the experiment and is not easily removed mechanically. The second zone is the gel layer, which is generally easy to remove mechanically. The gel layer has two interfaces - the glass-gel interface and the gel-solution interface. Both interfaces are used in the dissolution/precipitation model discussed in the next section.

Although the gel layer is for the most part formed in place, the process is, from a thermodynamic point of view, identical to dissolution followed by precipitation (i.e., thermodynamic properties are path independent). Thus, glass is treated as a congruently dissolving phase followed by precipitation of insoluble phases. The congruency of the glass dissolution has been observed (Grambow 1984; Pederson 1987; McGrail et al. 1988). Hence, the term "dissolution" is used with respect to the glass/water interaction as opposed to "leaching," which implies selective removal of elements.

3.2 PERFORMANCE ANALYSIS MODEL

Several models have been proposed for use in determining the long-term dissolution performance of nuclear waste glasses. Physico-chemical processes that have been incorporated into computational models for the dissolution of

glasses include 1) diffusion in a growing surface layer (Wallace and Wicks 1983); 2) formation of protective surface films (Hench, Clark, and Yen-Bower 1979; Bunker et al. 1983; and Malow 1982); 3) sorption at surface sites (Kuhn and Peters 1983); 4) alkali/hydrogen interdiffusion and first order dissolution (Machiels and Pescatore 1982; Harvey, Litke, and Boase 1984) and 5) diffusion of water or hydronium ions into the glass (Doremus 1975; Harvey and Larocque 1989). In addition, the thermodynamic stability of the component oxides and silicates of a glass relative to their hydrated states has been correlated with the chemical durability of the glasses (Plodinec, Jantzen, and Wicks 1984). However, none of these models can be used in the fashion outlined above (Section 3.0). That is, none of these models can be used with a simple set of variables to predict the dissolution rate of a glass in a number of repository situations. For instance, in a model based on diffusion, a different diffusion constant is usually required for each element in the glass and for any new dissolution environment.

3.2.1 Description of the Dissolution/Precipitation Model

A dissolution/precipitation model developed by Grambow (1984) has been applied to an extensive data base compiled from the dissolution of glass under a wide variety of conditions or simulated geochemical environments. These conditions include solution composition (Grambow and Strachan 1988; JSS 1987a; and Crovisier et al. 1986), flowing solution systems (Grambow and Strachan 1988), the bentonite/glass/water system (Grambow et al. 1986), the steel corrosion product/glass/water system (JSS 1987a,b), and the natural basalt glass/sea water system (Crovisier et al. 1986). The dissolution/precipitation model is based on solution chemistry, glass alteration products, and transition state theory. For any glass at a given temperature, a single set of four parameters is needed in the dissolution/precipitation model to calculate the dissolution of the glass under the variety of conditions shown above.

The underlying rate equation used in the dissolution/precipitation model, when diffusion of $H_4SiO_4(aq)$ in the gel layer can be neglected, is

$$R = k_+ \left(1 - \frac{K^*}{K} \right) \quad (3.1)$$

where R = the dissolution rate, including reactions which slow the rate

k_+ = forward dissolution rate

K^* = solubility expression for the rate-limiting species in the dissolution mechanism, which, for glass, is the activity (a_{Si}) of silicic acid (H_4SiO_4)

K = the equilibrium constant for the rate-limiting species in the dissolution mechanism, which, for glass is the H_4SiO_4 activity at saturation.

To include the effect of transport of H_4SiO_4 through the gel layer, Grambow proposed the following modification of Equation 3.1

$$R = \frac{D}{L} \left(a_{\text{Si},s} - a_{\text{Si},b} \right) + R_f \quad (3.2)$$

where D = the diffusion coefficient of H_4SiO_4 in the growing surface layer, m^2/s

L = the layer thickness, m

$a_{\text{Si},s}$ = the H_4SiO_4 activity at the surface of the glass, mol/m^3

$a_{\text{Si},b}$ = the bulk solution activity of H_4SiO_4 , mol/m^3

R_f = the final rate of glass dissolution when the solution is saturated with respect to an SiO_2 solid; i.e., $a_{\text{Si},s}$ is constant.

Initially $a_{\text{Si},b} \sim 0$, the rate of dissolution is rapid when the solution concentration of silicic acid (H_4SiO_4) is undersaturated with respect to the glass.^(a) Hence, K_+ is obtained from experiments at very early time when the activity of H_4SiO_4 is near zero. As the solution concentration of H_4SiO_4 increases, the rate of glass reaction decreases (Pederson et al. 1983). However, because glass is a thermodynamically unstable phase with respect to the potential alteration products in an aqueous environment, the rate of dissolution does not decrease to zero at saturation, but to a final rate (Grambow 1984).

(a) Glass saturation is an empirical quantity that differs from glass to glass, yet the saturation constants are remarkably similar. This glass saturation is close to the solubility constant of chalcedony, an SiO_2 polymorph, and between those of quartz and amorphous SiO_2 . This quantity is used in the model to account for the observed decrease in dissolution rate with increasing H_4SiO_4 .

The remaining constants K , D , and K_d are determined empirically for each glass. The equilibrium constant, K , for relatively low ionic strength solutions (excludes brines) is determined from very long-term experiments or from experiments in which a high ratio of surface area of glass to solution volume (SA/V) is used. These same experiments may also be used to estimate the final rate. The diffusion coefficient for H_4SiO_4 is best estimated using flow tests.

To calculate the mass balance of the various solution species, precipitating phases, dissolving phases, and the effects of environmental parameters such as temperature, a computer code (i.e., PHREEQE, EQ3/6, etc.) can be used to calculate the effect on solution composition as glass dissolves. Virtually any geochemical code may be used and the results of the calculations will be the same if the associated thermodynamic data base is the same. These codes typically are accounting tools for the mass-action reactions that take place as a glass dissolves. The output from these codes can be used along with Equation (3.2) to calculate the changes in solution activities as a function of time. However, it is, again, more convenient if one has a computer code with which to perform these calculations.

Grambow (JSS 1987b) has written a kinetic code - GLASSOL - incorporating Equation (3.2). The geochemical code PHREEQE (Parkhurst, Thorstenson, and Plummer 1980) is used to calculate the activities of the constituent elements as the glass is allowed to dissolve in water. These activities are passed to the GLASSOL code in which B is used to calculate reaction progress and the activity of H_4SiO_4 is used according to Equation (3.1) or (3.2).

The EQ3/6 geochemical code package (Wolery 1983; Wolery et al. 1990) may also be used for kinetic calculations, but with some extensive modifications (Aines 1986). It would also be possible to modify the output from EQ3/6 to be compatible with the GLASSOL code or modify the GLASSOL code to use the EQ3/6 output.

Bruton (1988) has used the EQ3/6 package to perform reaction progress calculations similar to the calculations performed with the PHREEQE code and reported here. However, there are some differences in the two approaches. In Bruton's work, the mass-transfer calculations were restricted to the

precipitation of only the crystalline SiO_2 phases. The modeling approach used in our study is to suppress all phases that are known to be kinetically hindered from precipitating. Secondly, phases that are found to be very much oversaturated are also suppressed.

To determine which phases to include in the simulation, dissolution test data are used to calculate the saturation indices for the solid phases in the PHREEQE data base. The saturation index is the value derived by dividing the equilibrium expression for a particular phase by the equilibrium constant. A value of 10 or greater for the saturation index generally indicates that this mineral is not present as a secondary phase in the test. If these grossly oversaturated, but thermodynamically stable, phases are allowed to precipitate during the simulation, the calculated solution concentrations of the constituent elements would be far below the observed concentrations. This approach is needed because the most thermodynamically stable phase may not always be the first phase that precipitates in a given geochemical environment; the most readily precipitated phase may be metastable. The point to be made here is that a geochemical simulation must be interpreted relative to what is observed in the laboratory before it can be used to simulate the long-term behavior of a glass. Unless the precipitation kinetics of the secondary phases are known, it is not possible to calculate a priori which phases precipitate first. If the precipitation kinetics are known, they are not useful with the PHREEQE code in which precipitation and dissolution kinetics do not appear.

A somewhat more realistic approach is being taken at Lawrence Livermore National Laboratory in work for the Yucca Mountain Project. In this approach the gel layer is treated as an assemblage of a solid-solution phase plus other crystalline phases (Bourcier et al. 1990). This approach is more realistic because a major portion of the gel layer (see Section 2.1) is amorphous and is more-or-less a solid solution. This approach is just being developed and appears quite promising. However, the rate equations used by Bourcier et al. (1990) are similar to those used by Grambow.

3.2.2 Use of Dissolution/Precipitation Model for Vapor Phase Attack and/or High Surface Area-to-Solution Volume Ratios

Vapor phase attack on the glass waste form has been suggested as a potential mechanism for rapid release of radionuclides (Bates et al. 1988). This effect is not treated directly here, but is addressed in Section 5.2.4. Although models have been applied to systems in which the sample surface area-to-solution volume (S/V) ratio is very high, none have been successfully applied to the case of water vapor attack on glass. Conceptually, it is possible to increase the S/V ratio to very high values to mimic the interaction of vapor and glass. However, experience with obsidians would suggest that another mechanism dictates the rate at which the glass is attacked by water vapor (McGrail et al. 1988). Even though diffusion appears to be one of the dominant rate-controlling steps in the water vapor attack on glass, experiments performed at PNL using deuterated water vapor suggest the same mechanism that is present during liquid water attack on glass (McGrail et al. 1988).

In the dissolution mechanism proposed by Grambow (1984), the first interaction between glass and water is one in which ion exchange occurs between alkali ions in the glass and H^+ in the H_2O . This interaction eventually forms a transition zone that remains the same thickness during the rest of the glass/water interaction. The presence of such a zone was indicated by the D_2O experiments of Pederson (1987). In these experiments with simple glasses, the early time interaction could be classified diffusive, but with a deuterium effect (i.e., the rate changes according to the square root of the ratio of the atomic mass of D and H). This means that part of the rate limiting reaction involves the breaking of a chemical bond involving D or H. Because the time to set up the transition zone is short and the transition zone is thin relative to the rest of the gel layer on the surface of monolithic glass surfaces, the ion exchange portion of the reaction has little effect on the overall solution concentrations. However, as the S/V is increased, the thickness of the transition zone relative to the thickness of the gel layer becomes more and more significant as does the contribution to the solution chemistry by the material leached to form the transition zone. Thus, Bates, Piepel, and Johnston (1989) and Vernaz, Advocat, and Dussosoy (1989) note departures from the trend in solution concentration with time when glass dissolution data are

scaled to the $(S \cdot t)/V$. This departure is not calculated by the glass dissolution/precipitation model because the model was developed based on the assumption that the glass/water interaction was at relatively low S/V where the formation of the transition zone has an insignificant effect on the solution concentrations. The ion exchange contribution can, however, be approximated by assuming a depth of ion exchange and including this change in the starting solution composition in the PHREEQE simulation.

An ion exchange depth can be estimated from the experiments reported by McGrail et al. (1988). By increasing the alkali concentration of the solution used as the starting solution in the simulation by the amount of alkali in the transition zone, one must increase the pH in order to maintain electrical neutrality for the solution. The higher pH means that more glass needs to dissolve depending on composition before saturation with respect to SiO_2 can occur.

