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**OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT**
**ANALYSIS/MODEL COVER SHEET**

1. QA: QA

Page: 1 of: 51

***Complete Only Applicable Items***

2. ☐ Analysis — Check all that apply

Type of Analysis
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☐ Performance Assessment
☐ Scientific

Intended Use of Analysis
☐ Input to Calculation
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Describe use:

3. ☒ Model — Check all that apply

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# OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT
# ANALYSIS/MODEL REVISION RECORD
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| REV 00 | Initial Issue |

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# ACRONYMS AND ABBREVIATIONS

| | |
|---|---|
| AMR | Analysis and Model Report |
| ANL | Argonne National Laboratory |
| ASTM | American Society for Testing and Materials |
| CSG | A Simple 5 – Component Analogue Glass |
| DIRS | Document Input Reference System (database) |
| DOE | U.S. Department of Energy |
| DOE/RW | U.S. Department of Energy Office of Civilian Radioactive Waste Management |
| DWPF | Defense Waste Processing Facility |
| HLW | High-Level Waste |
| MCC-1 | Material Characterization Center – Test Method 1 |
| MW | Magnox Waste |
| PA | Performance Assessment |
| PCT | Product Consistency Test |
| PCT-A | Product Consistency Test – Method A |
| QA | Quality Assurance |
| S/V | Glass Surface Area to Solution Volume Ratio |
| TSPA-SR | Total System Performance Assessment - Site Recommendation |
| TSPA-VA | Total System Performance Assessment - Viability Assessment |
| TBVs | to be verified |
| VHT | Vapor Hydration Test |
| WASRD | Waste Acceptance System Requirements Document |
| WVDP | West Valley Demonstration Project |

## 1. PURPOSE

The purpose of this Analysis/Model Report (AMR) is to document the analyses that were done to develop models for radionuclide release from high level waste glass dissolution that can be integrated into performance assessment (PA) calculations conducted to support site recommendation and license application for the Yucca Mountain site. This report was developed in accordance with the Development Plan for *Waste Package Materials Department Analysis and Modeling Reports Supporting the Waste Form PMR* (CRWMS M&O 2000). It specifically addresses the item, "Defense High Level Waste Glass Degradation," of the product development plan and is in compliance with procedure AP3.10Q. Because the release of radionuclides from the glass will depend on the prior dissolution of the glass, the dissolution rate of the glass imposes an upper bound on the radionuclide release rate. The approach taken to provide a bound for the radionuclide release is to develop models that can be used to calculate the dissolution rate of waste glass when contacted by water in the disposal site. The release rate of a particular radionuclide can then be calculated by multiplying the glass dissolution rate by the mass fraction of that radionuclide in the glass and by the surface area of glass contacted by water.

The scope includes consideration of the three modes by which water may contact waste glass in the disposal system: contact by humid air, dripping water, and immersion. The models for glass dissolution under these contact modes are all based on the rate expression for aqueous dissolution of borosilicate glasses. The mechanism and rate expression for aqueous dissolution are adequately understood; the analyses in this AMR were conducted to provide models and parameter values that can be used to calculate the dissolution rates for the different modes of water contact.

The analyses were conducted to identify key aspects of the mechanistic model for glass dissolution to be included in the abstracted models used for PA calculations, evaluate how the models can be used to calculate bounding values of the glass dissolution rates under anticipated water contact modes in the disposal system, and determine model parameter values for the range of potential waste glass compositions and anticipated environmental conditions. The analysis of a bounding rate also considered the effects of the buildup of glass corrosion products in the solution contacting the glass and potential effects of alteration phase formation. Note that application of the models and model parameter values is constrained to the anticipated range of HLW glass compositions and environmental conditions.

The effects of processes inherent to exposure to humid air and dripping water were taken into account by means of empirically measured parameter values rather than being modeled explicitly. These include the rates at which water sorbs onto the glass, drips onto the glass, and drips off of the glass. The dissolution rates of glasses that were exposed to humid air and dripping water measured in laboratory tests are used to estimate model parameter values for contact by humid air and dripping water in the disposal system.

## 2. QUALITY ASSURANCE

The Quality Assurance (QA) program applies to this analysis. All types of WPs were classified (per QAP-2-3) as Quality Level-1. CRWMS M&O (1999a, p. 7) in *Classification of the MGR Uncanistered Spent Nuclear Fuel Disposal Container System* is cited as an example of a WP type. The development of this analysis is conducted under activity evaluation *1101213FM3 Waste Form Analysis & Models –PMR* (CRWMS M&O 1999b), which was prepared per QAP-2-0. The results of that evaluation were that the activity is subject to the *Quality Assurance Requirements and Description* (DOE 2000) requirements.

The analysis documented in the references Ebert (2000a through k) were performed following the requirements in the quality assurance (QA) plan for Yucca Mountain Project activities performed at Argonne National Laboratory.

# 3. COMPUTER SOFTWARE AND MODEL USAGE

No software is used to support the analyses or models. Commercial off the shelf software Microsoft Excel 98 was used to compile test data, perform simple arithmetic calculations, and calculate the mean and standard deviation values that are used in this AMR. No developed applications, software routines, or macros were used with the software; only mathematical functions and statistical routines provided with the commercially available version were used. No external models were used in the development of this AMR.

Commercial off the shelf software Microsoft Kaleidagraph Version 3.0.5 was used to plot the data within this AMR. No developed applications, software routines, or macros were used with the software; only plotting functions provided with the commercially available version were used. The originator and checker have verified the plots against the original data.

# 4. INPUTS

## 4.1 DATA AND PARAMETERS

Much of the data used in this analysis report were measured at Argonne National Laboratory (ANL) (YMP WBS Element 1.2.2.3.1.2). Some of the data used to corroborate parameter values used in the abstracted model were measured in other tasks conducted at ANL under other Quality Assurance Plans that were compliant with DOE/RW-0333P (DOE 2000). Other corroborative data used in the analyses were taken from the open literature; those references are listed in Section 8. The results taken from some literature sources were further analyzed to extract information from the data that was not directly provided by the authors or to convert the measured values to different units. The data sources used directly in the analyses are listed below with identification of the section of the AMR in which the data or the results of the analysis are used. Data used in this AMR are not directly used in producing a technical product that provides any estimates for any of the principal factors or potentially disruptive events and processes and is thus labeled qualified verification level 2.

CRWMS M&O 1998. The rate expression given in Eq. 6-37 from Chapter 6 page 6-77 of CRWMS M&O 1998 was used as the mechanistic rate expression that was abstracted for degradation upon immersion and exposure to humid air or dripping water in section 6 of this AMR. The expression for the fractional increase in the surface area of a glass log given in Chapter 6 pages 6-79 and 6-80 of CRWMS M&O 1998 was used in the expression for the surface area of a glass log in section 6.1.2 of this AMR. The description in Chapter 6 page 6-79 of CRWMS M&O 1998 was used as the origin of the term for $k_{long}$ in section 6.2.3.1 of this AMR

Ebert 2000k. This reference provides the rate expression for the forward dissolution that is used in section 6.1.1 (Eq. 2) of this AMR.

DTN: LL000210651021.121. This reference provides the values of the intrinsic dissolution rate, pH dependence, and activation energy for CSG glass dissolution in acidic and alkaline solutions that are used in section 6.2.1 (Table 1) of this AMR.

DTN: LL000210551021.120. This reference provides PCT-A results from the ANL Task "Evaluating the Relationship Between PCT-A and Long-Term Behavior." ANL file no. AMR-006. Argonne, Illinois: Argonne National Laboratory. These results are used in section 6.2.3.2 (Table 4) of this AMR.

## 4.2 CRITERIA

The models developed in this AMR are not based on or affected by design criteria.

## 4.3 CODES AND STANDARDS

Data collection and analyses for data used to directly support this analysis were done following the American Society for Testing and Materials (ASTM) standard practices and test methods:

ASTM C1174-97. *Standard Practice for Prediction of the Long-Term Behavior of Materials, Including Waste Forms, Used in Engineered Barrier Systems (EBS) for Geological Disposal of High-Level Radioactive Waste.*

ASTM C1285-97. *Standard Test Methods for Determining Chemical Durability of Nuclear, Hazardous, and Mixed Waste Glasses: The Product Consistency Test (PCT)*

ASTM C 1220-98. *Standard Test Method for Static Leaching of Monolithic Waste Forms for Disposal of Radioactive Waste.*

# 5. ASSUMPTIONS

The following assumptions have been made in this AMR:

- The dissolution rate of the glass provides an upper bound to the release rates of radionuclides. This assumption is based on the corrosion behavior of waste glasses observed in laboratory tests. Tests with a wide range of waste glass compositions have shown radionuclides are released to solution more slowly than boron and other soluble glass matrix components. Since the parameter values used in the abstracted model developed in this AMR are based on the release of boron, they will provide conservative upper bound to the release rate of radionuclides. This assumption does not impact the form of the model or the values of model parameters. No further verification of this assumption is needed. Other effects may further limit transport of radionuclides. This assumption is used throughout this AMR.

- The form of the rate expression for glass dissolution documented in the *Waste Form Characteristics Report* (Stout and Leider 1998) and the *Total System Performance Assessment Viability Assessment Report (TSPA-VA) Analyses Technical Basis Document* (CRWMS M&O 1998) is adequate for calculating the glass dissolution rate. This assumption is based on the consistency of that expression with test results for a wide range of waste glass compositions and the use of similar forms of the rate expression by waste management programs throughout the world. However, that rate expression cannot be fully implemented in performance assessment calculations because processes affecting the reaction affinity will not be tracked. These include processes that affect the concentration of dissolved silica in the solution contacting the glass, such as the formation of alteration phases. This is the impetus for simplification of the mechanistic models into abstracted models. No further verification of this assumption is needed. This assumption is used throughout this AMR.

- The expression for the dependence of the glass dissolution rate on pH and temperature is assumed to be the same for all waste glass compositions. This assumption is based on the analysis of literature data for tests conducted with reference glasses and the fact that the same algebraic forms for the pH and temperature dependencies have been used to interpret test results by waste management programs throughout the world. No further verification of this assumption is needed. This assumption is used in Section 6.1.1.

- The model parameter values take into account the influence on the glass dissolution rate of any inclusion phases (both amorphous and crystalline) that may be present in the glass as a result of incomplete vitrification or devitrification. This assumption is based on the fact that the measured dissolution rates are used directly to determine model parameter values. No further verification of this assumption is needed. This assumption is used throughout this AMR.

- Glass dissolution behavior upon contact by humid air or dripping water is a special case of aqueous corrosion at a very high glass surface area/solution volume (S/V) ratio. This assumption is based on the fact that the reaction controlling the dissolution rate is the same under all three scenarios. The only difference is the solution chemistries that evolve as the glass dissolves. This assumption is verified in the sense that the dissolution behavior in aqueous solutions is used as an upper bound to dissolution in humid air or dripping water. No further verification of this assumption is needed. This assumption is used in Section 6.3.2. Tests are in progress that can be used to validate this assumption.

- The same rate expression can be used for glass dissolution in humid air and in dripping water. The rate constant used in that expression is extracted from test results and includes the combined effects of water sorption or dripping onto the glass, glass dissolution, and dripping off of the glass. This assumption is based on the results of laboratory tests with dripping water discussed in Section 6.3.2. Tests are in progress that can be used to validate this assumption for the case of humid air.

- The temperature dependence for glass degradation in humid air and in dripping water follows

Arrhenius behavior. This assumption is based on laboratory tests that show that the same mechanism controls glass dissolution in humid air and dripping water as when glass is immersed in water. Tests are in progress that can be used to validate this assumption.

- The glass corrosion rate is nil when glass is exposed to humid air at less than 80% relative humidity. This assumption is based on the absence of detectable corrosion in tests conducted at low relative humidity. No further verification of this assumption is needed. This assumption is used in Section 6.3.1.

# 6. ANALYSIS/MODEL

## 6.1 INTRODUCTION

The models described in this report were developed to calculate corrosion rates of waste glasses that are immersed in water or contacted by humid air or dripping water in the event that the waste container and pour canister are breached. The glass dissolution rate is used as an upper limit to the release rates of radionuclides from the glass as it corrodes. The release rate of a particular radionuclide can then be calculated by multiplying the glass dissolution rate by the mass fraction of that radionuclide in the glass and by the surface area of glass contacted by water.

The rate expressions used to calculate the dissolution rate of glass exposed to humid air, dripping water, or immersed in water are all derived from the rate expression for the dissolution of glass in aqueous solutions. The same rate expression that has been documented in Chapter 6 of the TSPA-VA technical basis document (CRWMS M&O 1998, Eq. 6-37, p. 6-77) is used in the analyses described in this AMR. The rate expression includes parameters for the effects of glass composition, pH, temperature, and dissolved silica. The abstractions of that rate expression and the determination of parameter values that can be used to determine the rate of waste glass dissolution in different water contact scenarios are described in this report. The analysis of the rate expression is summarized below.

### 6.1.1 Mechanistic Rate Expression for Aqueous Dissolution

The rate expression used to calculate the dissolution of waste glass immersed in water is a slight modification of the rate expression that was developed for aluminosilicate minerals (Bourcier 1994, pp. 17-22). The rate expression for the dissolution of glass in an aqueous solution that was given in the TSPA-VA (CRWMS M&O 1998, Eq. 6-37, p. 6-77) is:

$$\text{Rate} = S\ \{ k \bullet [1-(Q/K)] + k_{\text{long}} \} \qquad \text{(Eq. 1)}$$

where

Rate = the dissolution rate of the glass, in units of mass/time

S = the surface area of glass immersed in water, in units of area

k = the glass dissolution rate, which is a function of the glass composition, temperature, and solution pH, in units of mass/(area•time)

Q = the concentration of dissolved silica in the solution, in units of mass/volume

$K$ = a quasi-thermodynamic fitting parameter equal to the apparent silica saturation concentration for the glass, in units of mass/volume
$k_{long}$ = minimum long-term dissolution rate, in units of mass/(area•time)

The rate expression contains two main parts: the forward rate, k, which represents the dissolution rate in the absence of feed-back effects of dissolved silica, and the reaction affinity term, (1-Q/K), which quantifies the feed-back effects and is determined based on how far the silica concentration (Q) is from the quasi-thermodynamic saturation concentration (K). The value of K depends on the glass composition. Because the value of Q can range between zero and K, the value of the affinity term is mathematically constrained to values between one and zero. A glass will dissolve at the highest rate possible (at a given temperature and pH value) when the value of the affinity term is one (i.e., when $Q = 0$). The dissolution rate will decrease as the value of the affinity term decreases (i.e., as the value of Q approaches K) until a minimum is reached. The constant term $k_{long}$ was included in the rate expression to account for the long-term dissolution. The terms k, K, and perhaps $k_{long}$ are characteristics of the glass, while the terms S and Q depend on the contact conditions. Note that Equation 1 itself is a simplification of the mechanistic dissolution rate in that only the hydrolysis of Si-O bonds and only the effect of dissolved silica on that reaction are modeled (Bourcier 1994, p. 19).

The forward rate depends on the glass composition, solution pH, and temperature. These dependencies can be expressed explicitly as (Ebert 2000k):

$$k = k_o \bullet 10^{\eta \bullet pH} \bullet \exp(-E_a/RT) \qquad \text{(Eq. 2)}$$

where

$k_o$ = the intrinsic dissolution rate, which depends only on glass composition, in units of mass/(area•time)
$\eta$ = the pH dependence coefficient, which is dimensionless
$E_a$ = the effective activation energy, in units of kJ/mol
$R$ = the gas constant, which is $8.314 \times 10^{-3}$ kJ/(mol•K) (accepted value)
$T$ = the temperature, in Kelvin

This expression is assumed to be applicable to all waste glasses. The full rate expression is obtained by combining Equations 1 and 2, which yields Equation 3:

$$\text{Rate} = S\ \{ k_o \bullet 10^{\eta \bullet pH} \bullet \exp(-E_a/RT) \bullet [1-(Q/K)] + k_{long}\} \qquad \text{(Eq. 3)}$$

Application of this rate expression requires knowledge of several parameter values that depend on the glass composition ($k_o$, $\eta$, $E_a$, K, and $k_{long}$) and of several variables related to the exposure conditions (S, pH, T, and Q). This report describes how the rate expression is used to calculate dissolution rates under the different water contact modes to which the waste glass may be exposed. It also provides estimates of the parameter values based on experimental data and identifies parameter values that can be used to bound the dissolution rates of a range of potential waste glass compositions. The bounding approach is adopted to accommodate uncertainties in the database and rate expressions.

The rate expression in Equation 3 can be used for different water contact modes because the dissolution rate does not depend directly on the volume of water that is in contact with the glass or whether the contact is static or dynamic. Instead, the rate depends on the chemistry of the water through the pH and the concentrations of dissolved silica (the latter dependence is expressed through the affinity term). Note that the rate does not have explicit time dependence. The impact of time on glass degradation in the disposal system will occur indirectly through changes in the temperature, relative humidity, the solution chemistry, and exposure mode (i.e., whether glass is contacted by humid air, dripping water, or is immersed).

The rate expression for the dissolution of silicate waste glasses when contacted by water in the disposal system is given by Equation 3. Use of this rate expression requires knowledge of five parameter values ($k_0$, $\eta$, $E_a$, K, and $k_{long}$) for each waste glass composition and tracking of three variables: the solution pH, ion activity product, Q, and the fractions of the accessible surface area that are contacted by humid air, dripping water, or are immersed. It is assumed that it will not be possible to track the value of Q or processes that affect it during performance assessment calculations. In addition, it is assumed that model parameter values will not be available for the range of waste glass compositions that will be present. Therefore, bounding approximations to the form of the rate expression and parameter values are made for anticipated waste glass compositions and water-contact scenarios.

The rate expression in Equation 3 is simplified by combining the terms for the intrinsic dissolution rate and the reaction affinity into a single term referred to as $k_{eff}$, where $k_{eff}=k_0 \bullet (1-Q/K)$. Also, as will result in the abstraction of a bounding rate expression in Section 6.2.3, the value of $k_{long}$ can be neglected relative to the first term of the rate expression. The abstracted model requires knowledge of three parameter values: $k_{eff}$, $\eta$, and $E_a$.

The abstraction of the rate expressions and the model parameter values that provide bounding rates for each contact mode (humid air, dripping water, or immersion) were determined based on the results of laboratory experiments in which that contact mode was dominant. For contact by humid air vapor hydration tests (VHTs) were used. For contact by dripping water the results of drip tests were used. For contact by immersion, the results of MCC-1 static leach tests, Soxhlet tests, and product consistency tests (PCTs) were used. The analyses conducted to determine the abstractions of the rate expression and determination of the parameter values are discussed in the following sections.

If different models were to be used for each water contact mode (i.e., immersion in water, contact by humid air, and contact by dripping water) in performance assessment calculations, the fractions of the total area exposed to humid air or dripping water or are immersed must be known to calculate the mass of glass that dissolves. The glass surface area that is exposed to humid air, dripping water, and accumulated water in the disposal environment is difficult to characterize. The logs of waste glass will crack within the pour canister due to thermal and mechanical stresses generated as the glass cools and as the waste form is handled (including accidental drops or other impact). Cracking of the glass log will result in surfaces that may be contacted by water or humid air.

### 6.1.2 Estimation of the Exposed Surface Area of Waste Glass

The surface area of glass that is exposed in a laboratory test can be determined geometrically, if the specimens are large enough, or based on the sieve fraction in the case of crushed samples. The geometric surface area is sometimes multiplied by a roughness factor to take into account the fact that prepared surfaces are not smooth on a microscopic scale. A similar approach has been taken to estimate the surface area of logs of waste glass, wherein the geometric surface area of the glass log is determined by the dimensions of the pour canister and the fill height. Fractures caused by thermal and mechanical stress have been estimated to result in a surface area for an average glass log that is 20 times the geometric surface area. A surface increase factor of 20.85 is calculated in CRWMS M&O 1998, pages 6-79 and 6-80 to account for surfaces within fractures formed due to thermal and mechanical stress; that value, which is referred to as the cracking factor, $f_{cracking}$. An expression to calculate the initial surface area of a fractured cylindrical glass log is simply the geometric area times the cracking factor:

$$S_0 = f_{cracking} \bullet (2\pi r_o^2 + 2\pi r_o \bullet L_o) \qquad \text{(Eq. 4)}$$

where

$S_0$ = the initial exposed surface area of a glass log including that due to fracturing
$r_o$ = the initial radius of a glass log
$L_o$ = the initial length of a glass log
$f_{cracking}$ = the cracking factor

The dimensions of the HLW Standard Form in the Waste Acceptance System Requirements Document (DOE 1996, Section 3.2.3.1.1.3) are: total length = 3.000 meters (+0.005 m, -0.020 m); diameter = 61 cm (+1.5 cm, -1.0 cm); weight ≈2500 kg; fill height ≈80% canister volume. The dimensions for canisters for West Valley Demonstration Project (WVDP), Defense Waste Processing Facility (DWPF), and Hanford glass waste forms and the expected weights of glass are given in Stout and Leider (1998; Table 2.2.1.1-1, p. 2-343). For the DWPF canister, the mass of an average glass log is 1682 kg and the density (ρ) is about 2.69 g/cm$^3$ (which corresponds to 2690 kg/m$^3$) at 825°C (Stout and Leider 1998; Table 2.2.1.1-3, p. 2-345). The initial radius of the glass log ($r_0$) is simply one-half of the value of the outside diameter, which is 61 cm, minus the wall thickness, which is 9.5 mm (which corresponds to 0.95 cm). The initial radius of the glass log ($r_0$) is $(61 - 2\bullet 0.95)/2$ cm = 29.55 cm, which corresponds to 0.30 m (rounded to two significant figures). The length of the glass log ($L_0$) is calculated by treating the canister as a right cylinder of radius 0.30 m, equating the expression for the volume of a right cylinder (volume = $\pi \bullet r_0^2 \bullet L_0$) with the volume calculated from the total weight of the glass and the glass density (volume = weight/ρ), and solving the expression for the length. The initial length of the glass log is calculated to be $L_o$ = 2.21 m (to same accuracy as radius). The geometric surface area of the glass log is calculated using the formula for the surface area of a right cylinder ($2\pi r_o^2 + 2\pi r_o \bullet L_o$); the calculated surface area is 4.78 m$^2$. Multiplying this by the cracking factor gives the initial surface area of a DWPF glass log: $S_o$ = 94.6 m$^2$. Based on the dimensions and weights for the glass logs given in Stout and Leider (1998; Tables 2.2.1.1-2 and 2.2.1.1-4), the corresponding values for WVDP and Hanford glass waste forms are: $r_0 = 0.30$ and 0.30 m, $L_0 = 2.49$ and 2.21 m, and $S_0 = 105$ and 94.6 $m^2$, respectively.