3.3 REVIEW OF AVAILABLE DWPF GLASS DISSOLUTION DATA

Over the years, the composition of the nuclear waste glass to be produced at the Savannah River Plant has changed as the composition of the waste stream became better known and the process flow sheet became better developed. One of the early glass dissolution studies performed at the Savannah River Laboratory (SRL) was by Plodinec (1979, 1980). The result of this optimization study was a glass with the label "SRL-131." A large number of studies have included this glass formulation. More analytical data on the potential waste for the DWPF led to the formulation of three potential waste streams--two worst cases and one average. A statistical study of glass formulations based on these waste streams (Soper et al. 1983) led to the formulation of a new glass "SRL-165." Recently, Jantzen (1988) has looked at some of the changes to the process flow sheet for the DWPF and has recommended new glass formulations and an "SRL-202" series of glasses. These glasses are minor variations of the SRL-165 glass formulation.

It took some time for researchers outside of SRL to convert from SRL-131 to the SRL-165 formulation in their glass reaction studies. Hence, there are not many publicly available data from studies on SRL-165 and none on the

latest series of SRL-202 glasses. However, in later generations of this document, SRL-202 glass dissolution data will be available for discussion and use. A few of the studies on SRL-165 are summarized here.

Short-term dissolution tests of 182 days or less have been performed using SRL-165 glass by Bates, Fischer, and Gerding (1986); Bunnell, Maupin, and Oma (1986); Bibler (1986); Bibler and Jurgensen (1988); Bibler, Wicks, and Oversby (1985); Jantzen and Bickford (1985); and Phinney et al. (1987). The longest test reported was by Zhu et al. (1986). This test was 2 years in length, but only the depths of surface layers were reported. In the study by Bunnell, Maupin, and Oma (1986), long-term tests of three glasses were carried out by varying the $(S \cdot t)/V$ from $10 \text{ d} \cdot \text{m}^{-1}$ to approximately $5 \times 10^5 \text{ d} \cdot \text{m}^{-1}$. Of the above-mentioned studies, only the one by Jantzen and Bickford (1985) reported information on the dissolution behavior of the glasses made with the worst-case simulated wastes, i.e., high-Al and high-Fe wastes. The glass formulation with average waste composition was used in the remaining studies.

The above-mentioned studies may be most easily summarized using the plot from Bunnell, Maupin, and Oma (1986) (Figure 3.1). This plot shows the dissolution behavior of the simulated nuclear waste glasses PNL 76-68, SRL-165, and EMS-11. Two characteristic portions of the curves in this plot are evident. One is the forward reaction rate [k_f in Equation (3.1)] or the rate at which a glass dissolves when the solution in which it is immersed is undersaturated with respect to the H_4SiO_4 concentration. This is the portion of the curves at $<100 \text{ d} \cdot \text{m}^{-1}$. The second characteristic is the final dissolution rate [R_f in Equation (3.2)], $(S \cdot t)/V > 10^4 \text{ d} \cdot \text{m}^{-1}$. Since this is a log-log plot, the portions of the curves corresponding to constant rates are shown as straight lines with unit slope. In Figure 3.1, the normalized B concentration is used as an indicator of the extent of glass dissolution because B is typically the most soluble of the glass constituents. The B concentration is normalized to the B content in the glass so that glasses of different composition can be compared readily.

FIGURE 3.1. A Plot of Glass Dissolution for PNL 76-78, SRL-165, and EMS-11 Glasses. This is a combination of several tests run at different surface area-to-volume ratios and for different times at 90°C. The dashed lines represent an extrapolation of the curve above and below the range of the data.

3.4 PERFORMANCE ASSESSMENT OF DWPF GLASSES

No modeling efforts have been carried out to understand the long-term dissolution behavior of the SRL-165 or SRL-202 glasses. Of the studies outlined above, only one reported short-term information on the behavior of the glasses containing high Al and Fe waste concentrations (Jantzen and Bickford 1985). Due to the lack of data, it was not possible as part of the current study to perform a detailed modeling study regarding the long-term dissolution rates of the DWPF glasses. Rather, the results of a very preliminary modeling effort and a comparison between SRL-202 glasses and other glasses of similar composition will be discussed. In future generations of this document, results from revised calculations will be reported in which the currently

available data are modeled, missing data identified, and predictions made concerning the dissolution behavior of these glasses in contact with water.

The target compositions of the SRL-165 and SRL-202 glasses are shown in Table 3.1 (Jantzen 1988). The differences between the three SRL-165 glasses and the three SRL-202 glasses are the waste compositions, which range from wastes containing high concentrations of Al (SRL-165AL and SRL-202AL) to wastes containing high concentrations of Fe (SRL-165FE and SRL-202FE); average waste compositions are included (SRL-165AV and SRL-202AV). The changes in composition from SRL-165 to SRL-202 have to do with the projected composition of the precipitated waste, which will have more Na₂O, K₂O, Cs₂O, and B as B₂O₃ than previously anticipated.

Because there are essentially no published dissolution data on the SRL-202 glasses and because the available data are from relatively short-term (28-d) tests, we have not completed kinetic modeling of the SRL-202 glasses. However, a large amount of information can be obtained from modeling the dissolution of the SRL-202 glass in water without invoking the kinetic model

TABLE 3.1. Target Compositions of SRL-165 and SRL-202 Glasses

Component	Amount in Glass (wt%)					
	165AL	165AV	165FE	202AL	202AV	202FE
SiO ₂	52.1	54.0	51.0	51.7	53.6	50.5
B ₂ O ₃	7.2	7.3	7.1	7.4	7.5	7.4
Li ₂ O	5.1	5.1	5.0	4.4	4.5	4.4
Na ₂ O	11.0	10.5	11.3	7.5	6.8	7.8
MgO	0.8	0.8	0.8	1.3	1.3	1.3
CaO	0.4	0.9	1.3	0.4	0.9	1.3
ZrO ₂	0.7	0.7	0.7	--	--	--
TiO ₂	--	--	--	1.7	1.7	1.7
Fe ₂ O ₃	4.1	11.8	18.0	4.1	11.7	17.7
Al ₂ O ₃	14.7	4.6	0.5	14.5	4.6	0.5
MnO ₂	3.3	3.3	1.2	3.2	3.2	1.2
NiO	0.6	1.0	3.1	0.6	1.0	3.0
K ₂ O	0.04	0.03	0.04	3.2	3.2	3.2
	100.04	100.03	100.04	100.0	100.0	100.0

(e.g., calculating the glass dissolution behavior as a function of mass of glass dissolved rather than as a function of time). In the figures that follow, normalized elemental concentrations, calculated using PHREEQE/GLASSOL,^(a) for several of the main glass constituents are calculated as a function of reaction progress. Reaction progress is expressed simply as the mass of glass dissolved in a cubic meter of water. The units of reaction progress are $\text{g}\cdot\text{m}^{-3}$. Normalized elemental concentration is the mass of an element released by the glass to a cubic meter of water normalized to the elemental content of the glass. Normalized elemental concentration also has units of $\text{g}\cdot\text{m}^{-3}$. Thus, if an element in the glass is released to solution such that it does not precipitate or sorb, then the normalized elemental concentration equals the reaction progress and a plot of the data will have unit slope. Any element that precipitates or is sorbed will deviate to the right from the unit slope line. For a more complete discussion of these plots, see Appendix B.

Radionuclide concentrations are not shown in these plots because the main emphasis in this section is the evolution of the solution composition with respect to the glass matrix and because no SRL-202 glasses containing radionuclides have been prepared. The changes in solution composition with respect to the dissolution of radionuclide-containing glass can be calculated for those radionuclides where thermodynamic data are available. The ratio at which a particular radionuclide appears in solution has an upper bound that is the dissolution rate of the glass matrix. In Section 4.0, the concentrations of some radionuclides are shown to be dependent on solubility constraints; others depend on the dissolution rate of the glass matrix.

Predicted concentrations of glass-matrix elements released during the dissolution of SRL-202 glasses in deionized water at 90° are summarized in Figures 3.2, 3.3, and 3.4. The minerals included in the thermodynamic data base are the same minerals that have been used in past studies (Grambow and Strachan 1988; JSS 1987b). It needs to be emphasized here, as it was in the

(a) Reaction progress is one of the parameters that is calculated using GLASSOL.

FIGURE 3.2. A Reaction Progress Plot for SRL-202FE, the High Iron Waste-Containing Glass. Arrows point to reaction progress at which a mineral precipitates.

earlier studies, that these minerals have not in most cases been observed, but the solution data are consistent with the calculated solubilities of these minerals. Grambow and Strachan (1988) found that a single set of minerals could be used to account for the solution behavior of most elements released by the dissolution of nuclear waste glasses. The mineral assemblage consists of hydroxides {ferrihydrate $[\text{Fe}(\text{OH})_3]$ and gibbsite $[\text{Al}(\text{OH})_3]$ }, silicates {chalcedony $[\text{SiO}_2]$, $\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$, analcime $[\text{Na}(\text{AlSi}_2\text{O}_6) \cdot \text{H}_2\text{O}]$, amorphous sepiolite $[\text{Mg}_2\text{Si}_3\text{O}_6(\text{OH})_4]$, and montmorillonite $[\text{Na}_{0.3}(\text{Si}_{3.96}\text{Al}_{0.04})(\text{Al}_{1.55}\text{Fe}_{0.2}\text{Fe}_{0.01}\text{Mg}_{0.24})\text{O}_{10}(\text{OH})_2]$ }, and carbonates {calcite $[\text{CaCO}_3]$ and rhodochrosite $[\text{MnCO}_3]$ }. Some of these minerals may be considered as end members of a more complicated solid solution mineral. During a simulation (calculation), the

FIGURE 3.3. A Reaction Progress Plot for SRL-202AV, the Average Waste-Containing Glass

glass composition will dictate how early or whether the solution becomes saturated with respect to each mineral.

A simulation of the dissolution of the high-Fe or the average-waste glass compositions result in the precipitation of chalcedony (SiO_2) at a reaction progress of about $0.01 \text{ g} \cdot \text{m}^{-3}$ (Figures 3.2 and 3.3). This means that for the two glasses SRL-202FE and SRL-202AV the net rate of dissolution [R in Equations (3.1) and (3.2)] will reach a low rate (typical of silica-saturated solutions) on the order of $0.01 \text{ g}/(\text{m}^2 \cdot \text{d})$ based on the results from SRL-165 glass (Figure 3.1). However, chalcedony is not calculated to precipitate when the high-Al glass (SRL-202AL) is dissolved in water (Figure 3.4). The Al_2O_3 content of the glass is sufficiently high, along with the Na and Si, to cause analcime [$\text{Na}(\text{AlSi}_2\text{O}_6)\text{H}_2\text{O}$] to precipitate in sufficient mass during the simulations that chalcedony cannot precipitate. Because chalcedony is prevented from precipitating in the simulations, the SRL-202AL glass is likely to exhibit a higher long-term dissolution rate than the other two SRL-202

FIGURE 3.4. A Reaction Progress Plot for SRL-202AL, the High Aluminum Waste-Containing Glass

glasses. How much higher the rate will be cannot be predicted a priori, but the prediction must be validated through experimentation.

Because solution data from dissolution tests of SRL-202 glasses have not been compared with solubility calculations, it is possible that the actual solute concentrations are different from those predicted in these calculations. If the chalcedony solubility used in these calculations was too high and the analcime solubility was too low compared with the solubilities of the actual phases, then chalcedony may precipitate. However, the possibility also exists that chalcedony precipitates first followed by analcime later in reaction progress as was observed by van Iseghem and Grambow (1988). This would cause the rate of glass dissolution to increase after apparent approach to the final dissolution rate.

In the work by van Iseghem and Grambow (1988), the low- Al_2O_3 glass (SM58; Figure 3.5a) initially dissolved at a higher rate than the high- Al_2O_3 glass (SAN60; Figure 3.5b). By 10 days at an $\text{S/V} = 100 \text{ m}^{-1}$ the SM58 glass had

FIGURE 3.5a. Experimental Data for SM58 Glass in Distilled Water at 90°C (ESA/V=100 m⁻¹) and Calculated Results

FIGURE 3.5b. Experimental Data for SAN60 Glass in Distilled Water at 90°C (SA/V = 100 m⁻¹) and Calculated Results

released about ten times more B, Li, Na, and Si to solution than had SAN60. This is because the silica concentration at which the rate decreased for SAN60 was about a factor of about 10 lower than for SM58. As the glasses approached final reaction rates, both experimentally and through modeling, the SAN60 glass began to dissolve at a higher rate. This process was predicted by Grambow and was calculated to be due to the precipitation of analcime. Arguments based on mass balance for the silica in the system showed that once analcime began to precipitate, chalcedony had to dissolve to maintain mass balance in the system. Once chalcedony had dissolved, the H_4SiO_4 concentration began to decrease because of the precipitation of analcime. The reduced H_4SiO_4 concentration forced the glass to dissolve at a higher rate [Equation (3.2)].

To determine if the same or similar effect will occur in the SRL-202 series of glasses, a variety of long-term tests at moderately high S/V ratios need to be performed. These experiments need to be performed with the idea that a model, such as the dissolution/precipitation model developed by Grambow, will be used to determine the long-term (beyond the laboratory time frame) behavior. These experiments should also include a number of glasses with varying amounts of Al_2O_3 so that the predicted solute concentrations can be checked against the measured solute concentrations. A geochemical code such as PHREEQE or EQ3/6 can be used to determine the reaction progress needed to precipitate different minerals as was calculated by van Iseghem and Grambow (1988). This modeling approach would be useful in determining the regions of glass composition that could result in high dissolution rates.

3.5 IMPACT OF CORROSION PRODUCTS

As the waste package container corrodes, corrosion products having significant sorptive capacity are precipitated. It has been shown that the presence of corrosion products in contact with a dissolving glass accelerates the dissolution rate of the glass because of " SiO_2 " sorption on the corrosion products (Tsukamoto et al. 1988; Shade, Pederson, and McVay 1984; McVay and Buckwalter 1982). Although this has been modeled using the dissolution/precipitation model discussed above (Grambow et al. 1987), the effect has not been modeled here because insufficient kinetic data exist for this series of

glasses. However, the effect of corrosion products on the dissolution of glass is expected to depend on the mass of corrosion products, their sorption capacity for dissolved H_4SiO_4 , and the number of sorption sites that are filled prior to the time the glass is contacted by water.

4.0 GLASS WASTE PACKAGE PERFORMANCE

The purpose of this section is to evaluate the release of radionuclides from a single waste package containing DWPF glass, of which SRL-202 is the latest formulation. Two limiting chemical boundary conditions are examined 1) control of concentration by the dissolution rate of glass, and 2) control of concentrations by formation of secondary, solubility-limiting phases. In the previous section, the dissolution behavior of the individual waste glass cylinders was examined. As mentioned, actual measured dissolution rates on SRL-202 glass are not available. Therefore, in this section, data from the literature will be used to provide an estimate for the dissolution rate of DWPF glass. The fractional release rates of selected radionuclides from waste packages containing DWPF glass are calculated using the AREST code (Apted and Engel 1988). Similar calculations using the PANDORA code (Apted et al. 1990; O'Connell and Drach 1986) are in general agreement with these results.

4.1 OVERVIEW OF WASTE PACKAGE RELEASE MODEL

Experimental results on pore water interactions with DWPF glasses (see Section 3), as well as other waste forms, indicate the release of radionuclide from the waste form can be divided into two limiting categories. In the first category, the concentrations of highly soluble nuclides are assumed to be controlled by the long-term dissolution rate of the waste form. This may be referred to as "reaction-rate limited." For the second category, the concentration of a nuclide at the waste form surface is solubility-limited by the formation of secondary alteration solids. This may be referred to as "solubility limited." Mass-transfer analyses (Zavoshy et al. 1985), confirmed by experimentation and geochemical modeling (e.g., Bruton 1988), indicate that essentially all radionuclides will be solubility-limited. Unfortunately, a general lack of thermodynamic data on some nuclides, and their solubility-limiting solids, makes it necessary to assume a certain number of nuclides (e.g., ^{99}Tc , ^{135}Cs , ^{245}Cm) may be reaction-rate limited.

Mass transport models for radionuclide release from waste packages have been developed by Chambré, Pigford and coworkers for both categories (Pigford

and Chambré 1988). These models are analytical solutions to the time-dependent, diffusional mass transport of nuclides from a spent-fuel waste form surrounded by a shell of porous material (buffer, backfill, air gap, or equivalent) material imbedded in a porous (or fractured) host rock. There are several assumptions made in these models: 1) near-field transport is dominated by diffusion, 2) waste containers provide no resistance to mass transfer, and 3) linear-sorption isotherms are sufficiently accurate for calculation of the retardation coefficients. These analytical solutions to mass transfer equations have been implemented into the AREST code (Liebetrau et al. 1987) and used for the analyses in this study. Similar models have been developed for OCRWM by other groups, including the University of California at Berkeley (Pigford and Chambré 1988) and the Lawrence Livermore National Laboratory (O'Connell and Drach 1986).

For the general, solubility-limited release model, the concentration of a nuclide i at the waste form surface is imposed by the solubility (C_i) of the most stable solid that contains nuclide i as a principal component. Initially, the concentration of nuclide i outside the waste form is zero. A spherical configuration is evaluated, with the waste-form surface area chosen to equal the surface area of an actual cylindrical waste container. The mass transfer rate for nuclide i , M_i , was about a factor of about 10 lower than for SM58. As the glasses approached final reaction rates, both experimentally and through modeling, the rate of dissolution for SAN60 was about a factor of about 10 lower than for SM58. As the glasses approached final reaction rates, both experimentally and through modeling, the SAN60 (r, t), as a function of distance from the waste form surface (r) and time after initiation of release (t), is given by (Chambré et al. 1985):

$$M_i(r, t) = 4\pi\epsilon_1 DR_0 r C_i^s \psi_i(r, t), \quad R_0 \leq r \leq R_1, \quad t \geq 0 \quad (4.1)$$

where the term $\psi_i(r, t)$ is a complex function of the porosity of the packing (ϵ_1) and host rock (ϵ_2), the diffusion coefficient for nuclide i in water (D), the waste form radius (R_0), the radius to the waste package/host rock boundary (R_1), the packing/air-gap thickness ($b = R_1 - R_0$), the respective retardation

coefficients for nuclide i in the packing/filled air-gap region (K_1) and host rock (K_2), and the radioactive decay constant (λ) or half-life ($t_{1/2}$) for nuclide i .

The mass transfer rate for highly soluble, inventory-limited nuclides, evaluated at the waste package/host rock boundary, has been derived previously (Chambré et al. 1988):

$$M_i(R_i, t) = 2K_1\epsilon_1 N_0 S_v \omega_i(t) \quad (2)$$

where N_0 is the initial concentration of nuclide i assuming that the available mass inventory of nuclide i dissolves instantaneously in the water-filled, interior volume (V_v) of the waste package container, S_v is the surface area of the cylindrical waste package container, and $\omega_i(t)$ is a complex function of ϵ_1 , ϵ_2 , K_1 , K_2 , λ , D , b , V_v , and S_v .

4.2 SELECTION OF RELEASE MODE FOR PRELIMINARY ANALYSES

Preliminary release calculations using both the "wet-drip" and "moist-continuous" release modes at Yucca Mountain have been made for waste packages containing spent fuel (Apted, Liebetrau, and Engel 1989). This work represents a joint project conducted by OCRWM-sponsored scientists at the Lawrence Livermore National Laboratory, the University of California at Berkeley, and the Pacific Northwest Laboratory. It represents a consensus evaluation of the various modes of radionuclide release from nuclear waste packages (summarized below), as well as sample release calculations of selected radionuclides for each of these various modes.

The various release models utilized in the work with spent fuel waste packages are based on different transport processes as discussed in Section 2.0 of this report. Despite different release modes, releases for a wide range of radionuclides are calculated to be similar between the "wet-drip" and "moist-continuous" release modes, if the same thermodynamic data base and geochemical conditions are used. This is probably attributable to the fact that, at the assumed low velocity for pore water at Yucca Mountain (<1 mm/year), diffusional transport rate equals or exceeds the convective transport rate (Pigford and Chambré 1986) if a continuous pathway were to be

established between waste form and host rock. Because of the broad similarity in previous results for "wet-drip" and "moist-continuous" release modes, only "moist-continuous" release calculations are performed for this study.

The following release calculations are for a single waste package containing DWPF waste glass. It is expected that at least 90% of all waste packages will remain dry for 10 000 years at the Yucca Mountain site. No release of radionuclides would occur from these dry packages. Scaling these results for a single package to an entire EBS must account for this factor. If 10% of waste packages are undergoing release as calculated for this one waste package, then the EBS release rate will be a factor of ten lower. Similarly, it is possible that only 1% of the waste packages will be contacted by water (i.e., 99% remain dry); in this case, the EBS release rate will be two orders of magnitude lower than the values described in this section for a single package. Further aspects of System-Level Analysis are described in Section 5.0.

4.3 DATA USED FOR WASTE PACKAGE PERFORMANCE ANALYSES

The data used in the release models are summarized in Tables 4.1 and 4.2. Waste package dimensions and physical properties in Table 4.1 are adopted from recent DOE reports (USDOE 1986 and 1988). A vertical emplacement geometry is assumed. The time of containment failure can directly affect the magnitude of the release rates. Generally, a broader distribution in failure times will correspond to lower peak release rates (Apted and Engel 1988; Pigford and Chambré 1988). Currently, there are no reliable estimates of the distribution of containment failures for waste packages as a function of time. To be consistent with previous studies on spent fuel (Apted, Liebetrau, and Engel 1989) and ongoing analyses by the staff at the Office of System Integration and Regulations in DOE's OCRWM, arbitrary and conservatively narrow "instantaneous" failure times of 1000 and 5000 years after permanent repository closure are selected in the analyses presented here.

Liquid-phase diffusion coefficients in crushed and intact rock have been recently measured under controlled, partially saturated conditions (Conca

TABLE 4.1. Physical Parameters for Release Calculations on DWPF Glass

Diffusion Coefficient (m^2/s)	$1 \times 10^{-9} (1.00 \times 10^{-13})^{(a)}$
Water Flux (mm/yr)	1.00
Cross-Sectional Area (m^2)	1.00
Water Flow Rate (L/yr)	1.00
Spherical Waste Form Radius (m)	0.859
Borehole Radius (m)	0.889
Air Gap Thickness (mm)	30
Canister Head-Space (L)	108
Porosity of Filled Air Gap	0.5
Porosity of Intact Tuff	0.1
Bulk Density of Filled Air Gap ($10^3 \text{ kg}/\text{m}^3$)	1.29
Bulk Density of Intact Tuff ($10^3 \text{ kg}/\text{m}^3$)	2.33
Percent Saturated	0.75%

(a) Second value of the diffusion coefficient used in this study (see text).