The specific surface area of a glass log ($S_{sp}$) is calculated by dividing its surface area by its weight. For the DWPF glass log considered above, the specific surface area is (94.6 $m^2$) / (1682 kg) = $5.62 \times 10^{-2}$ $m^2/kg$. The specific surface areas for the WVDP and Hanford glass logs are $5.53 \times 10^{-2}$ and $5.73 \times 10^{-2}$ $m^2/kg$, respectively. Hence, the range of the specific surface area is $5.53 \times 10^{-2}$ to $5.73 \times 10^{-2}$ $m^2/kg$, with a mean value of $5.63 \times 10^{-2}$ $m^2/kg$.. The surface area that remains as the glass degrades (S) is calculated as the product of the specific surface area and the mass of glass that remains.

The reactivity of surfaces in the tight fracture cracks that result from thermal or mechanical stresses will be determined by the glass composition, temperature, and the chemistry of the water that fills the crack in the same way these factors affect the dissolution rate at free surfaces. The key difference between the dissolution rates of the glass within cracks and at the outer surface is the transport rates of reactants into the crack and reaction products out of the crack. Short-term dissolution tests showed that, while more glass dissolved in tests with samples of fractured glass than in tests with samples of a glass that was not fractured, the difference was less than the estimated increase in the surface area. It had been concluded previously from the results of tests in which various crack widths were simulated with platinum wire spacers that "the assumption that crack surfaces leach as readily as the external surface is unduly conservative" (Perez and Westsik 1981, p. 168). The amounts of glass components released to solution from cracks and from free surfaces cannot be distinguished based on solution results alone. Analysis of test specimens reacted under test conditions similar to those used by Perez and Westsik (1981) indicated that the amount of altered glass in cracks near the surface (which were probably formed during sample preparation) was similar to the amount of altered glass that remained at free surfaces (Pederson et al. 1983, Fig. 6, p. 156). The cracks containing altered glass were observed only near the surface; it could not be determined if the cracks penetrated into the glass beyond what was altered. Sufficient information is not available to quantify either the fraction of cracks that are accessible to water or the difference between the corrosion rates in cracks and at an outer surface. The free surface of a waste glass log will be at the top. Other surfaces will be fracture surfaces within the glass or between the glass and the pour canister; connected voids within the glass will also provide free surfaces. The most conservative approach is to assume all surfaces corrode at the same rate when exposed to water.

## 6.2 DISSOLUTION OF GLASS IMMERSED IN WATER

The rate expression for glass dissolution (Equation 3) was developed based primarily on the results of tests conducted with minerals and glass immersed in water (Bourcier 1994, pp. 4-12). This rate expression has been used extensively for modeling waste glass corrosion (e.g., Advocat et al. 1990; CRWMS M&O 1998; Ebert 1993; Knauss et al. 1990; McGrail et al. 1997a). In addition to waste glasses, the rate expression has been applied to describe the alteration of basalt on the sea bed (Grambow et al. 1986, p. 2710); basalt is used as a natural analogue for waste glass. To determine the appropriate bounding approximations for the rate expression for the dissolution of waste glass in water, the forward rate and affinity terms are considered separately. The dependence of the forward rate on the glass composition, pH, and temperature is analyzed first. These dependencies are measured under test conditions in which the value of the affinity term is maintained near one. The rate expression for glass dissolution under conditions in which the value of the affinity term is equal to one is given in Equation 2. Tests conducted at constant temperature and pH values are used to measure the forward dissolution rates (defined as k in Eq. 2) from which the values of $k_0$, $\eta$, and $E_a$ are determined.

In the following analysis, the forward rates measured for several borosilicate glasses are evaluated to estimate the range of parameter values for various waste glass compositions. The pH- and temperature-dependencies measured for a simple borosilicate glass are used to estimate the values of $\eta$ and $E_a$ for waste glasses. Other literature data are used for corroborative purposes. These parameters are independent of the glass composition, so the same values are used for all waste glasses. Tests were conducted with several reference waste glasses to expand the database used to evaluate the composition dependence and estimate the range of values of $k_0$ for waste glasses. Based on the available measured forward dissolution rates, parameter values that provide a likely bound for the anticipated range of waste glass compositions can be determined. The parameter value of $k_0$ will not be used directly in the models developed for glass dissolution when immersed in water. Rather, the parameter $k_0$ will be coupled with a bounding value of the affinity term in the abstracted model. However, the effect of glass composition on the value of $k_0$ is evaluated separately in order to later evaluate the effect of composition on the combination of several parameters and select the range of parameter values that covers the range of waste glass compositions.

### 6.2.1 The Forward Dissolution Rate (defined as k in Eq. 2)

The forward dissolution rates of three alkali borosilicate glasses have been measured to determine the pH and temperature dependence of the dissolution rate. Single-pass flow-through tests were conducted with a 5-component glass that was formulated to represent an early reference glass for the DWPF (Knauss et al. 1990, p. 372). Tests were conducted at temperatures of 20, 40, and 70°C in pH buffer solutions spanning the range from pH 1 to pH 13. The dissolution rate of this glass was found to have a "V-shaped" pH dependence, with a minimum rate occurring at near-neutral pH values and higher rates occurring at lower pH values (the low pH or acidic leg) and at higher pH values (the high pH or basic leg) (Knauss et al. 1990, Fig. 2, p. 374). The "V-shaped" pH dependence was corroborated in tests with SRL 165 glass (Bourcier et al. 1992, Fig. 2, p. 83). Following Bourcier et al. (1992, p. 82), the simple 5-component analogue glass tested by Knauss et al. (1990) is referred to as CSG glass. Similar pH dependencies have been observed in tests with a nonradioactive analogue of the magnox waste (MW) glass (Abraitis et al. 1998, Fig. 1b, p. 51) and with aluminosilicate minerals (Brady and Walther 1989, Figs. 4, 5, 6, pp. 2825, 2826; Oelkers et al. 1994, Fig. 2, p. 83). The "V-shaped" pH dependence is probably the result of different reactions or reaction mechanisms being predominant at low and high pH values (Brady and Walther 1989, abstract, p. 2828; Carrol et al. 1994, p. 535). For convenience, the pH value at the minimum rate is referred to as $pH_m$ and dissolution at pH values lower and higher than the minimum are referred to as "the low pH leg" and "the high pH leg," respectively.

In contrast to the results of Knauss et al. (1990), Bourcier et al. (1992), and Abraitis et al. (1998), neither a minimum rate nor an increase in the rate with decreasing pH was observed in tests with

R7T7 glass conducted at 90°C and at pH values as low as 4.5 (Advocat et al. 1991, Fig. 4, p. 63), nor were they observed in tests with LD6-5412 glass conducted at 20, 40, 70, and 90°C and at pH values as low as 6 (McGrail et al. 1997a, Fig. 12, p. 186). While it is possible that the compositions of some waste glasses will be such that a low pH leg does not occur, the relationship between glass composition and dissolution behavior is not known well enough to predict whether or not the rate increases at decreasing pH values. By including the acid leg in the model, it is unlikely that the dissolution rate of any waste glass will exceed the calculated value. Therefore, separate rate expressions and separate values of $k_0$, $\eta$, and $E_a$ are determined to calculate the glass dissolution rate under acidic and basic conditions. The values of $\eta$ and $E_a$ determined by Knauss et al. 1990 in tests with the CSG glass at 70°C under acidic and basic conditions are used to determine the model parameters. The results of tests with other glasses are used to corroborate these parameter values. The value of $k_0$ is determined based on the results of short-term MCC-1 tests with reference waste glasses.

Single-pass flow-through tests were conducted to measure the pH and temperature dependencies for CSG and LD6-5412 glass. For the R7T7 glass, Soxhlet tests were used to measure the temperature dependence (Delage and Dussossoy 1991, p. 41; see Delage and Dussossoy 1991 for a description of the Soxhlet test method) and MCC-1 tests were used to measure the pH dependence (Advocat et al. 1991, p. 57). MCC-1 tests were also used in tests with the Magnox Waste (MW) glass (Abraitis et al. 1998, p. 49). The values of $\eta$ and $E_a$ determined for these glass compositions are summarized in Table 1. The values of $k_0$ shown in Table 1 were extracted from the cited results as follows. McGrail et al. (1997a) reported the value of $\log_{10} k_0$ in units of $g/(m^2 \bullet s)$; these were converted to units of $g/(m^2 \bullet d)$. Both Knauss et al. (1990) and Advocat et al. (1991) presented the rate constants without separating the intrinsic and temperature-dependent components. They reported rates as $\log_{10} \kappa$, where $\log \kappa = \log_{10} k_0 + \log_{10}\{\exp(-E/RT)\}$. The rates presented in Table 3.5.1-1 of the Waste Form Characteristics Report (Stout and Leider 1998, p. 3-172), which are based on the data of Knauss et al. (1990), were analyzed (DTN: LL000210651021.121) to determine the values of $\log_{10} k_0$ and $\eta$ that are presented in Table 1 (DTN: LL000210651021.121). The activation energies for the Knauss et al. (1990) results were determined from Arrhenius plots of the natural logarithms of the tabulated rates versus the reciprocal temperature at constant pH. The mean and standard deviation for results at pH values of 1, 2, 3, 4, and 5 were used for the activation energy of the low pH leg, and the mean and standard deviation for results at pH values of 7, 8, 9, 10 and 12 were used for the activation energy of the high pH leg. The result for the high pH leg is in agreement with the value of 20±2 kcal/mol that was reported by Knauss et al. (1990, p. 376; The value of 20 kcal/mol is equivalent to 84 kJ/mol using the conversion factor 4.181 kJ/kcal.) The values of $\log_{10} k_0$ were then extracted from the rates presented in Table 3.5.1-1 of the Waste Form Characteristics Report (Stout and Leider 1998, p. 3-172) using the pH and temperature dependencies in Table 1 (DTN: LL000210651021.121). The values of $\log_{10} k_0$ given in Table 1 are the mean and standard deviation for the values calculated at the pH values included in the low and high pH legs.