1990).^(a) The measured values range between 10^{-13} and $10^{-14} \text{ m}^2/\text{s}$ (estimated errors of $\pm 20\%$), depending on the water content (i.e., degree of saturation) and grain size of the crushed rock. In previous studies of diffusional release for "wet-continuous" conditions, a diffusion coefficient of $1 \times 10^{-9} \text{ m}^2/\text{s}$ was used - four orders of magnitude greater than the measured values. Steady-state release rates of radionuclides under "wet-continuous" conditions will be directly proportional to the diffusion coefficient. Because of the sensitivity of the calculated release behavior to diffusion coefficient, bounding values of 1×10^{-9} and $10^{-13} \text{ m}^2/\text{s}$ are used in these calculations of radionuclide release under "wet-continuous" conditions.

Based on inventory information for the wastes at the Savannah River Plant (Plodinec 1988), at least twenty nuclides have inventories above the exclusion limit (see Appendix A). Of these, the following nuclides are selected for these preliminary analyses based on the availability of data and

(a) This diffusion coefficient is not the same diffusion coefficient in Equation 3.2. This diffusion coefficient is for the diffusion external to the waste form.

TABLE 4.2. Chemical Parameters for Release Calculations on DWPF Glass

Element/ Nuclide	Half-Life (years)	SRL-165 Glass Inventory (curies/canister)		Solubility (g/m ³) ^(c)	Sorption Coefficient K _d ^(d)
		Emplacement ^(a)	1000-Years ^(b)		
Tc ⁹⁹ Tc	2.15E5	2.83E0	2.82E0		0.11
Cs ¹³⁵ Cs	3.00E6	9.00E-2	9.00E-2	6.31E-1 ^(e)	417
Pb ²¹⁰ Pb	2.23E1	0	5.07E1	2.10E-2 ^(f)	5
Ra ²²⁶ Ra	1.60E3	0	5.08E1	NE ^(g)	NE
Th ²³⁰ Th	8.0E4	1.44E2	1.43E2	NE	NE
U ²³⁴ U	2.47E5	8.65E-2	8.65E-2	5.98E-2	1.8
²³⁸ U	4.51E9	8.16E-3	8.16E-3		
Np ²³⁷ Np	2.14E6	1.12E-2	1.35E-2	2.98E-4	4.9
Pu ²³⁸ Pu	8.6E1	2.26E2	DP ^(h)	3.02E-10	208
²³⁹ Pu	2.44E4	2.56E0	2.49E0		
²⁴⁰ Pu	6.58E3	1.74E0	1.52E0		
²⁴¹ Pu	1.32E1	5.28E2	DP		
²⁴² Pu	3.79E5	2.44E-3	2.44E-3		
Am ²⁴¹ Am	4.58E2	1.21E1	3.20E0	1.53E-3	1070
²⁴³ Am	7.95E3	6.65E-3	5.87E-3		
Cm ²⁴⁵ Cm	8.50E3	6.66E-6 ^(j)	6.16E-6 ^(j)	2.45E-1 ⁽ⁱ⁾	1200
Total		4.47E4	2.60E2		

(a) Data from M. J. Plodinec, written communication, 1989a.

(b) Data from T. H. Pigford, written communication, 1989.

(c) Data from Bruton (1988) except where noted.

(d) Data from U.S. DOE (1986; 1988).

(e) Datum from Bennington, Beyer, and Johnson (1983).

(f) Datum from Goodwin and Guenther (1988).

(g) Not evaluated.

(h) Decayed to insignificant amount.

(i) Datum from U.S. DOE (1986).

(j) Assumed value, from M. J. Plodinec, written communication, 1989b.

representative range of chemical characteristics: ^{99}Tc , ^{135}Cs , ^{238}U , ^{237}Np , ^{239}Pu , ^{240}Pu , ^{242}Pu , and ^{245}Cm . It should be recognized that actual inventories (hence, allowable release rates) for the DWPF glass are uncertain because of sampling uncertainties and continued optimization in production.

Sorption values (Table 4.2) for the selected nuclides are within the ranges reported (USDOE 1986 and 1988). The preliminary radioelement solubilities calculated by Bruton (1988) for DWPF glass reacting at 90°C with J-13 water from the Yucca Mountain site have been used in these release calculations, supported by values from other sources. A value of 0.01 g/(m²·d) is assumed for the long-term dissolution rate of glass [R_f in Equation (3.2)]. This value falls within the range of predicted long-term dissolution rates of other borosilicate glasses (Grambow and Strachan 1988; see Figure 3.1 in Section 3.4).

4.4 RESULTS FROM THE ASSESSMENT OF DWPF PACKAGES

The fractional release rates of solubility limited nuclides using a diffusion coefficient of 0.1 m²/s are shown in Figure 4.1. The calculated release rates for ^{237}Np , ^{238}U , ^{239}Pu , ^{240}Pu , and ^{242}Pu are well below the allowable release rate limits. The early, transient-release period (first 1000 years after release begins) is characterized by release rates higher than the final steady-state values. This behavior arises from a complex interplay of diffusion rate, sorption, and radioactive decay during nuclide migration from the waste form surface to the host rock. The relatively higher and more rapid releases during this transient for the Pu isotopes are attributable to the significantly higher sorption coefficient for Pu compared to U and Np at these geochemical conditions. Essentially identical results are calculated for containment failure at 5000 years after repository closure.

Figure 4.2 presents calculated fractional release rates from the waste package for relatively soluble nuclides that are dissolution-rate limited. A diffusion coefficient of 1×10^{-9} m²/sec is used. The dashed line represents the upper limit to release of radionuclides for which the concentrations are not controlled by solubility based on a dissolution rate of 1.0×10^{-2} g/(m²·d). All of these calculated release rates are below one part in 10^5 per year for the assumed dissolution rate of the glass. Because its low

FIGURE 4.1. Fractional Release Rates of Solubility-Limited Nuclides from a Single Waste Package of Glass That Failed at 1000 years

sorption coefficient, high solubility, and relatively long half-life, the fractional release rate of ^{99}Tc quickly rises to near the diffusion rate limit. The concentration slowly decreases with time because "fractional release rate" is normalized against a fixed 1000-yr inventory, even though the nuclide inventory in the glass decreases from radioactive decay. The release rate of highly sorptive, long-lived ^{135}Cs rises more slowly but also closely approaches the reaction rate limit to release. For highly sorptive ^{245}Cm , the

FIGURE 4.2. Fractional Release Rates of Reaction-Rate-Limited Nuclides from a Single Waste Package of Glass

AREST calculations indicate the time to reach peak release rate is also greatly delayed. Furthermore, because of its relatively short half-life, the peak release rate is well below that of the reaction rate limit because of decay during transport to the host rock. Because Am is expected to be highly sorptive, the relatively short-lived ^{241}Am and ^{243}Am isotopes are expected to follow release curves similar to ^{245}Cm . The approximate effect of K_0 on release for soluble nuclides can be evaluated by comparing the slopes for ^{99}Tc , ^{135}Cs and ^{245}Cm at early time (up to 10 000 years) in Figure 4.2. There is a progressive increase in K_0 from 0.11 for ^{99}Tc , to 417 for ^{135}Cs to 1200 for ^{245}Cm . No specific sensitivity studies on the effect of variation in K_0 values were attempted; the value of K_0 merely affects the rate (i.e. time) at which the release rate approaches the "Reaction-Rate Limit," which is conservatively estimated to be below the NRC one part in 10^5 release rate requirement.

Release rate calculations using a diffusion coefficient of $10^{-13} \text{ m}^2/\text{s}$ show two effects when compared with releases calculated using a value of $1 \times 10^{-9} \text{ m}^2/\text{s}$. The first is that the steady-state release rates are four orders of magnitude (i.e., proportionally) lower for the calculations based on the lower diffusion coefficient. This result is expected based on the analytical equations used in these AREST calculations (Apted and Engel 1988; Chambré et al. 1985). The second notable feature is that the predicted time to reach peak release rate is also greatly increased for the case with the lower diffusion coefficient. The extremely low diffusion coefficient causes the 30-mm-thick air gap (assumed to be filled with tuff rubble) to perform as an effective barrier to the transport of sorptive radionuclides. This result is also expected, although its magnitude is a complex function of the diffusion coefficient and the radionuclide retardation coefficient (Chambré et al. 1985).

5.0 SYSTEMS-LEVEL PERFORMANCE ANALYSES

The NRC has established allowable fractional release rates for mined geologic repositories in the period following 300 to 1000 years postclosure where substantially complete containment is required (10 CFR 60, 1983). A detailed discussion of the implications and nuances associated with the application of the NRC regulations can be found elsewhere (Apted, Liebetrau, and Engel 1989). For the purposes of this section, the key aspect of the regulation is that the release rate limit is imposed at the engineered barrier system boundary. The direct implication of this requirement is that fractional release rates must be calculated from the total radionuclide inventory. The total inventory includes radionuclide inventories from both spent fuel and borosilicate glass, both of which will be placed in the repository. This requirement can be quantitatively expressed by

$$f_i(t) = \frac{\sum_{n=1}^N R_n^{i,f} + \sum_{m=1}^M R_m^{i,g}}{I_{1000}^{i,f} + I_{1000}^{i,g}} \quad (5.1)$$

where f_i = total fractional release rate

$R_n^{i,f}$ = time-dependent release rate of the i th radionuclide from the n th failed spent fuel container

$R_m^{i,g}$ = time-dependent release rate of the i th radionuclide from the m th failed glass canister

$I_{1000}^{i,f}$ = total inventory of radionuclide i at 1000 years post-closure in N total spent fuel containers

$I_{1000}^{i,g}$ = total inventory of radionuclide i at 1000 years post-closure in M total DWPF glass containers.

The AREST code (Liebetrau et al. 1987) was used to calculate the time-dependent release rate for each waste package ($R_n^{i,f}$ or $R_m^{i,g}$). Later modifications to the waste package release module for hydrologically unsaturated geologic media (Reimus et al. 1988) were included. Various controlling release mechanisms were considered for radionuclides with high and low

solubilities under repository conditions to determine the relative contributions of radionuclides released from glass and spent fuel to the overall system release.

The authors emphasize that the purpose of this systems-level analysis is to predict the relative radionuclide release rates of glass and spent fuel and identify key parameters affecting the predicted the release. The results should not be construed as actual predictions of the performance of the Yucca Mountain site or the Nevada Nuclear Waste Storage Investigations EBS design. For example, it is expected that over 90% of all waste packages will remain dry at the subsurface geohydrological conditions expected within Yucca Mountain for at least 10 000 years. Therefore, no aqueous release is expected for the great majority of waste packages. This factor greatly reduces the magnitude of any calculated release from the engineered barrier system, but is not explicitly incorporated in this co-analysis of spent fuel and DWPf glass. Furthermore, the entire aspect of the far-field and its considerable role in mitigating releases is outside the scope of this report and has not been considered here.

5.1 INPUT DATA FOR PERFORMANCE ASSESSMENT ANALYSES

The AREST code requires three basic categories of information to conduct an analysis (Apted, Liebetrau, and Engel 1989):

- containment-failure times
- radionuclide data
- repository data.

The input to the AREST calculations in this analysis is discussed according to these categories.

5.1.1 Containment-Failure Times

A theoretical containment failure distribution was selected for analysis to represent a possible distribution of containment failures. For simplicity and consistency with previous analyses for spent fuel (Apted, Liebetrau, and Engel 1989), a normal (Gaussian) distribution with mean $\mu = 5000$ years and standard deviation $\sigma = 200$ years was selected.

5.1.2 Radionuclide Data

When placed in the repository, both spent reactor fuel and DWPF glass will contain 90 to 100 different radionuclides. However, site screening analysis (U.S. DOE 1986b) has identified approximately 20 key radionuclides that affect long-term performance. Table 5.1 lists the inventory per waste package container and total repository inventory for those key radionuclides present in both borosilicate glass and PWR spent fuel considered in this study. Where needed, radionuclide mass fractions were calculated from Table 5.1 by normalizing the spent fuel inventories by the mass of ^{238}U and the borosilicate glass inventories by assuming 1683 kg glass per canister.

TABLE 5.1. Inventory of Individual Nuclides for Spent PWR Fuel and Borosilicate Waste Glass. (Note: These values differ from those reported in Table 4.2 because they are reported in grams rather than in curies. Table 4.2 lists radionuclides only for the glass waste form.)

Nuclide	Waste Package		Repository ^(a)		Total
	Spent Fuel g	Glass ^(b) g	Spent Fuel g	Glass g	
^{241}Am	3.49E+02	3.74E+00	8.73E+06	5.61E+04	8.78E+06
^{243}Am	2.27E+02	3.60E-02	5.68E+06	5.40E+02	5.68E+06
^{245}Cm	3.83E-01	3.83E-01	9.58E+03	5.75E+03	1.53E+04
^{135}Cs	9.89E+02	1.02E+02	2.47E+07	1.53E+06	2.62E+07
^{59}Ni	1.28E+00	3.23E-01	3.20E+04	4.85E+03	3.68E+04
^{237}Np	2.69E+03	1.59E+01	6.73E+07	2.39E+05	6.75E+07
^{239}Pu	1.48E+04	4.18E+01	3.70E+08	6.27E+05	3.71E+08
^{240}Pu	5.86E+03	7.67E+00	1.47E+08	1.15E+05	1.47E+08
^{242}Pu	1.33E+03	6.27E-01	3.33E+07	9.41E+03	3.33E+07
^{79}Se	1.86E+01	3.70E+00	4.65E+05	5.55E+04	5.21E+05
^{126}Sn	5.46E+01	1.91E+01	1.37E+06	2.87E+05	1.65E+06
^{99}Tc	2.47E+03	1.66E+02	6.18E+07	2.49E+06	6.42E+07
^{234}U	4.08E+02	4.29E+00	1.02E+07	6.44E+04	1.03E+07
^{238}U	3.10E+06	2.44E+04	7.75E+10	3.66E+08	7.79E+10

(a) Total repository inventories calculated assuming emplacement of 25 000 spent fuel canisters and 15 000 DWPF canisters.

(b) M. J. Plodinec, private communication, 1988.

5.1.3 Repository Data

The necessary repository site data for the AREST calculations are listed in Table 4.1. The cylindrical waste form was converted to spherical coordinates by conserving the volume of the waste form as described by Liebetrau et al. 1987. Liquid-phase diffusion coefficients less than $0.1 \text{ m}^2/\text{s}$ have been measured [e.g., see Conca (1990)]. However, a diffusion coefficient of $0.1 \text{ m}^2/\text{s}$ was used, because it provides an upper-bound, worst-case scenario.

5.2 RESULTS FROM SYSTEMS-LEVEL ANALYSES

To reduce the number of variables that must be considered, the radionuclide release models implemented in AREST were reformulated to calculate relative release rates of spent fuel and DWPF glass by introducing the parameter Γ_i :

$$\Gamma_i = \frac{f_i^f}{f_i^g} \quad (5.2)$$

where f_i^f = fractional release rate of the i th radionuclide from spent fuel

f_i^g = fractional release rate of the i th radionuclide from DWPF glass.

In the following sections, we will show how this approach permits a direct determination of the relative importance of radionuclide release from DWPF glass in predicting the overall performance of the system by eliminating several variables in the transport equations. From Equations (5.1) and (5.2), it is easy to show that Γ_i is given by

$$\Gamma_i(t) = \frac{\sum_{n=1}^N R_n^{i,f}}{\sum_{m=1}^M R_m^{i,g}} \quad (5.3)$$

The release from the waste package calculated using AREST is based on either matrix dissolution rate or the diffusive-convective mass transport rate, depending on which results in the smallest predicted release rate. The following sections illustrate results first from convective, then from diffusive mass transport, and finally matrix dissolution-limited release. The special case of release of gap and grain boundary radionuclides is treated separately in Section 5.2.4.

One process that has received considerable attention in the literature is radionuclide release by colloid transport. Bates, Ebert, and Gerding (1990) have found actinide colloids in their wet-drip release experiments with several waste glasses. These results are consistent with the other considerable evidence in the literature for colloid formation in closed-system tests reacting glass with water (Oloffson et al. 1982; McVay and Buckwalter 1983; Avogadro and de Marsily 1984; Shade, Ames, and McGarrah 1984; McGrail 1986). However, the formation or potential for formation of colloids in the near-field is not at issue. What is considerably less clear is the potential for transport of any colloids that do form out of the EBS.

An often-cited example where colloid transport may have occurred in unsaturated tuff is a low-level waste site at Los Alamos National Laboratory. This site contains four shallow buried beds containing approximately 10 Ci of plutonium that was discharged between 1945 and 1952. Core samples taken from these beds in 1978 have shown that the plutonium had migrated vertically downward over 30 m (Nyan et al. 1984). The migration distance is much further than expected from calculations using a simple 1-D transport model. Travis and Nuttall (1985) were able to better model the observed concentration profile using a colloid transport code.

The problem with these studies is that there is no direct evidence that colloid migration was the cause of the more rapid transport of plutonium than expected. Indeed, equally plausible arguments could be made for an inadequate understanding of the hydrologic conditions of the site or the fact that aqueous complexation reactions were not considered that could have affected the retardation of Pu. Also, the prevailing hydrologic conditions under shallow-burial conditions of the low-level waste site have little resemblance to the expected conditions hundreds of meters below ground. Indeed, it is difficult

to see how the colloid size particles could be transported in partially saturated tuff where solute diffusion coefficients on the order of 10^{-13} to 10^{-14} m^2/s have been measured (Conca 1990). The small diffusion coefficients in unsaturated tuff are thought to be due to the discontinuous nature of thin water films on the mineral surfaces. Because of the large degree of uncertainty in the probability of colloidal transport in unsaturated tuff and the lack of a defensible colloid transport model, we have not considered radionuclide releases associated with colloids in conducting the preliminary PA analyses in this section.

5.2.1 Wet-Drip/Convective Mass Transport

If convective mass transport is assumed to be the dominant release mechanism, then the release rate can be conservatively calculated by a simple wet-drip model. The volume of water entering and exiting the waste package is assumed in this model to be saturated with respect to each waste element (Kerrisk 1985; see also Section 2.2). The release rates from the glass and spent fuel waste packages are given by

$$R^{i,f}(t) = N(t)Q(t)C^{i,f} \quad (5.4)$$

$$R^{i,g}(t) = M(t)Q(t)C^{i,g} \quad (5.5)$$

where $N(t)$ = number of failed spent fuel containers at time t

$M(t)$ = number of failed glass containers at time t

$Q(t)$ = volumetric flow rate per package (= pore velocity $\cdot$ cross sectional area)

$C^{i,f}$ = saturation concentration of nuclide i with respect to spent fuel

$C^{i,g}$ = saturation concentration of nuclide i with respect to DWPF glass.

It is implicit in Equations (5.4) and (5.5) that the volumetric flow rates are equivalent between the spent fuel and DWPF glass waste packages. Some variation between packages may be expected because of different heat generation rates, spatial variations in host rock hydrologic properties, etc.

For the special case of $C^{i,g} = C^{i,f}$, $r_i = N(t)/M(t)$, which is simply the ratio of the number of spent fuel and DWPF glass containers that have failed at any given time. Assuming that the distributions of failures for both spent fuel and DWPF glass containers follow the same normal distribution with $\mu = 5000$ years and $\sigma = 200$ years, probability curves for the variability of r_i can be calculated as shown in Figure 5.1. At long times, after all the spent fuel and DWPF glass containers have failed, the probability curves converge to a steady-state value for r_i of 1.7 (25 000 spent fuel containers/15 000 DWPF containers). At early times, r_i can become zero if some glass containers but no spent fuel containers have failed. Conversely, if no glass containers have failed, $r_i \rightarrow \infty$. However, the value of r_i is of no practical interest when only a few containers have failed, because repository release rates will not be high enough to approach regulatory limits. In general, the value of r_i is

FIGURE 5.1. Level Curves of Probability for the Variability of Relative Release Rate Ratio (r_i) as a Function of Time. Container failures were assumed to follow a normal distribution with a mean of 5000 years and standard deviation of 200 years.

not highly dependent on the shape of the container failure distribution if the failure distributions for spent fuel and DWPF glass waste packages are similar.

For the long-term release from DWPF glass to contribute more significantly to overall release from the repository, the solubility of a radionuclide released into the groundwater immediately surrounding the glass waste packages must exceed the solubility of that released into the groundwater surrounding the spent fuel waste packages by at least a factor of 2. This seems unlikely from both geochemical modeling studies (Bruton 1988) and laboratory experiments with spent fuel (Oversby and Wilson 1985) and borosilicate glass (Bates, Lam, and Steindler 1983). Results from these studies show comparable if not lower concentrations of most radionuclides released from the DWPF glass relative to spent fuel.

Furthermore, depending on the magnitude of the groundwater flow rate predicted in the repository and the solubility of the individual radionuclide, it may be possible to ignore the radionuclide release contribution from DWPF glass. For example, if release rates from spent fuel are much less than one part in 10^5 as calculated using Equation (5.4), then accounting for the additional contribution from the glass is insignificant in terms of demonstrating compliance with the NRC regulatory requirements, assuming that the solubilities are not significantly higher for a DWPF glass waste package. However if release rates are predicted near one part in 10^5 , then the contribution from the DWPF glass waste packages may need to be taken into account.

5.2.2 Moist-Continuous/Diffusive Mass Transport

The simple convective mass transport model used above results in non-conservative release rate predictions at very low flow rates if a connective pathway exists between the waste container and the host rock where diffusive mass transport can occur. Under such a moist-continuous release scenario (see Sections 2.3 and 4.1) diffusive mass transport release rates for radionuclides from the spent fuel and glass are calculated in AREST as follows [Chambré et al. 1985; also see Equation (4.1)]:

$$R^{i,f}(t) = 4\pi\epsilon D r_1 C^{i,f} \psi^i(t) N(t) r_0^f \quad (5.6)$$

$$R^{i,g}(t) = 4\pi\epsilon D r_1 C^{i,g} \psi^i(t) M(t) r_0^g \quad (5.7)$$

where $N(t)$ = number of failed spent fuel containers at time t

$M(t)$ = number of failed glass containers at time t .

ϵ = porosity of the host rock normalized by degree of hydrologic saturation

D = diffusion coefficient

r_0^f = radius of the spent fuel

r_0^g = radius of the glass container

r_1 = radius of the waste package

$\psi^i(t)$ = nuclide specific mass transport function

$C^{i,f}$ = saturation concentration of nuclide i with respect to spent fuel

$C^{i,g}$ = saturation concentration of nuclide i with respect to DWPF glass.

If the radionuclide solubilities based on release from spent fuel and DWPF glass waste packages are assumed to be equivalent, and the radii of the two containers are not significantly different, and retardation coefficients and rock porosity are similar between packages, then $r_1 = N(t)/M(t)$, which is identical to the ratio found for the convective mass transport analysis. Even under conditions controlled by diffusive mass transport, release from spent fuel is predicted to exceed release from the borosilicate glass by approximately a factor of 2, and similar arguments can be made about the need to consider release from the glass based on the magnitude of the predicted release rates.