Table 1. Values of $\log_{10}k_0$, $\eta$, and $E_a$ for Borosilicate Glasses

| Glass | Temperature (°C) | $\log_{10} k_o$[a] | $\eta$ | $E_a$ (kJ/mol) | Literature Reference |
|---|---|---|---|---|---|
| | | | Low pH Leg | | |
| CSG | 25 | 9.4[b] | -0.48 | 58±15[b] | Knauss et al. 1990 |
| CSG | 50 | 10[b] | -0.70 | 58±15[b] | Knauss et al. 1990 |
| CSG | 70 | 10[b] | -0.69 | 58±15[b] | Knauss et al. 1990 |
| MW | 20 | -- | -0.7[c] | 32.4±0.8 | Abraitis et al. 1998 |
| MW | 60 | -- | -0.6[c] | 32.4±0.8 | Abraitis et al. 1998 |
| | | | High pH Leg | | |
| CSG | 25 | 6.6[b] | 0.51 | 84±7[b] | Knauss et al. 1990 |
| CSG | 50 | 6.6[b] | 0.51 | 84±7[b] | Knauss et al. 1990 |
| CSG | 70 | 7.7[b] | 0.40 | 84±7[b] | Knauss et al. 1990 |
| MW | 20 | -- | 0.1[c] | 36.0±0.6 | Abraitis et al. 1998 |
| MW | 60 | -- | 0.4[c] | 36.0±0.6 | Abraitis et al. 1998 |
| LD6-5412 | 20 | 6.99 ±0.55[d] | 0.40±0.03 | 74.8±1.0[d] | McGrail et al. 1997a |
| LD6-5412 | 40 | 6.99 ±0.55[d] | 0.40±0.03 | 74.8±1.0[d] | McGrail et al. 1997a |
| LD6-5412 | 70 | 6.99 ±0.55[d] | 0.40±0.03 | 74.8±1.0[d] | McGrail et al. 1997a |
| LD6-5412 | 90 | 6.99 ±0.55[d] | 0.40±0.03 | 74.8±1.0[d] | McGrail et al. 1997a |
| R7T7 | 90 | -- | -- | 59±2 | Delage and Dussossoy 1991, page 47 |
| R7T7 | 90 | 5.27[e] | 0.41±0.02 | -- | Advocat et al.1991, page 63 |

NOTES: [a] Calculated for $k_0$ in units of g/(m$^2$•d)

[b] Calculated from data in cited reference (see DTN: LL000210651021.121)

[c] Calculated from data in cited reference (see Ebert 2000b)

[d] Calculated from data in cited reference (see Ebert 2000h)

[e] Calculated from data in cited reference (see Ebert 2000c)

### 6.2.1.1 Dependence on pH

The measured pH dependence in the high pH leg is about the same for these glasses. Advocat et al. (1991) provided results for tests at 90°C only. McGrail et al. (1997a, Fig. 12, p. 186) found the results for tests at 20, 40, 70, and 90°C could be regressed with the same pH dependence, whereas Knauss et al. (1990, Table 1, p. 375) regressed their data for tests at 25, 50, and 70°C separately so that different values of $\eta$ were determined at different temperatures. In the models for waste glass dissolution developed in this AMR, the values of $\eta$ used for the low pH and high pH legs do not depend on the temperature. The value $\eta = 0.4 \pm 0.1$ is selected for the high pH leg for all waste glasses based on the results of Knauss et al. (1990) for tests at 70°C. This value is corroborated by the results for other glasses shown in Table 1.

The fact that an acid leg has been observed in tests with the CSG (Knauss et al. 1990, Fig. 2, p. 374), SRL 165 (Bourcier et al. 1992, Fig. 2, p. 83), and MW glasses (Abraitis et al. 1998) but not with LD6-5412 (McGrail et al. 1997a, Fig. 12, p. 186), or R7T7 (Advocat et al, 1991, Fig. 4, p. 63) glasses lends more uncertainty to the selection of a value for the acid leg. The values of $\eta$ determined from the results of Knauss et al. (1990) and Abraitis et al. (1998) between 20 and 70°C do not show a trend with the temperature. A value of $\eta = -0.6 \pm 0.1$ is used for the acid leg. The high end of this range is consistent with the values measured at 50 and 70°C by Knauss et al. (1990). The low end of the range was selected based on the value of $\eta$ measured by Knauss et al. (1990) at 25°C, rounded to one significant figure. Although the dissolution rates of some glasses are known not to increase as the pH becomes more acidic, the abstracted model in this AMR takes into account the possibility that the dissolution rates of some waste glasses may increase at low pH values. Thus, the abstracted model provides an upper bound to the dissolution rate.. The extraction of the other parameter values from the results of tests conducted under neutral or alkaline conditions and under acidic conditions are discussed separately. [Note: the term $pH_m$ is used to identify the pH value at which the rate at a particular temperature is a minimum (i.e., the minimum in the "V") and to distinguish between the low pH and high pH legs. Calculation of $pH_m$ is discussed in Section 6.2.3.3.]

#### 6.2.1.2 Dissolution under Neutral or Alkaline Conditions ($pH \geq pH_m$)

Dissolution of waste glasses will result in an increase in the solution pH due to dealkalization reactions. Corrosion tests with reference waste glasses have resulted in glass dissolving under neutral or alkaline conditions, and these conditions are expected to prevail in the vicinity of waste glasses.

**Dependence on Temperature**–The differences between the temperature dependencies measured for the CSG, LD6-5412, and R7T7 glasses at neutral and alkaline pH values are statistically significant. It has been reported that "the activation energies for a very large number of [borosilicate glass] compositions cluster between 60 and 90 kJ/mol" (White 1986, p. 439). The values measured for dissolution in basic solutions given in Table I nearly span this range. From the Arrhenius expression, the sensitivity of the rate to changes in the temperature increases slightly with the activation energy. For a given temperature change, the change in the rate when the activation energy is 60 kJ/mol is about 2/3 the change in the rate when the activation energy is 90 kJ/mol. For example, a change in temperature from 40 to 30°C will result in a decrease in the rate by factors of about 2.1 times, 2.8 times, and 3.1 times, respectively, when the activation energy is 60, 80, and 90 kJ/mol. The activation energy calculated as mean value plus one standard deviation from the data of Knauss et al. (1990) in alkaline solutions was used as the high end of the range for the activation energy; that value is 91 kJ/mol. The activation energy calculated as mean value minus two standard deviations from the data of Knauss et al. 1990 in alkaline solutions was used as the low end of the range for the activation energy; that value is 70 kJ/mol. The activation energy is biased lower than the values measured by Knauss et al. (1990) to add conservatism to the values calculated at low temperatures. The activation energy is expressed to one significant figure as 80 ± 10 kJ/mol.

**Dependence on Glass composition**–The effect of the composition on the glass dissolution rate is quantified in Equations 2 and 3 by the intrinsic dissolution rate constant ($k_0$). The value of $k_0$ cannot be measured directly but is determined by deconvoluting the contributions of the pH and temperature terms from the measured forward rate. The value of $k_0$ that is extracted from the measured forward rate will depend on the values used for the pH and temperature dependencies. This can be seen clearly by taking the logarithm of Equation 2:

$$\log_{10}k = \log_{10}k_0 + \eta \bullet pH + \log_{10}\{\exp(-E_a/RT)\} \qquad \text{(Eq. 2')}$$

Thus, although the dissolution rates that were measured for the CSG, LD6-5412, and R7T7 glasses at a given temperature and pH values are similar, the values of $\log_{10}k_0$ for the three glasses are significantly different because different temperature dependencies were used.

Tests were conducted to determine the values of $k_0$ for glass compositions that are representative of likely waste forms for DWPF, WVDP, and Hanford wastes (Ebert 2000j). The suite of glasses used in the study was selected to study the sensitivity of $k_0$ to the concentrations of key glass components. Glasses were selected to span the range of possible aluminum contents for waste glasses. The aluminum content is known to affect the durability of waste glasses in short-term tests (Ellison et al. 1994, pp. 35, 39, 42, 47) and is suspected to affect the propensity for the formation of zeolite alteration phases (Van Iseghem and Grambow 1988, pp. 631 and 639; Ellison et al. 1994, p. 46). The glasses are listed in Table 2 in decreasing order of aluminum content. The PNL 76-68 glass was included in the study as a glass with no aluminum. The LD6-5412 composition was developed for low-activity wastes and has higher sodium content than anticipated for high level waste glasses. While these glass compositions may be outside the range of likely high level waste glasses, they provide useful measures of the sensitivity of $k_0$ at the lower bound of aluminum content and upper bound of sodium contents.

Samples of these glasses were subjected to MCC-1 tests at 90°C for durations between 1 and 15 days to measure the forward dissolution rates. The pH values attained in the tests were all greater than 9, so the results were analyzed using the parameters for the high pH leg. The values of $k_0$ were extracted from the measured rates (which were based on the release of boron) by deconvoluting the effects of the pH and temperature using the values $\eta = 0.40$ and $E_a = 80$ kJ/mol (see sections 6.2.1.1 and 6.2.1.2). Note that all pH values were measured at room temperature. The measured pH values were decreased by 0.8 to estimate the pH values at 90°C to take into account the temperature dependence of the ionization constant of water. This has the effect of lowering all calculated values of $\log_{10} k_0$ by a factor of $0.40 \bullet 0.8 = 0.32$. The results are included in Table 2 (see Ebert 2000j). The mean and standard deviation of $\log_{10} k_0$ calculated for all nine glasses are $\log_{10} k_0 = 7.91 \pm 0.16$ g/(m$^2\bullet$d) (Ebert 2000j). The mean and standard deviation for only the reference high-level waste glasses (i.e., when the results of the Hanford-L, PNL 76-68, and LD6-5412 glasses are excluded from the average) are $\log_{10} k_0 = 7.86 \pm 0.12$ g/(m$^2\bullet$d).

Table 2. Values of $\log_{10} k_0$ Measured for Reference Waste Glasses[a]

| Glass | Mass Fraction Al | $\log_{10} k_0$ | Glass | Mass Fraction Al | $\log_{10} k_0$ |
|---|---|---|---|---|---|
| LD6-5412 | 0.068 | 7.78 | SRL 165U | 0.022 | 7.99 |
| Hanford-L | 0.063 | 8.02 | SRL 202U | 0.020 | 7.75 |
| Hanford-D | 0.054 | 7.89 | SRL 131U | 0.017 | 7.99 |
| WV ref 6 | 0.032 | 7.87 | PNL 76-68 | 0 | 8.19 |
| SRL 51S | 0.028 | 7.69 | | | |

NOTE: [a] Values of log $k_0$ are given for $k_0$ in units g/(m$^2\bullet$d).

The intrinsic dissolution rate of LD6-5412 glass that was measured with MCC-1 can be compared with the value measured with single-pass flow-through tests by McGrail et al. (1997a) if the same activation energy and value of $\eta$ are used to deconvolute the temperature and pH effects from the measured rates. The value of $\log_{10} k_o$ calculated from the MCC-1 test results using the values are $\eta = 0.40$ and $E_a = 75$ kJ/mol is $\log_{10} k_0 = 7.00$ g/(m$^2$•d). This is well within the uncertainty of the value reported by McGrail et al. (1997a), which was $\log_{10} k_0 = 6.97 \pm 0.55$ g/(m$^2$•d). (The rate reported in McGrail et al [1997a] was $\log_{10} k_0 = 2.05 \pm 0.16$ g/(m$^2$•s); conversion of units is documented in Ebert [2000h].) This comparison shows that the MCC-1 test method and single-pass flow-through tests provide the same estimate the value of $\log_{10} k_0$. It also demonstrates the sensitivity of the calculated value of $\log_{10} k_0$ to the value of the activation energy that is used. Namely the value of $\log_{10} k_0$ extracted from the measured rate using an activation energy of 80 kJ/mol is 0.78 g/(m$^2$•d) greater than the value extracted using an activation energy of 75 kJ/mol. This difference will not impact the rates that are calculated with the rate expression, however, since the sum of the values of $\log_{10} k_0$ and the temperature term is the same in both cases.

The following parameter values are selected for use in calculations for total system performance assessment site recommendation (TSPA-SR) to bound the forward dissolution rate on the high pH leg (at $pH \geq pH_m$):

$\log_{10} k_0 = 7.9 \pm 0.3$ g/(m$^2$•d)
$\eta = 0.4 \pm 0.1$
$E_a = 80 \pm 10$ kJ/mol.