5.2.3 Matrix Dissolution Controlled Release

Under expected sub-surface geohydrologic conditions at the Yucca Mountain site, the release of most radionuclides will be limited by solubility constraints, and the analysis of either Section 5.2.1 or 5.2.2 applies. However, there are several important fission product species, ^{79}Se , ^{129}I , ^{99}Tc , ^{135}Cs , for example, with solubility limits so high that matrix dissolution

control their release rates. If release of these nuclides from DWPF glass and spent fuel is assumed to be congruent, then the release rates are given by:

$$R^{i,f}(t) = z^{i,f}(t) A^f \sum_{n=1}^{N(t)} R_n^f \quad (5.8)$$

$$R^{i,g}(t) = z^{i,g}(t) A^g \sum_{m=1}^{M(t)} R_m^g \quad (5.9)$$

where $z^{i,f}$ = mass fraction of soluble nuclide i in the spent fuel waste form

$z^{i,g}$ = mass fraction of soluble nuclide i in the glass waste form

A^f = surface area of the spent fuel waste form

A^g = surface area of the glass waste form

R_n^f = dissolution rate of spent fuel in the n th waste package

R_m^g = dissolution rate of the DWPF glass in the m th waste package.

Dividing Equation (5.8) by Equation (5.9) gives:

$$\Gamma_i(t) = \frac{z^{i,f}(t) A^f \sum_{n=1}^N R_n^f}{z^{i,g}(t) A^g \sum_{m=1}^M R_m^g} \quad (5.10)$$

Because calculating the time-dependent matrix dissolution rate of both spent fuel and DWPF glass under repository conditions is a very complex task, Γ_i has been evaluated for a range of fuel to glass dissolution rate ratios as illustrated in Figure 5.2 for ^{79}Se , ^{99}Tc , and ^{135}Cs . From the values given in Figure 3.1, an average dissolution rate for the glass is estimated to be $0.01 \text{ g}/(\text{m}^2 \cdot \text{d})$.

FIGURE 5.2. Relative Release Rate Ratio (Γ) as a Function of the Ratio of Glass and Spent Fuel Matrix Dissolution Rate. The glass and spent fuel surface area were assumed to be equal.

Matrix dissolution rates for spent fuel were derived from a range of reported values from laboratory tests. Assuming a maximum dissolution rate of $0.027 \text{ g}/(\text{m}^2 \cdot \text{d})$ (Reimus et al. 1988), and minimum of $0.00014 \text{ g}/(\text{m}^2 \cdot \text{d})$ (Wilson and Gray, personal communication) gives R^f/R^g ratios ranging from 5 to 0.02. For R^f/R^g ratio exceeding approximately 0.5, spent fuel dissolution will dominate the release contribution from the EBS. However, for R^f/R^g ratio less than ≈ 0.005 , dissolution of the glass will dominate EBS release for these soluble radionuclides. Based on the data plotted in Figure 5.2, and the uncertainty in the R^f/R^g values, it is clear that release from DWPF glass may contribute a significant fraction of the overall release of the soluble fission product radionuclides from a repository. Still, the predicted release rate based on a R^g of $0.01 \text{ g}/(\text{m}^2 \cdot \text{d})$ for DWPF glass shows a release rate of less than one part in 10^5 for these same radionuclides. As the repository

temperature decreases with time, the glass reaction rate would also be expected to decrease, resulting in an even smaller predicted fractional release rate.

The above analysis is applicable after long time periods where matrix dissolution rates of both spent fuel and borosilicate glass control the release rates of the soluble fission product radionuclides. At earlier times, it is necessary to account for the rapid release of these same nuclides from the gap and grain boundaries of the spent fuel. Figure 5.3 shows the results from AREST calculations of the fractional release rate of ^{99}Tc from spent fuel assuming a normal distribution of container failures centered at 5000 years post-closure. The scatter in the predicted release rate is due to peculiarities of the numerical algorithm used to sum the instantaneous release from each waste package in discrete time steps (Apted, Liebetrau, and Engel 1989). For the purposes of this analysis, we have approximated the complex

FIGURE 5.3. Predicted Fractional Release Rate of ^{99}Tc from Spent Fuel. (This calculation assumes a normal distribution of container failures centered at 5000 years and standard deviation of 2000 years.)

distribution shown in Figure 5.3 by a simple step function (solid line, Figure 5.3). Figure 5.4 shows the predicted variation in r values as a function of time and R^f/R^g ratio for two values of spent fuel dissolution rate, 10 and 10^{-2} g/(m²·yr), and also using the step function shown in Figure 5.3 to describe the container failure distribution. Figure 5.4 illustrates that at early times, depending on the spent fuel and glass dissolution rates, the rapid release of fission product radionuclides from the spent fuel gap and grain boundaries can dominate their release from the repository system (relative to the glass) by several orders of magnitude. If the distribution of container failures could be confidently predicted to be even broader than the distributions used here, then over the time period of regulatory concern, the release contribution from DWPF glass would be negligible relative to the release contribution from spent fuel.

5.2.4 Vapor Phase Hydration and Gap Inventory Release

Apart from those radionuclides incorporated in the UO₂ matrix of spent fuel, approximately 2% of the inventory of volatile (at in-reactor fuel temperatures) fission-product nuclides is distributed between the fuel/cladding gap and UO₂ grain boundaries. The release of these fission products from the gap and grain boundaries is expected to occur very rapidly if liquid water contacts the spent fuel in the waste package. For those waste packages that fail early and expose a DWPF glass to high-temperature water vapor, an analogous rapid release of radionuclides could occur from the porous alteration layer that develops from vapor-phase hydration (Bates et al. 1988). Assuming that $\sigma_f N$ spent fuel containers and $\sigma_g M$ DWPF glass containers have failed at the time (t_s) upon contact with liquid water, where σ_f and σ_g are the fraction of spent-fuel and glass waste packages, respectively, that fail prior to resaturation, we can write:

$$r_i(t_s) = \frac{I^{i,f} \sigma_f N \theta^{i,f}}{I^{i,g} \sum_{m=1}^{\sigma_g M} \theta_m^{i,g}} \quad (5.11)$$

a) Spent Fuel Dissolution Rate of $0.027 \text{ g}/(\text{m}^2 \cdot \text{d})$

b) Spent Fuel Dissolution Rate of $2.7 \times 10^{-5} \text{ g}/(\text{m}^2 \cdot \text{d})$

FIGURE 5.4. Variation in Relative Release Rate Ratio (r_i) as a Function of Time and Fuel to-Glass Matrix Dissolution Rate Ratio

where $I^{i,f}$ and $I^{i,g}$ = inventory of radionuclide i per spent fuel and glass waste package (Table 5.1), respectively

$\theta^{i,f}$ and $\theta^{i,g}$ = fraction of available inventory per spent fuel and glass waste package, respectively, that can be rapidly released.

Although $\theta^{i,g}$ will be a complex function of temperature and time, it will be assumed for simplicity here that $\theta^{i,g}$ is equivalent for each glass waste package as was assumed for the spent fuel waste packages. Equation (5.11) then reduces to:

$$\Gamma_i(t_g) = \frac{I^{i,f} \sigma_f N \theta^{i,f}}{I^{i,g} \sigma_g M \theta^{i,g}} \quad (5.14)$$

Equation (5.14) can be further simplified by assuming that $\sigma_f = \sigma_g$. The numerator of Equation (5.14) can be determined by conservatively assuming that $\theta^{i,f} = 0.02$, or that 2% of the entire fission product inventory of the spent fuel resides in the gap and grain boundaries and is subject to rapid release (Baker et al. 1987; Barner 1985). Figure 5.5 is a plot of Γ_i calculated from Equation (5.14) as a function of a range of $\theta^{i,g}$ values. Figure 5.5 shows that Γ_i values do not approach 1 (i.e., release rate of spent fuel and glass equal) unless 50 to 100% of the glass in those waste packages that fail early has been vapor phase altered. Evidence from natural analogues for the slow rate of vapor phase hydration (Ewing and Haaker 1979) indicates that such extensive alteration is unlikely. However, additional work is needed with complex waste glasses to demonstrate similarly small vapor phase alteration rates under repository conditions. Vapor-phase hydration of DWPF glass could then be ignored as an important release mechanism for predicting the systems-level performance of the repository.

FIGURE 5.5. Relative Release Rate Ratio (Γ_r) as a Function of the Fraction Vapor Phase Altered Borosilicate Glass. (The plot was constructed assuming 2% of the total fission product inventory in the spent fuel is available for rapid release.)

6.0 PERFORMANCE ASSESSMENT AND THE WASTE ACCEPTANCE PRELIMINARY SPECIFICATIONS

The Defense Waste Processing Facility (DWPF) at the Savannah River site near Aiken, South Carolina, is scheduled to begin producing high-level radioactive waste glass in 1992. Before this vitrified waste is produced, it is desirable to have some assurance that the material will perform adequately in the geohydrological conditions of interest. To achieve this assurance in part, the DOE established the Waste Acceptance Process in July 1985. A key component of this process is the requirement that the waste form producers demonstrate compliance with Waste Acceptance Specifications. At the present time, Waste Acceptance Preliminary Specifications (WAPS) have been proposed (U.S. DOE 1986a).

The WAPS impose a number of criteria on the canistered waste, including heat and radiation loading, combustibility, etc. However, one of the key specifications requires that the waste-form producer demonstrates

"... that the radionuclide release properties of the waste form can be controlled during production. The producer shall relate the method of control to the repository-site-specific tests or perform the repository-site-specific tests."

Few assessment analyses had been performed at the time that a radionuclide release rate criterion for defense high-level waste glass was promulgated for the WAPS (DOE 1986a), making it difficult to define "acceptability." The specification imposed on the waste form is that the normalized releases of B, Na, U, and other selected elements do not exceed $1 \text{ g}/(\text{m}^2 \cdot \text{d})$ averaged over 28 days in an MCC-1 leach test^(a) (Oversby 1984). At the present time, no documented approach exists as to how the results from this test will or can be used in assessing the long-term performance of a waste package containing DWPF glass. In addition, it is not clear whether a glass meeting this specification will indeed perform acceptably in a potential repository. Consequently,

(a) The MCC-1 Test is a standard dissolution test developed by the Materials Characterization Center (MCC) (Strachan, Turcotte, and Barnes 1982).

the DOE/OCRWM staff requested that the PASS program staff assess the impacts of the performance assessment analyses performed here relative to the WAPS.

The impact from two (Sections 3 and 5) of the three levels of performance-assessment analyses are discussed here.

6.1 IMPACT OF THE GLASS WASTE FORM PERFORMANCE ANALYSIS

There are clear indications that dissolution data from the present waste acceptance test are not relevant to predicting the long-term release rate of a glass waste form. There are many glass compositions that will yield a value of about $28 \text{ g} \cdot \text{m}^{-2}$ or less in a 28-day MCC-1 test, but have long-term dissolution rates that are quite divergent. Two studies can be used to demonstrate the difference between short-term and long-term dissolution rates: van Iseghem and Grambow (1988) (see Figures 3.5a and 3.5b) and Chick et al. (1984).

In the van Iseghem and Grambow study, SM58 and SAN60 glass compositions yielded 28-day MCC-1 dissolution rates that were less than $1 \text{ g}/(\text{m}^2 \cdot \text{d})$, but have much different long-term rates. In fact, the 28-day dissolution rate for SAN60 is much lower than the rate for SM58, but the long-term rate for SAN60 is much higher than the long-term rate for SM58. The preliminary modeling calculations performed here (Section 3.0) indicate that the same effect may be observed in the SRL-202 glass series.