These parameter values were selected based on a limited database. The available evidence indicates that the rates calculated with these parameter values will bound the forward dissolution rates for the full range of waste glass compositions at high pH values.

### 6.2.1.3 Dissolution under Acidic Conditions ($pH < pH_m$).

Although the dissolution of waste glasses is not expected to result in solution pH values below 6, the groundwater that comes into contact with the waste glass could be acidified due to radiolysis of moist air or the corrosion of other materials in the engineered barrier system. Only the results of Knauss et al. (1990) and Abraitis et al. (1998) are available to quantify the waste glass dissolution rate in acidic solutions.

**Dependence on Temperature**–For dissolution in solutions with pH values less than $pH_m$, the mean and standard deviation of the activation energies extracted from the results of Knauss et al. (1990) for tests conducted at pH values less than pH 6 are 58 ± 15 kJ/mol (see DTN: LL000210651021.121). This is lower than the activation energy for the high pH leg for CSG glass. This value is used to provide a conservative estimate of the dissolution rates all waste glasses when $pH < pH_m$.

**Dependence on Glass composition**–The average value of the intrinsic dissolution rate for CSG glass calculated from the results of Knauss et al. (1990) for the low pH leg is $\log_{10} k_0 = 10$ g/(m$^2$•d) at 50 and 70°C and $\log_{10} k_0 = 9.4$ g/(m$^2$•d) at 25°C (see DTN: LL000210651021.121). The bounding values are selected to span the range measured by Knauss et al. (1990) for these temperatures: $\log_{10} k_0 = 9 \pm 1$ g/(m$^2$•d). The lower value of this range corresponds to the mean value measured at 25°C minus one standard deviation, and the higher value of this range corresponds to the mean value measured at 70 and 50°C plus one standard deviation, both rounded to one significant figure. Notice that the value of $\log_{10} k_0$ for dissolution under acidic conditions is significantly larger than the value of $\log_{10} k_0$ for dissolution under alkaline conditions. This is a consequence, in part, of the different values of $\eta$ and $E_a$ used to extract log $k_0$ from the measured dissolution rate, but may also be an indication that different rate-determining steps are operative under acid and alkaline conditions, as stated earlier in section 6.2.1 (Brady and Walther 1989, abstract, p. 2828; Carrol et al. 1994, p. 535).

The following parameter values are selected for use in TSPA-SR calculations to bound the forward dissolution rate on the low pH leg (at $pH < pH_m$):

$\log_{10} k_0 = 9 \pm 1$ g/(m$^2$•d)
$\eta = -0.6 \pm 0.1$
$E_a = 58 \pm 15$ kJ/mol.

These parameter values were selected based on a limited database. The available evidence indicates that the rates calculated with these parameter values will bound the forward dissolution rates for the full range of waste glass compositions at low pH values.

### 6.2.2 Effects of the Affinity Term (defined as {1-Q/K} in Eq. 3)

The affinity term provides a measure of the feedback effects of solutes that are reactants in the reverse of the rate-determining step for glass dissolution (Bourcier 1991, abstract, p. 13). The value of the affinity term will have a predominant effect on the glass dissolution rate under disposal conditions. When the value of the affinity term is one, glass dissolves at the forward rate. When the value of the affinity term is zero, the forward and reverse rates are equal and the net dissolution rate is zero. The most conservative upper bound for the dissolution rates is the forward rate. However, this is an overly conservative bound, because the value of the affinity term cannot remain one when the glass becomes contacted by water. If a thin film of water contacts the glass, the value of the affinity term will decrease significantly after very little glass has dissolved. For immersion, the amount of dissolved silica present in the incoming groundwater itself causes the affinity term to be significantly less than one immediately. The analyses in this section were done to determine if the use of a bound to the dissolution rate that is less conservative than the forward rate is justified.

It is instructive to consider glass corrosion behavior in terms of three stages that are related to three characteristic values of the affinity term. Stage I occurs when the value of the affinity term is one and glass dissolves at the forward rate for the specific temperature and pH conditions involved. Stage I will not occur when glass is contacted by groundwater due to the presence of dissolved silica in the groundwater.

Stage II occurs as the buildup of solutes slows the glass dissolution and the value of the affinity term approaches zero. The value of the affinity term cannot become zero, because glass is thermodynamically unstable and cannot equilibrate with the solution. An ad hoc constant rate term was included in the rate expression for waste glasses in the TSPA-VA, namely, $k_{long}$, to insure that the calculated rate remained greater than zero.

Stage III occurs when the dissolution rate increases concurrent with the formation of alteration phases. The formation of alteration phases is believed to cause a decrease in the value of Q due to the consumption of dissolved silica as silica-bearing phases form (Advocat et al. 1990, p. 244; Patyn et al. 1990, pp. 303 and 304). It has been hypothesized that the formation of some alteration phases establishes saturation limits that are lower than the effective limits set by the glass (i.e., lower than the limits set by K) (Van Iseghem and Grambow 1988, p. 633). This results in the value of Q being maintained at a lower value than K and, thereby, establishes a maximum value for the ratio of Q/K. This also results in a lower limit for the value of the affinity term.

Stage III behavior has been observed with several test methods, including long-term PCTs (Ebert et al. 1993, pp. 573, 575; Patyn et al. 1990, Fig. 1, pp. 301; Feng et al. 1993, p. 195, Fig. 3 p. 200), vapor hydration tests (Bates and Steindler 1983, abstract, p. 85; Abrajano et al. 1986, pp. 254, 255 and Fig. 1, p. 255; Ebert et al. 1991a, Fig. 2, p. 211), accelerated dissolution tests (Ebert et al.1996, p. 573), and unsaturated flow-through tests (McGrail et al. 1997b, p. 257). It has been observed in tests conducted with crushed and monolithic samples, with water vapor, demineralized water, and tuff groundwater, and at temperatures between 70 and 240°C.

However, Stage III behavior has not been observed for all glasses that have been studied with the laboratory tests listed above. In some cases, the test durations may not have been long enough for the critical alteration phases to nucleate and the reaction to progress to Stage III. This may be due to variations in the nucleation kinetics of rate-affecting phases. In other cases, the composition of the glass may be such that the alteration phases that form do not measurably affect the reaction affinity. Attempts have been made to relate the likelihood of reaching Stage III behavior with the glass composition (Van Iseghem and Grambow 1988, p. 637).

It is important to note that Stage III behavior has not been observed in drip tests with high level waste glass. This is probably because the solution flow in these tests is sufficient to prevent the solution contacting the glass from becoming saturated with respect to alteration phases that affect the dissolution rate. The phases observed on samples from drip tests include clays and sparingly soluble phases such as iron silicates, uranium silicates, and calcium thorium phosphate (Fortner and Bates 1996, abstract, p. 209.). The zeolite phases typically observed to form when Stage III occurs (such as analcime, hershelite, and phillipsite) have not been detected in drip tests. Therefore, the possibility that corrosion enters Stage III is only considered for glass corroding under immersion conditions.

Although the formation of silicon-bearing alteration phases (and the consequent decrease in the value of the affinity term) has been suggested as the trigger to Stage III, tests in which Stage III behavior has been observed show no obvious changes in the solution concentration of silicon to occur immediately before or after the dissolution rate increases. Tests with some glasses show an increase in the solution pH after Stage III is reached, but tests with other glasses show a decrease. The change in pH is probably a result of the increased dissolution rate and the formation of alteration phases rather than a cause. It may not be possible to measure the change in the silicon concentration that triggers Stage III due to the high sensitivity of the dissociation of orthosilicic acid to alkaline pHs. It is difficult to accurately measure the pH of solutions with high concentrations of dissolved glass components because of the sodium effect on the electrode response. Without knowing the conditions that trigger entry into Stage III, it is not possible to predict when Stage III occurs in performance assessment calculations. The conservative approach is to select the bounding value of the affinity term so that the rates that have been measured for glasses that have progressed to Stage III are bounded in the PA calculations.

The effective value of the affinity term for corrosion in Stage III is not expected to increase significantly as the assemblage of rate-increasing alteration phases evolves. This expectation is made based on the hypothesis that alteration phases control the dissolution rate in Stage III by fixing the value of Q equal to the solubility limit for silicon that is established by the assemblage of alteration phases that have formed. The increase in the dissolution rate as the reaction progresses from Stage II to Stage III occurs because the solubility limit set by the assemblage of alteration phases in Stage III (and, therefore, the maximum value of Q) is much lower than the effective solubility limit in Stage II. In Stage II, the value of Q can become similar to the value of K, in which case the value of the affinity term (1-Q/K) becomes nearly zero (see Equation 1). In Stage III, alteration phases maintain Q at a value lower than the value of K. The change in the solubility limit as the assemblage of alteration phases evolves will be small compared to the change that occurs when the alteration phases form initially. This is supported by the fact that, although changes in the assemblage of alteration phases have been detected after glass corrosion enters Stage III, the dissolution rate in Stage III has not been observed to increase. In fact, the rate in Stage III has been observed to decrease over time in long-term PCTs (Ebert and Tam 1997, Fig. 2, p. 155). This may be due to the effects of the precipitation rate of the alteration phases or mass transport limitations in the test.

### 6.2.3 Abstraction of a Bounding Rate Expression

In the absence of a method to predict whether or not corrosion of waste glass will enter Stage III, it is conservative to assume that all disposed waste glasses will progress to Stage III immediately if they become immersed in water. As discussed above, the effect of Stage III on the dissolution rate occurs through the affinity term when the reaction is in Stage III. Since the value of the affinity term is assumed to remain constant in Stage III, the value of the affinity term, which is denoted as $(1\text{-}Q/K)_{III}$, can be combined with the intrinsic dissolution rate constant to simplify the rate expression in Equation 3 as the following abstraction:

$$\mathrm{Rate}/S = k_{eff} \bullet 10^{\eta \bullet pH} \bullet \exp(-E_a/RT) \qquad \text{(Eq. 5)}$$

where

$$k_{eff} = k_0 \bullet (1\text{-}Q/K)_{III} \qquad \text{(Eq. 6)}$$

Note that the term $k_{long}$ in Equation 3 has been dropped from the abstracted rate expression in Equation 5. The term $k_{long}$ was included in the rate expression given by Equation 3 to maintain a nonzero rate in the event that the conditions were such that the value of the affinity term was calculated to be less than or equal to zero (CRWMS M&O 1998, p. 6-79). In the present abstraction of the rate expression for glass dissolution (Equation 5), the affinity term is fixed at a value that (as will be shown below) is greater than zero and cannot become less than or equal to zero. Neglect of the term $k_{long}$ in the abstracted rate expression will be shown to be justified because the rates calculated using the abstracted rate expression are always greater than $k_{long}$ (see Section 6.4).

### 6.2.3.1 Determining the Values of $k_{eff}$ for Stage III Rates

In the following analysis, the range of values of $k_{eff}$ that bound the dissolution rates of waste glasses in Stage III as measured in long-term PCT is determined. The reactivities of those glasses in PCT-A are then compared to the dissolution rates in Stage III as measured in long-term PCT to evaluate whether the results of PCT-A can be used to define an equivalent range of $k_{eff}$ for waste glasses. As discussed in Section 6.2.1, the intrinsic dissolution rate constant is only weakly dependent on the glass composition. The composition dependence of $k_{eff}$ will be primarily through the affinity term. The composition dependence of $k_{eff}$ is determined empirically by comparing the values of $k_{eff}$ that are extracted from rates measured for reference glasses in PCT-A with the values extracted from the rates measured for glasses in Stage III.

Stage III rates have been measured for only a few reference waste glasses and, only a small database is available for the analysis. Although Stage III behavior has been observed with several test methods, the most reliable rates were extracted with PCTs conducted for long durations. The Stage III rates measured for several glasses are listed in Table 3 along with the averages of the final pH values that were measured in the tests (DTN: LL000210551021.120). (Note: the SRL 131A and SRL 202A glasses were made by doping the SRL 131U and SRL 202U glasses with of radionuclides (about 0.01 mass % total). The dissolution behaviors of the SRL 131U and SRL 202U glasses and the corresponding radionuclide-doped glasses are compared directly in this analysis.) Values of $k_{eff}$ for these glasses were extracted from the measured rates (based on the release of boron) using Equation 5 with $\eta = 0.4$ and $E_a = 80$ kJ/mol. Note that all pH values were measured at room temperature. The measured pH values were decreased by 0.8 to estimate the pH values at 90°C to take into account the change in the ionization constant of water with temperature. This has the effect of lowering all calculated dissolution rates by a factor of about 2.1 (and the values of $\log_{10} k_{eff}$ by 0.32).

The mean and standard deviation for the Stage III rate constants measured for these six glasses are $\log_{10}k_{eff} = 6.19 \pm 0.64$ g/(m$^2$•d). These values are significantly lower than the values measured from the forward rates of similar glasses, which were $\log_{10} k_o = 7.91 \pm 0.16$ g/(m$^2$•d). The composition dependence of $\log_{10} k_{eff}$ for the different glasses as measured by the percent relative standard deviation is 9.6%. The percent relative standard deviation in $\log_{10} k_0$ for the suite of glasses in Table 2 is 2.0%. These results indicate that variations in the values of $k_0$ and $(1\text{-}Q/K)_{III}$ with glass composition are of similar magnitude.

Table 3. Dissolution Rates and $\log_{10}k_{eff}$ in Stage III[a]

| Glass | Stage III Rate, $g/(m^2 \bullet d)$[a] | pH for Stage III | $\log_{10}k_{eff}$[b] | Data Reference |
|---|---|---|---|---|
| SRL EA | 0.070[c] | 12.3[c] | 5.76[c] | Ebert et al. (1998) |
| SRL 131A | 0.037 | 12.1 | 5.56 | Ebert (2000a) |
| SRL 202A | 0.032 | 12.0 | 5.54 | Ebert (2000a) |
| SRL 200S | 0.87[d] | 12.2[d] | 6.89[d] | Feng et al. (1993) |
| SAN 60 | 0.074[e] | 9.8[e] | 6.78[e] | Patyn et al. (1990) |
| LD6-5412 | 0.4 | 12.0 | 6.63[f] | Ebert et al. (1996) |

NOTES: [a] Rates are based on release of boron in tests at 90°C and 20,000 $m^{-1}$.
[b] Value of $\log_{10}k_{eff}$ for $k_{eff}$ in units of $g/(m^2 \bullet d)$
[c] see Ebert (2000e)
[d] see Ebert (2000f)
[e] see Ebert (2000i)
[f] see Ebert (2000d)

### 6.2.3.2 Relationship Between PCT-A Rates and Stage III Rates

While the Stage III rates measured for the glasses discussed above could be used to determine a bounding value of $k_{eff}$, the database is too small to provide confidence that the value that is determined will bound the dissolution rates of the wide range of glass compositions that may be disposed. It is believed that confidence in the bounding values can be enhanced by first showing that the long-term dissolution rates of these glasses (i.e., the Stage III rates) are bounded by the average rates of the same glasses measured with PCT-A, and then selecting a value of $k_{eff}$ that bounds the rates that have been measured for a wider range of glass compositions using that test. The database of PCT-A rates can be more readily expanded with other glass compositions than can the database of Stage III rates. For example, all future waste glass compositions will be evaluated with PCT-A as a part of the waste acceptance procedure. These tests can also be used to confirm that their corrosion rates are bounded by the model. Therefore, the use of PCT-A rates for bounding the Stage III rates and selecting $k_{eff}$ was evaluated. The benefit of demonstrating that the PCT-A rate can also be used to bound the Stage III rate is that part of the slowing effects of the affinity term are taken into account.

The values of $\log_{10}k_{eff}$ were extracted from the PCT-A rates (which were calculated based on the release of boron in the tests) using Equation 5. As before, the pH term was estimated at 90°C by subtracting 0.8 from the pH measured at room temperature to take into account the affect of the temperature difference on the ion product of water. The results are given in Table 4. These are plotted against the values extracted from the Stage III rates measured with long-term PCT in Figure 1. (Comparison of the Stage III rates for SRL 131A and SRL 202A glasses with the PCT–A rates for SRL 131U and SRL 202U glasses are labeled SRL 131 and SRL 202 in Figure 1). The diagonal line shows where the values are equal. The values from the PCT–A rates are higher than the values from the Stage III rates for points that lie above the line, while the values from the Stage III rate are higher than the values from the PCT-A rate for points that lie below the line.

As can be seen in Figure 1, the values from the PCT-A rates do not provide an upper bound to the values from the Stage III rates for all glasses. The LD6-5412 glass was formulated in the development of low-activity Hanford waste forms but is not a reference waste form. The SAN 60 represents the Belgian HLW glass. The difference between the PCT-A and Stage III rates of the LD6-5412 and SAN 60 glasses is probably due to difference in the effects of the high aluminum contents in PCT-A and in Stage III (LD6-5412 and SAN 60 glass contain about 13 and 18 mass % $Al_2O_3$, respectively). The aluminum contents in the reference high level waste glasses are less 6 mass % $Al_2O_3$. In PCT-A, the high aluminum content increases the durability of the glass and leads to a low PCT-A rate. In Stage III, the availability of dissolved aluminum in solution results in a lower silica solubility limit after the formation of zeolite phases; this decreases the value of the affinity term and increases the dissolution rate in Stage III (Van Iseghem and Grambow 1988, p. 633).

Table 4. PCT-A Rates[a] and Calculated Values of $\log_{10}k_{eff}$ for Reference Waste Glasses

| Glass | Rate Measured in PCT-A, in $g/(m^2 \cdot d)$ | Measured pH (at room temperature) | $\log_{10}k_{eff}$ (at 90°C) | Data Reference |
|---|---|---|---|---|
| SRL EA | 1.2 | 11.85 | 7.15[b] | Ebert et al. (1998) |
| SRL 131U | 0.69 | 11.63 | 7.02 | LL000210551021.120 |
| SRL 202U | 0.043 | 10.42 | 6.29 | LL000210551021.120 |
| SRL 200S | 0.10[c] | 10.65[c] | 6.57[c] | Feng et al. (1993) |
| SAN 60 | 0.055[d] | 9.8[d] | 6.65[d] | Patyn et al. (1990) |
| LD6-5412 | 0.044 | 11.20 | 5.42 | LL000210551021.120 |
| SRL 51S | 0.038 | 10.66 | 6.15 | LL000210551021.120 |
| SRL 165U | 0.044 | 10.31 | 6.35 | LL000210551021.120 |
| WV ref 6 | 0.039 | 9.98 | 6.42 | LL000210551021.120 |
| PNL 76-68 | 0.18 | 9.43 | 7.30 | LL000210551021.120 |
| Hanford-D | 0.052 | 10.67 | 6.27 | LL000210551021.120 |
| Hanford-L | 0.095 | 10.96 | 6.28 | LL000210551021.120 |

NOTES: [a] Average rates for tests conducted at 90°C and 2000 $m^{-1}$ for 7 days
[b] Ebert (2000e)
[c] Ebert (2000f)
[d] Ebert (2000i)

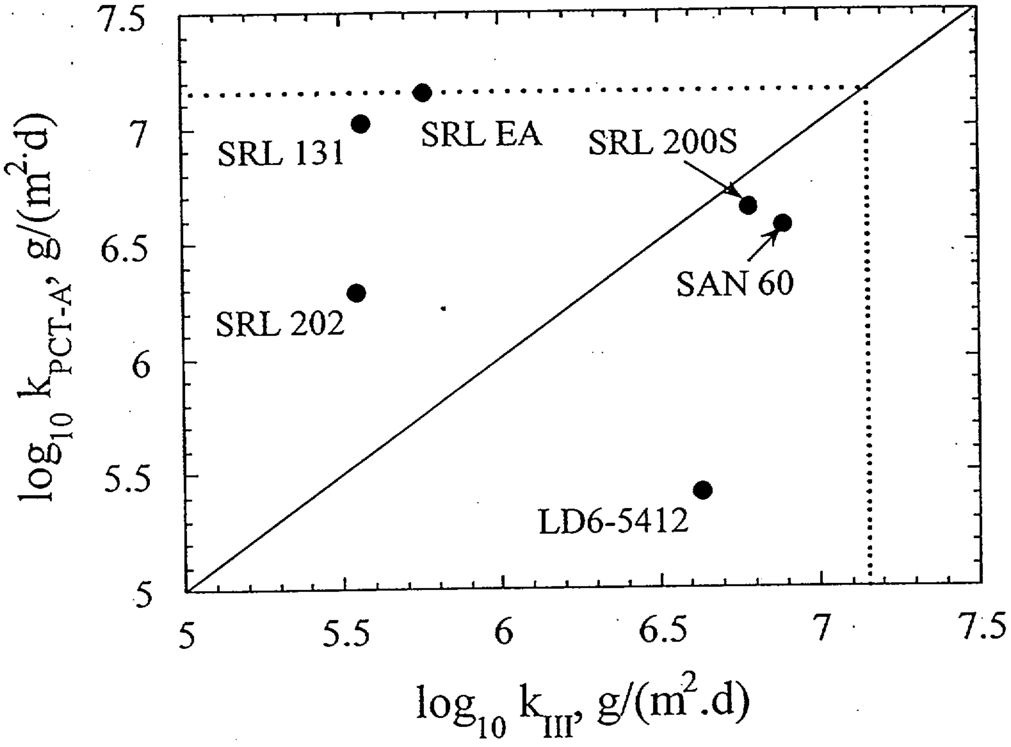

Figure 1. Comparison of Values of $\log_{10}k_{eff}$ Extracted from PCT-A Rates and Stage III Rates Measured with Long-Term PCTs.

The results shown in Figure 1 are interpreted to indicate that the PCT-A rates of reference waste glasses SRL 202A, SRL 131A and SRL EA bound their Stage III rates, but the PCT-A rates of SRL 200S, LD6-5412, or SAN 60 glasses do not bound their Stage III rates. However, the PCT-A rate of the EA glass does bound the Stage III rates of all glasses that were evaluated, including the LD6-5412 and SAN 60 glasses. The rate from PCT-A with SRL EA glass is $\log_{10}k_{PCT-A} = 7.15$ g/(m$^2$•d). The dotted lines in Fig. 1 show all of the measured rates to be bounded when $\log_{10} k_{PCT-A}$ and $\log_{10} k_{III}$ have the value of 7.15 g/(m$^2$•d).