In a study performed by Chick et al. (1984) for the development of a nuclear waste glass for West Valley Nuclear Services, 108 glass compositions were studied. One of the tests used in this study was the MCC-1 test at 90°C for 28 days and another test was the MCC-3 test for 7 days. Due to the higher surface area of the sample used in the MCC-3 test, the test can be used as an indicator of longer-term behavior relative to the MCC-1 test. Unfortunately, the B concentration was measured in the MCC-1 test, but not in the MCC-3 test. So, for an approximate comparison, the silicon-release data can be used from both tests. In Table 6.1, several of the glasses that meet the specification of $1 \text{ g}/(\text{m}^2 \cdot \text{d})$ or $28 \text{ g}/\text{m}^2$ in 28 days are listed. The data show that the ranking of glasses based on the 28-d test is not the same as the ranking based

TABLE 6.1. Comparison of Glass Performance Under Two Test Conditions [The data were taken from Chick et al. (1984) and are for the MCC-1 test and the MCC-3 test. Values are normalized elemental mass loss (g/m^2)^(a).]

Glass or Melt No.	Boron MCC-1, 28d, 90°C	Silicon MCC-1, 28d, 90°C	Silicon MCC-3, 7d, 90°C
4-44	11.3	9.5	0.41
7-34	16.7	13.2	3.10
8-62	13.8	13.9	0.44
14-67	18.4	16.6	0.69
16-58	17.2	18.7	0.17
41-63	9.7	9.0	0.35
51-66	9.5	6.7	0.46
75-26	5.8	8.4	0.97
101-80	11.1	8.7	0.16
22-27	223.3	56.0	0.81
82-24	2704.0	271.3	7.31

(a) To obtain the value that corresponds to the specification, divide the MCC-1 values by 28 d to get a rate in $\text{g}/(\text{m}^2 \cdot \text{d})$.

on the MCC-3 test. Included in Table 6.1 are two glasses that have dissolution rates 10 and 100 times the specification based on the 28-day MCC-1 test, but compare favorably with the other glasses when judged on the MCC-3 data.

The results from these studies suggest that the proposed WAPS test for glass dissolution needs to be replaced with a test that is more relevant for long-term performance assessment. However, it is clear from the available data that even data from this new test should be only one indication of whether the glass being tested is a "good" glass or not. Many more tests with glasses that contain nonradioactive elements and glasses that contain radioactive isotopes are needed to support a claim that a glass composition or a limited range of glass compositions will meet a long-term dissolution rate criterion. Once a "safe" composition range is determined using a combination of dissolution tests and modeling calculations, then one can use a single test

and test criterion as an indicator that the glass performance will be acceptable in geohydrological conditions of interest. This single test must also be combined with tight control on the composition of the waste form as is already planned for the DWPF (SRL 1988).

In Section 4.0, it was not presupposed that the one-part-in- 10^5 criterion will be imposed on each DWPF glass waste package. However, comparing the one-part-in- 10^5 criterion with predictions for the release rate from each glass waste package is not necessarily unreasonable. To demonstrate that a glass waste form alone may meet this criterion, a line representing the one-part-in- 10^5 is added to Figure 3.1 (Figure 6.1). In Figure 6.1, it can be seen that even on the laboratory time-scale, glass compositions exist that dissolve at approximately the rate required by the one-part-in- 10^5 criterion.

FIGURE 6.1. A Plot of Glass Dissolution for PNL 76-68, SRL-165, and EMS-11 Glasses Showing the Relationship Between Glass Performance and the One-Part-in- 10^5 Criterion

Thus, it is possible to take credit for the durability of the glass, using the redundancy of the remainder of the waste package to demonstrate a viable system.

6.2 IMPACT OF THE SYSTEMS-LEVEL PERFORMANCE ANALYSIS

From a systems-level point of view, the WAPS for radionuclide release gives unsatisfactory results in terms of demonstrating compliance with the 10 CFR 60 requirements. If the only dissolution data available on the actual glass being produced at the DWPF are those required by the WAPS, a fractional release per year (Figure 6.2) can then be calculated for the soluble radionuclides contained within the glass matrix.

Figure 6.2 shows the results from AREST calculations of fractional release rates for ^{79}Se , ^{99}Tc , and ^{135}Cs over a wide range of matrix dissolution rates for borosilicate glass. At the waste acceptance specification of

FIGURE 6.2. Predicted Fractional Release Rates for Fission Product Radionuclides as a Function of Glass Matrix Dissolution Rate. The WAPS specification is shown as $0.976 \text{ g}/(\text{m}^2 \cdot \text{d})$ [$356 \text{ g}/(\text{m}^2 \cdot \text{yr})$] and K_f as $0.0055 \text{ g}/(\text{m}^2 \cdot \text{d})$ [$2 \text{ g}/(\text{m}^2 \cdot \text{yr})$].

1 g/(m²·d), fractional release rates for each of these radionuclides exceed the one-part-in-10⁵ criterion. This result is not surprising because a 1 g/(m²·d) matrix dissolution rate is very near the forward rate of reaction of a typical nuclear waste glass at 90°C. However, under repository conditions, a considerably slower reaction rate is expected, as was calculated in Equation (5.12) using simple mass balance considerations. This simple model gives a long-term reaction rate of only 0.006 g/(m²·d), or 2 g/(m²·yr). As shown in Figure 6.2, this results in a predicted fractional release rate of less than one part in 10⁵.

6.3 SUMMARY

A number of glasses have been shown to meet the WAPS specification of 1 g/(m²·d) in a 28-day MCC-1 test. However, the long-term dissolution behavior of these glasses cannot be predicted by the results from the MCC-1 test. Thus, the specification cannot be connected to the long-term performance of glasses under geohydrological conditions of interest. A new specification and dissolution test with a relationship to long-term behavior are needed.

The 1 g/(m²·d) dissolution rate criterion in the WAPS is only applicable to those radionuclides with very high solubility because release of solubility-limited radionuclides will be controlled by diffusive-convective mass transport. However, even for these few radionuclides, the WAPS specification provides no direct assurance of adequate performance because releases in excess of one part in 10⁵ are predicted for glasses meeting the WAPS dissolution rate specification. This does not mean that borosilicate glass will be inadequate as waste form, but that a technically defensible criterion and associated test method need to be developed. Instead of an arbitrary dissolution rate specification, the acceptance criterion must be based on waste form properties such as dissolution rate that have demonstrable impact on repository performance.

7.0 CONCLUSIONS

Three levels of analyses were used to perform a preliminary performance assessment of the DWPF glass at geohydrologic conditions that might be expected at the Yucca Mountain site: 1) an initial systems-level performance assessment 2) a preliminary performance assessment of individual waste packages containing DWPF glass, and 3) an initial prediction of the final dissolution rate for DWPF glass. Separate conclusions are presented below for each level of analysis.

7.1 SYSTEM-LEVEL ANALYSIS

A systems-level performance assessment analysis was conducted considering release from both spent fuel and borosilicate glass waste forms. For those radionuclides with relatively low solubilities under repository conditions, release from the spent fuel packages was found to exceed release from the glass waste packages by a factor of 2 as calculated by both convective-controlled and diffusion-controlled mass transport models.

For those radionuclides with very high solubilities under repository conditions, matrix dissolution rates control the overall release rate at long-times. Given the present uncertainty of our knowledge of long-term dissolution rates for spent fuel and glass, the results from the latter analyses were inconclusive as to whether release from spent fuel or DWPF glass would dominate. However, at short-times, release of radionuclides in the gap and grain boundaries from the spent fuel dominates the system by several orders of magnitude. Clearly, the long-term dissolution rates of both spent fuel and DWPF glass waste forms under repository conditions must be much better understood and predicted. In contrast, the systems-level analysis showed that rapid release of radionuclides from a glass altered by vapor phase hydration is unimportant compared with the analogous rapid release of radionuclides from the gap and grain boundaries from spent fuel.

The systems-level analysis also showed that the $1 \text{ g}/(\text{m}^2\cdot\text{d})$ dissolution rate criterion in the WAPS is only applicable to those radionuclides with very high solubilities. Release of solubility-limited radionuclides will be controlled by diffusive-convective mass transport. However, even for the few

radionuclides with high solubilities, the WAPS specification provides no direct assurance of adequate performance because releases in excess of one part in 10^5 per year are predicted for glasses meeting the WAPS dissolution rate specification and continuing to dissolve at that rate for the long-term. This does not mean that borosilicate glass will be inadequate as a waste form but does mean that a technically defensible criterion and associated test method need to be developed. Instead of an arbitrary dissolution rate specification, the acceptance criterion must be based on waste form properties such as long-term dissolution rate that have demonstrable impact on repository performance.

7.2 WASTE PACKAGE ANALYSIS

Calculations are presented for radionuclide-release from a single waste package containing DWPF glass, assuming a moist-continuous release scenario. One of two boundary conditions for the concentration of radionuclides at the waste glass surface is used in the diffusive mass transport models: 1) individual solubility limits for relatively insoluble radionuclides, or 2) congruent alteration rate of the glass for highly soluble radionuclides. Data on waste package design and host rock properties are taken from recent reports (U.S. DOE 1986 and 1988). Calculated solubilities (Bruton 1988) for radionuclides and an assumed long-term dissolution rate of 1.6×10^{-2} g/(m²·d) are used to constrain release rate.

Based on these data and assumed dissolution rate, the radionuclides examined in this study are all calculated to comply with NRC fractional release rate limits for a single waste package, and by extension, for the engineered barrier system. This is true even if containment failure of all waste packages occurs 1000 yr after repository closure and packages are contacted by water, assuming diffusion coefficients equal the conservatively high value for diffusion in water (1×10^{-9} m²/s). More realistic values for these diffusion parameters reduce the release rate of nuclides from the engineered barrier system. The major factors affecting the magnitude (and degree of compliance) of predicted releases are the long-term dissolution rate of the DWPF glass, radionuclide solubility, transport rate, and, paradoxically, the radionuclide

inventories. These calculated results are sensitively related to several assumptions and uncertainties regarding these factors.

Radionuclide solubilities are taken from thermodynamic calculations that simulate the radionuclide-bearing borosilicate glass reacting with a reference water composition (Bruton 1988). There are serious potential uncertainties and limitations to such calculated data, however, as noted by Bruton (1988). An approach for solubility-limited release based on thermodynamically calculated solubilities is inadequate, by itself, for a number of reasons. First, key solid phases containing radionuclides may be missing from the thermodynamic data base. Second, the low abundance of nuclides within DWPF glass will result in their solubility control by alteration phases in which they are trace, rather than major, components. Hence, solid-solution descriptions of co-precipitation may be needed for a rigorous, theoretical calculation. Third, temperature effects on the thermodynamic properties of many radioelement-bearing solids and aqueous species are lacking.

Laboratory studies of glass interaction with water must be conducted to support and, in some cases, supersede thermodynamic calculations of solubility. Such tests should be performed under conditions to promote and evaluate the formation of solubility-limiting alteration phases of DWPF glass. That is, tests designed to show the fate of radionuclides rather than tests designed to show only the fate (i.e., dissolution rate) of the glass. In many cases, it probably will not be possible to determine directly what alteration phase is controlling the concentration for a given trace radionuclide. However, it is possible through laboratory experiments and geochemical modeling simulations to bracket the solubility values and provide more realistic solubility values for release rate calculations.

A definitive study of diffusion under partially saturated conditions for intact and crushed rock is needed. Initial laboratory tests conducted at the PNL through the PASS Program show diffusion coefficients that are possibly four orders of magnitude lower than values previously used in release rate calculations. Because release rates may scale directly with the magnitude of the diffusion coefficient for the moist-continuous case, reduction in the

uncertainty for the diffusion coefficient represents the single most important and undetermined factor that may lead to greatly reduced release rates for all radionuclides.