### 6.2.3.3 Bounding Values of $k_{eff}$

It is now evaluated whether the value of $k_{eff}$ from the PCT-A rate of SRL EA glass provides an appropriate upper bound for the dissolution rates of other reference glasses. Values of $k_{PCT-A, ref}$ were extracted from the measured PCT-A rates of 11 different waste glasses for direct comparison with the value extracted from the measured PCT-A rate for SRL EA glass. The measured PCT-A rates, the measured final pH, and the extracted value of log $k_{eff}$ are summarized in Table 4. These results show that the value of $k_{eff}$ determined based on the PCT-A rate of

SRL EA glass bounds all the glasses that were evaluated except for PNL 76-68 glass, which is not a reference waste glass. The PNL 76-68 glass was included in the suite of glasses that were tested as a glass without added aluminum to provide a bound for measuring the effect of the aluminum content. The PNL 76-68 glass also had the highest intrinsic dissolution rate constant of the glasses that were evaluated (see Table 2). Nevertheless, it is important to note that the value of $\log_{10} k_{eff}$ for a glass that has a lower release of boron in PCT-A than the EA glass can have a higher value of $\log_{10} k_{eff}$ than the EA glass. This is because the influence of the pH on the dissolution rate in the PCT-A is taken into account in the extraction of $\log_{10} k_{eff}$ from the PCT-A results.

The options considered for selecting the values of $k_{eff}$ that are expected to bound the values for a range of potential waste glasses are summarized below in the order of increasing level of conservatism.

**Option 1**–Use the average PCT-A rate measured for reference glasses: $k_{eff} = k_{PCT\text{-}A,\ ref} \bullet (1\text{-}Q/K)_{PCT\text{-}A,\ ref}$.

This option uses the average value of the dissolution rates of six reference glasses measured with PCT-A directly to determine the value of the effective rate constant. The glass compositions that were tested span the expected composition range for waste glasses with regard to the aluminum, sodium, and silicon contents. From the values given in Table 4, the mean value of log $k_{eff}$ for the seven reference HLW glasses (SRL 131U, SRL 202U, SRL 200S, SRL 51S, SRL 165U, WV ref 6, and Hanford D) is $\log_{10}k_{PCT\text{-}A,\ ref} = 6.41$ g/(m$^2$•d) and the standard deviation is 0.27 g/(m$^2$•d). The mean for all glasses in Table 4 except EA glass is $\log_{10}k_{PCT\text{-}A,\ ref} = 6.41$ g/(m$^2$•d) and the standard deviation is 0.50 g/(m$^2$•d).

**Option 2**–Average dissolution rate of EA glass in PCT conducted in tuff groundwater: $k_{eff} = k_{PCT\text{-}B,\ EA} \bullet (1\text{-}Q/K)_{PCT\text{-}B,\ EA}$.

The dissolution rate in tuff groundwater is more repository-relevant than the rate measured in demineralized water with PCT-A because the composition of the leachant is similar to that of groundwater likely to first contact the waste glass. The average dissolution rate of EA glass in a tuff groundwater is about 0.64 g/(m$^2$•d) at pH 11.61, and the value of $\log_{10}k_{PCT\ B,\ EA}$ extracted from these results is 7.00 g/(m$^2$•d) (Ebert 2000e). The dissolution rate in tests in tuff groundwater based on the release of boron is about one-half of the rate measured with PCT-A in demineralized water (see option 3). This is because the dissolved silicon already present in the groundwater solution used in the tests (approximately 46 mg/L; Ebert et al. 1998, Table 2, p. 29) has a significant effect on the dissolution rate as measured by the release of boron.

**Option 3**–Use the average dissolution rate of EA glass in PCT-A: $k_{eff} = k_{PCT\text{-}A,\ EA} \bullet (1\text{-}Q/K)_{PCT\text{-}A,\ EA}$.

The average dissolution rate in PCT-A (which is referred to in this report as the PCT-A rate) is calculated by dividing the normalized mass loss by the test duration, which is seven days. The PCT-A rate includes the effect of the buildup of dissolved glass components during the test. The average boron concentration for PCT-A conducted with the EA glass at three different laboratories is 553 ± 30 mg/L and the average pH is 11.87 (Ebert 2000e). The average normalized dissolution rate is calculated by dividing the concentration by the mass fraction of boron in the EA glass, which is 0.0347, by the S/V ratio of the test, which is 2000 $m^{-1}$, and by the test duration, which is 7 days. The average dissolution rate in PCT-A is calculated to be about 1.17 $g/(m^2 \bullet d)$ at pH 11.87. The calculated value of $\log_{10}k_{eff}$ is 7.15 $g/(m^2 \bullet d)$; the uncertainty is estimated to be 0.05 $g/(m^2 \bullet d)$.

This option empirically relates the bounding dissolution rate to the product acceptance requirement for vitrified waste forms; the WASRD requires vitrified waste forms to have lower releases of soluble components than the EA glass in the 7-day PCT-A (DOE 1996, Sec. 1.3.1). This is tantamount to requiring the PCT-A rates of all accepted waste glasses to be less than the PCT-A rate of the EA glass. However, because different pH values will likely be attained in tests with different glasses, the values of $k_{eff}$ for all waste glasses accepted for disposal will not necessarily be less than $k_{eff}$ for the EA glass. Since the values of $k_{eff}$ for all future waste glass compositions will be available for comparison with $k_{eff}$ for the EA glass; this option provides a useful upper bound.

**Option 4**–Use the intrinsic dissolution rate measured for reference glasses: $k_{eff} = k_{0, ref}$.

This option uses the intrinsic dissolution rates that have been measured for reference waste glasses to determine the effective rate constant. Forward dissolution rates measured with short-term MCC-1 tests for six reference glasses likely to bound the compositions of waste forms for DWPF, WVDP, and Hanford were presented earlier in this report (see Table 3). The mean and standard deviation for the intrinsic dissolution rates of glasses that were analyzed is $\log_{10}k_{0, ref} = 7.91 \pm 0.16$ $g/(m^2 \bullet d)$ (Ebert 2000j).

The values of $k_{eff}$ extracted from these tests are summarized in Table 5 for values calculated based on the releases of boron. Bounding values are calculated as the mean plus two standard deviations in order to directly compare the values of $\log_{10}k_{eff}$. The highest bounding value of $\log_{10}k_{eff}$ is that calculated using the forward rates of the tests with reference glasses (Option 4, $k_{eff} = k_{f, ref}$); these provide the most conservative estimates that have been measured. However, this bound is overly conservative because it neglects the slowing effect of the affinity term on the dissolution rate. The lowest bounding value of $\log_{10}k_{eff}$ is that calculated using the PCT-A rates for tests with reference glasses ($k_{PCT\text{-}A, ref}$).

Table 5. Values of $\log_{10}k_{eff}$ for Different Options

| Option | Method | $\log_{10}k_{eff}$ (B), $g/(m^2•d)$[a] | |
|---|---|---|---|
| | | mean ± s[b] | Bounding Value[c] |
| 1 (all glasses) | $k_{eff} = k_{PCT-A, ref}$ | 6.47 ± 0.49 | 7.45 |
| 1 (all glasses except SRL EA) | $k_{eff} = k_{PCT-A, ref}$ | 6.41 ± 0.50 | 7.41 |
| 1 (HLW reference glasses) | $k_{eff} = k_{PCT-A, ref}$ | 6.41 ± 0.27 | 6.95 |
| 2 | $k_{eff} = k_{PCT-B, EA}$ | 7.00 ± 0.05 | 7.10 |
| 3 | $k_{eff} = k_{PCT-A, EA}$ | 7.15 ± 0.05 | 7.25 |
| 4 | $k_{eff} = k_{0, ref}$ | 7.91 ± 0.16 | 8.23 |

NOTES: [a] Effective rate constant based on release of boron.
[b] mean ± one standard deviation.
[c] Upper bound to value of $\log_{10}k_{eff}$ is calculated as the mean plus two standard deviations.

The range of values for $\log_{10} k_{eff}$ used in the abstracted model for TSPA-SR for dissolution in the high pH leg is based on the values determined with Option 1 with all glasses in Table 4 except SRL EA glass. The upper bound to the value of $\log_{10} k_{eff}$ for the high pH leg is taken as the mean value for $\log_{10} k_{PCT-A,ref}$ plus two standard deviations (which is 7.41 $g/(m^2•d)$) and the lower bound is taken as the mean value of $\log_{10} k_{PCT-A, ref}$ for HLW reference glasses (which is 6.41 $g/(m^2•d)$). The recommended range from 6.41 to 7.41 $g/(m^2•d)$ is expressed (to two significant figures) as 6.9 ± 0.5 $g/(m^2•d)$. The upper limit of 7.41 $g/(m^2•d)$ bounds the value extracted from the PCT-A rate for the SRL EA glass. It also bounds the value extracted for the PNL 76-68 glass, which is $\log_{10} k_{eff} = 7.30$ $g/(m^2•d)$ (see Table 4) and takes into account the possibility that a waste glass could be less reactive than the SRL EA glass in PCT–A, but still have a higher long-term (i.e., Stage III) dissolution rate than the SRL EA glass.

A similar analysis cannot be performed for dissolution in the low pH leg, because test results are not available. The dissolution of waste glasses in PCT-A and in long-term tests that enter Stage III results in pH values on the basic leg. The value of the affinity term that is needed to define a bounding rate expression for dissolution in acidic solutions cannot be determined from the results of Knauss et al. (1990), because those test conditions maintained the value of the affinity term near one. Instead, the mean value and standard deviation of the intrinsic rate constant measured by Knauss et al. (1990) for dissolution in acidic solutions, which was 9 ± 1 $g/(m^2•d)$ (Section 6.2.1.3), is used to set the bounds to the value of $\log_{10} k_{eff}$ for the low pH leg. The lower bound to the value of $\log_{10} k_{eff}$ for the low pH leg is taken as the mean value for $\log_{10} k_0$ minus one standard deviation and the upper bound is taken as the mean value plus one standard deviation. The recommended range is expressed as 9 ± 1 $g/(m^2•d)$.

The bounding rate expressions for dissolution of glass immersed in water selected based on evaluation of the available data are:

For the low pH leg ($pH < pH_m$):

$$\log_{10} rate = (9 \pm 1) + (-0.6 \pm 0.1) \bullet pH + \log_{10}(\exp((-58 \pm 15)\ kJ/mol/(RT))) \qquad \text{(Eq. 7)}$$

For the high pH leg ($pH \geq pH_m$):

$$\log_{10} \text{rate} = (6.9 \pm 0.5) + (0.4 \pm 0.1) \bullet pH + \log_{10}(\exp((-80 \pm 10)\ \text{kJ/mol}/(RT))) \qquad \text{(Eq. 8)}$$

The use of separate rate expressions for the low and high pH legs requires identification of the pH ranges at which the different expressions are used. This is done by calculating the pH at which the rates for Equations 7 and 8 are equal at a given temperature. By equating Equations 7 and 8, the pH values at which the rates are equal (i.e., the minimum of the "V") can be calculated for the mean values with the following expression:

$$pH_m = 2.1 + 1149/T \qquad \text{(Eq. 9)}$$

where $pH_m$ is the pH value at which the minimum rate occurs and T is the absolute temperature. If $pH < pH_m$ at the temperature of interest, then the rate parameters for the low pH leg are used. If $pH \geq pH_m$ at the temperature of interest, then the rate parameters for the high pH leg are used. The dissolution rates calculated with the mean values and using equations 8 and 9 at several temperatures and pH values are given in Table 6.