The release of highly soluble, low-sorptive radionuclides from waste packages containing DWPF glass will be controlled by the long-term dissolution rate of the glass and subsequent transport into the host rock. The performance assessment model for release must, therefore, combine a reaction-rate boundary condition with mass transport constraints (Pigford and Chambré 1988). Glass dissolution models based solely on empirical correlations of data, even massive amounts of data, will probably provide an inadequate basis for the long-term prediction of radionuclide release from waste packages containing DWPF glass. This approach may not be technically defensible. It provides no insight into the reaction mechanisms that control the dissolved concentrations or any basis for comparison to natural analogues. Therefore, it is vital for the dissolution rate model to be scientifically based on thermodynamics, kinetics, and a detailed, laboratory-based understanding of the chemical alteration of the DWPF glass over time.

Finally, an expanded set of radionuclides must be examined to fully establish the release performance of waste packages containing DWPF glass. The actual magnitude of allowable release rates for many radionuclides depends on the total 1000-year radionuclide inventory as well as their individual 1000-year radionuclide inventories. The producers of DWPF glass and other reprocessed waste forms will need to make better estimates of these values (or range of values) for these data.

7.3 GLASS WASTE FORM ANALYSIS

The existence of several glass dissolution models has been acknowledged, but only one of those models can be used to calculate the evolution of the solution concentrations resulting from the glass/water interaction with a simple set of variables. The dissolution/precipitation model is based on a thermodynamic and physical understanding of the dissolution process and has been tested for a variety of relevant geohydrologic conditions. Two other models with the same parentage have also been developed or are under

development. These glass dissolution models may be used with high surface-to-volume ratio or vapor phase attack experiments, but were not specifically developed to handle these situations.

Dissolution data on the latest set of glass compositions from the Savannah River Site are not publicly available and were unavailable at the time this report was written. However, the modeling studies performed here indicate that the high Al-content glass may dissolve significantly faster than the glass formulations which include either the high-Fe waste or the average waste composition. The relatively high dissolution rate forecasted for the high-Al content glass results from the formation of the mineral analcime, which causes a decrease in the concentration of dissolved H_4SiO_4 and a concomitant increase in the glass dissolution rate. Because of the current paucity of dissolution data, these conclusions must be verified through experimentation.

If these experiments also indicate a high dissolution rate for the glass containing high-Al waste, then modeling calculations and waste glass dissolution experiments need to be carried out to determine how much Al can be tolerated in the glass or how the composition can be varied to avoid high dissolution rates.

There is no connection between the long-term performance of the DWPF glass and the results from the MCC-1 test specified in the WAPS. Basically, many glasses may meet the WAPS criterion of $1 \text{ g}/(\text{m}^2 \cdot \text{d})$ but behave quite differently in the long-term. Consequently, the results from the WAPS provide no direct assurance that the actual glasses being produced at the DWPF will perform adequately in a repository relative to the regulatory guidelines.^(a) It is suggested that a test be developed that meets both the needs of the producer (product consistency) and the repository (long-term performance). An optimum test could be developed with an extensive data base and mechanistic understanding of glass dissolution. This test would be of short duration such that it could be run during DWPF operation, and would be sufficiently accelerated that, with the underlying data base and modeling results, it could be

(a) However, the intent of the WAPS was not to provide information or assurance of the long-term performance of the glass.

used as a reliable indicator of the long-term performance in the geohydrological conditions expected in an unsaturated repository.

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APPENDIX A

NRC RELEASE REQUIREMENTS FOR THE ENGINEERED BARRIER SYSTEM

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Spent fuel performance can be assessed with respect to specific federal regulations regarding acceptable releases of radionuclides from a mined geological disposal system. These requirements, or performance objectives, include those by the Nuclear Regulatory Commission (NRC) and the Environmental Protection Agency (EPA). The performance objectives established by these two agencies are applicable to the final safety assessment of spent fuel as a waste form and the licensing of a nuclear waste repository, as discussed in the next section. It is prudent, therefore, to consider the adequacy of spent fuel over the broadest possible set of safety and performance objectives in order to establish its adequacy as a waste form. The NRC and EPA objectives for nuclide release addressed in this evaluation are summarized in the following sections and are portrayed schematically in Figure A.1. Figure A.1 also includes the waste package boundary as designated by the U.S. Department of Energy's (DOE) Generic Requirements Document (GRD), which interprets the NRC and EPA requirements in its definitions of the mined geologic disposal system, its subsystems, and components. The GRD requirements are internal, baselined DOE requirements, and do not constitute a federal regulation. However, since the GRD governs DOE work, its requirements were also addressed in this assessment of spent fuel performance.

A.1 U.S. NUCLEAR REGULATORY COMMISSION 10 CFR PART 60 RELEASE RATE CRITERION

The NRC has established allowable fractional release rates for nuclides from the engineered barrier system (EBS) in the period following the 300 to 1000 years during which substantially complete containment is required (10 CFR 60, 1983). Section 60.113(a)(1)(ii)(B) of 10 CFR 60 states that:

"[T]he engineered barrier system shall be designed so that, assuming anticipated processes and events, . . . (B) The release rate of any radionuclide from the engineered barrier system following the containment period shall not exceed one part in 100,000 per

FIGURE A.1. Calculated Allowable Fractional Release Rates for Radionuclides in Defense High-Level Waste Glass (data from Plodinec 1988). Note extremely high 1000-year curie inventories for ^{230}Th , ^{226}Ra and ^{210}Pb may be artifact of designing all measured Th in curries defense waste to ^{230}Th rather than a mixture of Th isotopes.

year of the inventory of that radionuclide calculated to be present at 1000 years following permanent closure, or such other fraction of the inventory as may be approved or specified by the Commission; provided, that this requirement does not apply to any radionuclide which is released at a rate less than 0.1% of the calculated total release rate limit. The calculated total release rate limit shall be taken to be one part in 100 000 per year of the inventory of radioactive waste, originally emplaced in the underground facility, that remains after 1000 years of radioactive decay."

There are several important considerations in this NRC performance objective. First, the NRC release rate limit is established for "anticipated processes and events," which in turn has been defined (10 CFR 60, 1983) as meaning those natural processes and events that are reasonably likely to occur during the period in which the intended performance objective must be achieved. It may be assumed that those processes operating in the repository

host rock prior to waste emplacement will continue, provided appropriate allowance is made for the perturbations caused by the mining of the repository and the emplacement of the waste.

Second, the NRC release rate limit is imposed at the EBS boundary, not at the waste form surface. The EBS is defined (10 CFR 60, 1983) as the waste packages and the underground facility, including openings and backfilled tunnels (see Figure A.1). This necessarily means that the assessment of DWPF glass performance relative to the fractional release rate objective depends on DWPF glass characteristics, as well as the characteristics of spent fuel and the properties of any additional barriers that may be present in the EBS. Because site characterization and final EBS designs are not complete, the assessment of waste forms can only be made on a conditional basis at this time.

Third, 10 CFR 60 requires that the release rate objective must be met with "reasonable assurance." Although this term has not been explicitly defined, the NRC has indicated (50 FR 22288-22301) that the level of confidence associated with its concept of "reasonable assurance" is the same as that sought by the EPA term "reasonable expectation" (40 CFR 191, 1985). The EPA advocates reliance on a probabilistic approach in which the consequence of an event (e.g. a measurable fractional or cumulative release) is assessed relative to the probability of occurrence of that event (40 CFR 191, 1985). This approach recognizes and incorporates the qualitative judgments regarding the inherent uncertainty and variation in physical and chemical parameters upon which a quantitative performance assessment must be based. Demonstration of "reasonable assurance" will be based on two principles (51 FR 22288-22301): 1) that performance assessment analysis indicates a high (although unquantified) likelihood of meeting EPA and NRC release requirements, and 2) that the performance assessment is sufficiently conservative that actual performance will be within predicted limits.

Fourth, the allowable NRC fractional release rate for individual nuclides depends on the calculated inventory of that nuclide at 1000 years after permanent closure of the repository (Bensky and Oliver 1986). For nuclides with 1000-year inventories, $I(1000)_i$, greater than 0.1% of the total

1000-year inventory, $I(1000)_T$, the allowable annual fractional release rate is one part in 100 000 (i.e. 10^{-5}) of $I(1000)_i$. For nuclides with $I(1000)_i$ less than 0.1% (10^{-3}) but greater than 10^{-8} of $I(1000)_T$, the allowable fractional release rate is equal to the ratio of $I(1000)_T/I(1000)_i$, multiplied by 10^{-8} . Finally, nuclides with $I(1000)_i$ below 10^{-8} of $I(1000)_T$ can be exempted from the performance assessment analysis entirely.^(a) This dependence of allowable release rate on inventory for defense waste glass is shown in Figure A.1.

Lastly, compliance with the NRC performance objective for the specific nuclide release rates, "or such other fraction of the inventory as may be approved or specified by the Commission . . .," must be demonstrated for final licensing of a nuclear waste repository. It is apparent that, although the basis and formulation of the NRC release rate limit have been criticized (10 CFR 40, 1983), the NRC has expressly retained flexibility in applying and accepting alternate measures of safety assessment.

A.2 REFERENCES

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- (a) The lower inventory cutoff may not be appropriate for release occurring before 1000 years. For example, short-lived nuclides such as ^{137}Cs and ^{90}Sr fall below the inventory cutoff at 1000 years but represent significant fractions of the total curie content of high-level waste for many hundred years after repository closure. When evaluating release prior to 1000 years it is not clear that such nuclides can or should be dismissed under the NRC regulations on the basis of their 1000-year inventory.

APPENDIX B

A GUIDE TO THE UNDERSTANDING OF REACTION PROGRESS PLOTS

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A GUIDE TO THE UNDERSTANDING OF REACTION PROGRESS PLOTS

In Figures B.1 and B.2, reaction progress is measured as grams of glass dissolved in a cubic meter of water. This means, for instance, that x grams of glass has reacted with 1 m^3 of water. On the ordinate is plotted the normalized concentration in g/m^3 . The concentration of any element has been normalized to the fraction of that element in the glass. Thus, if x grams of glass dissolves in water and all of the glass constituents go into solution, then the normalized concentration will equal the reaction progress. This would result in a line of unit slope (Figure B.1) or congruent dissolution.

FIGURE B.1. A Plot Illustrating the Concept of Congruent Dissolution of a Glass

FIGURE B.2. A Plot Illustrating the Concept of Congruent Dissolution of a Glass with Precipitation of a Mineral Phase

As glass dissolves in water, however, some elements or combination of elements are likely to exceed solubility of a solid phase, such as $\text{Fe}(\text{OH})_3$. Since the new concentration will be lower than the concentration would be if all of the element went into solution, the line associated with the solubility of the precipitating phase will be lower than the congruent dissolution line (Figure B.2). Since the bulk solution concentration changes as a function of reaction progress (i.e., other glass constituents are going into solution and the pH of the solution is changing), the calculated solution concentration for the precipitated element will vary according to the solubility relation and the changing bulk solution concentrations. As the solubility limits of other solids are exceeded, these solids will precipitate and control the solution concentrations of the constituent elements to varying degrees in accordance

with the mass balances in the system. The predicted end result of reacting glass with water and calculating solution concentrations as a function of reaction progress (i.e., time) is a graph such as shown in Figures 3.2, 3.3, and 3.4.

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