Table 6. Dissolution Rates Calculated with Equations 7 and 8, values given as $\log_{10}$ rate, $g/(m^2 \bullet d)$

| | Rates Calculated with Equation 7 | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | pH | | | | | | | |
| Temperature (°C) | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| 15 | -2.12 | -2.72 | -3.32 | -4.52 | -5.12 | - | - | - |
| 20 | -1.94 | -2.54 | -3.14 | -4.34 | -4.94 | - | - | - |
| 25 | -1.77 | -2.37 | -2.97 | -4.17 | - | - | - | - |
| 30 | -1.60 | -2.20 | -2.80 | -4.00 | - | - | - | - |
| 35 | -1.44 | -2.04 | -2.64 | -3.84 | - | - | - | - |
| 40 | -1.28 | -1.88 | -2.48 | -3.68 | - | - | - | - |
| 45 | -1.13 | -1.73 | -2.33 | -3.53 | - | - | - | - |
| 50 | -0.98 | -1.58 | -2.18 | -3.38 | - | - | - | - |
| 55 | -0.84 | -1.44 | -2.04 | -3.24 | - | - | - | - |
| 60 | -0.70 | -1.30 | -1.90 | -3.10 | - | - | - | - |
| 65 | -0.56 | -1.16 | -1.76 | -2.96 | - | - | - | - |
| 70 | -0.43 | -1.03 | -1.63 | -2.83 | - | - | - | - |
| 75 | -0.31 | -0.91 | -1.51 | -2.71 | - | - | - | - |
| 80 | -0.18 | -0.78 | -1.38 | -2.58 | - | - | - | - |
| 85 | -0.06 | -0.66 | -1.26 | -2.46 | - | - | - | - |
| 90 | 0.05 | -0.55 | -1.15 | -2.35 | - | - | - | - |
| 95 | 0.17 | -0.43 | -1.03 | -2.23 | - | - | - | - |
| 100 | 0.28 | -0.32 | -0.92 | -2.12 | - | - | - | - |
| 105 | 0.38 | -0.22 | -0.82 | -2.02 | - | - | - | - |
| 110 | 0.49 | -0.11 | -0.71 | -1.91 | - | - | - | - |
| 115 | 0.59 | -0.01 | -0.61 | -1.81 | - | - | - | - |
| 120 | 0.69 | 0.09 | -0.51 | -1.71 | - | - | - | - |
| | Rates Calculated with Equation 8 | | | | | | | |
| | pH | | | | | | | |
| Temperature (°C) | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| 15 | - | - | -4.81 | -4.41 | -4.01 | -3.61 | -3.21 | -2.81 |
| 20 | - | - | -4.56 | -4.16 | -3.76 | -3.36 | -2.96 | -2.56 |
| 25 | - | -4.72 | -4.32 | -3.92 | -3.52 | -3.12 | -2.72 | -2.32 |
| 30 | - | -4.49 | -4.09 | -3.69 | -3.29 | -2.89 | -2.49 | -2.09 |
| 35 | - | -4.27 | -3.87 | -3.47 | -3.07 | -2.67 | -2.27 | -1.87 |
| 40 | - | -4.05 | -3.65 | -3.25 | -2.85 | -2.45 | -2.05 | -1.65 |
| 45 | - | -3.84 | -3.44 | -3.04 | -2.64 | -2.24 | -1.84 | -1.44 |
| 50 | - | -3.64 | -3.24 | -2.84 | -2.44 | -2.04 | -1.64 | -1.24 |
| 55 | - | -3.44 | -3.04 | -2.64 | -2.24 | -1.84 | -1.44 | -1.04 |
| 60 | - | -3.25 | -2.85 | -2.45 | -2.05 | -1.65 | -1.25 | -0.85 |
| 65 | - | -3.06 | -2.66 | -2.26 | -1.86 | -1.46 | -1.06 | -0.66 |
| 70 | - | -2.88 | -2.48 | -2.08 | -1.68 | -1.28 | -0.88 | -0.48 |
| 75 | - | -2.71 | -2.31 | -1.91 | -1.51 | -1.11 | -0.71 | -0.31 |
| 80 | - | -2.54 | -2.14 | -1.74 | -1.34 | -0.94 | -0.54 | -0.14 |
| 85 | - | -2.37 | -1.97 | -1.57 | -1.17 | -0.77 | -0.37 | 0.03 |
| 90 | - | -2.21 | -1.81 | -1.41 | -1.01 | -0.61 | -0.21 | 0.19 |
| 95 | - | -2.06 | -1.66 | -1.26 | -0.86 | -0.46 | -0.06 | 0.34 |
| 100 | - | -1.90 | -1.50 | -1.10 | -0.70 | -0.30 | 0.10 | 0.50 |
| 105 | - | -1.76 | -1.36 | -0.96 | -0.56 | -0.16 | 0.24 | 0.64 |
| 110 | - | -1.61 | -1.21 | -0.81 | -0.41 | -0.01 | 0.39 | 0.79 |
| 115 | - | -1.47 | -1.07 | -0.67 | -0.27 | 0.13 | 0.53 | 0.93 |
| 120 | - | -1.33 | -0.93 | -0.53 | -0.13 | 0.27 | 0.67 | 1.07 |

## 6.3 DISSOLUTION OF GLASS EXPOSED TO HUMID AIR OR DRIPPING WATER

### 6.3.1 Introduction

In the unsaturated environment of the proposed Yucca Mountain site, it is likely that waste glass will be contacted initially by humid air. When glass is exposed to humid air, water molecules will sorb onto specific sites on the glass surface, primarily silanol sites and alkali metal sites. The amount of water that sorbs on the glass will depend on the relative humidity of the air, the temperature of the glass surface, and the hygroscopicity of the glass surface. The sorption isotherm for water on a reference waste glass made with SRL 165 frit has been measured at about 23°C (Ebert et al. 1991b, Fig. 1b, p. 134). The measured isotherm was fit using the following equation:

$$\theta = \{-b / \ln(RH/100)\}^{1/r} \qquad \text{(Eq. 10)}$$

where $\theta$ is the number of layers of sorbed water, RH is the relative humidity, b and r are constants with values of $b = 3.2$ and $r = 1.5$ for SRL 165U glass. That isotherm is shown in Figure 2. The shape of the isotherm for the waste glass is similar to isotherms for water on silica and quartz (Hagymassy et al. 1969, p. 489). The first layer forms at a relative humidity of only a few percent. This corresponds to sorption at the primary sites. Subsequent layers form as water vapor bonds with sorbed water to form beads of water on the glass surface. The amount of sorbed water increases to about 6 layers when the relative humidity is about 60% and 10 layers when the relative humidity is about 80%. At relative humidities above about 80%, a sufficient amount of water has condensed to coalesce into a thin film covering the entire surface.

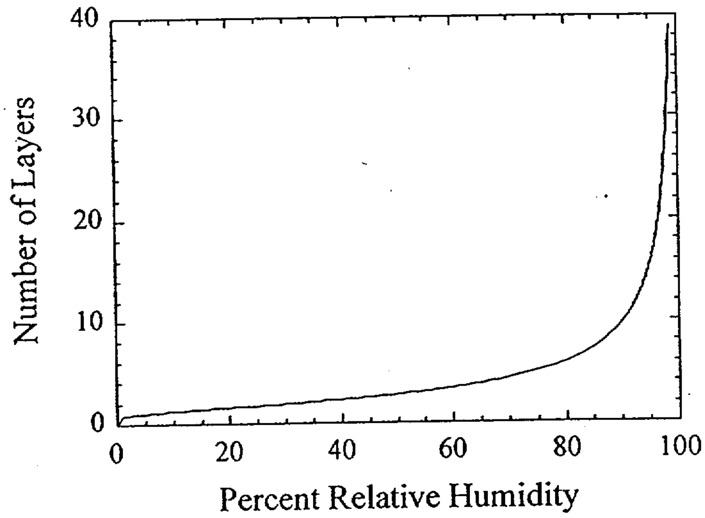

Figure 2. Sorption Isotherm for Water on SRL 165 Glass at Room Temperature

The thickness of the water film increases sharply at relative humidities above about 80% until about 40 layers form at 100% relative humidity. No hysteresis was observed in the isotherm collected for the waste glass, which indicates that the sorbed water did not react with the glass at this temperature and did not condense in tight pores during the time the isotherm was measured (several days).

Isotherms for the sorption of water on waste glass have not been measured at higher temperatures. It is presumed that a similar relationship between the amount of water that forms on the glass and the relative humidity occurs at higher temperatures. However, at higher temperatures the glass will react with the water. Initial reactions will likely result in the dissolution of alkali metals into the film of water. This will decrease the equilibrium vapor pressure of the film of water and cause more water to condense in the film. After the initial film of water is sorbed, the amount of water on the glass will likely be determined by the salinity of the film rather than the relative humidity. Therefore, the glass corrosion rate is assumed to be nil when the relative humidity is below 80% and is calculated as a function of the temperature when the relative humidity is between 80 and 100%.

In an open system such as the disposal system, water vapor will continually condense in the film of saline water on the exposed waste glass as the glass corrodes. For the various configurations in which fractured glass may be contacted by humid air or dripping water, water may drip or flow away from the glass or may accumulate over time while contacting the glass. Once alkali metals are released into the film of water, the hygroscopicity of the film will result in continuous condensation of water vapor. Continuous exposure to water-saturated air will result in a process of vapor condensation, flow across the sample, and dripping wherein dissolved species can be transported away from the glass as solution drips from the glass, and fresh water vapor continually condenses. The corrosion rate of the glass under these conditions will be affected by the rates at which water vapor condenses in the film, and solution drips from the sample. These processes will affect the glass dissolution rate through their effects on the solution chemistry of the film. The effects of the condensation, flow, and drip rates on the glass dissolution rate are taken into account in the model empirically in combination with other parameters by the use of an experimentally measured rate constant.

Two cases of corrosion in humid air that can be related to the availability of water vapor have been examined experimentally. In the first case, the film of water that forms on the glass remains static for long times if a limited amount of vapor contacts the glass. Vapor hydration tests conducted with a limited amount of water so that water does not drip from the glass during the test have been used to promote the formation of alteration phases to identify the phases that form, determine if they contain radionuclides, and determine if their formation increases the glass dissolution rate. Tests have shown that radionuclides become incorporated into alteration phases that form on the specimen surface (Ebert et al. 1991a, p. 212). Subsequent exposure of vapor-hydrated glass to liquid water results in a rapid release of radionuclides from the alteration layer into solution as dissolved and colloidal species (Bates et al. 1990, Table 5, p. 1100). Radionuclides that are retained in soluble phases (e.g., technetium, neptunium, uranium, etc.) during vapor hydration will be released when those phases are contacted by dripping water or become immersed. Radionuclides that are retained in sparingly soluble phases during vapor hydration are more likely to be released as radiocolloids from spalled alteration phases.

In the second case, either enough water is added to the vessel initially that dripping occurs or water is periodically added to the test vessel so that water drips from the sample. The release of radionuclides from glasses that were initially vapor-hydrated and subsequently contacted by dripping water over a long time showed similar behavior to static tests: soluble phases containing B and Np were dissolved from the altered surface rapidly upon initial contact with dripping water. Whereas, the release of components such as Pu from sparingly soluble phases was much slower (Ebert 2000g).

### 6.3.2 Modeling Corrosion in a Thin Film of Water as a Special Case of Aqueous Corrosion

The corrosion behavior of glass contacted by a thin film of water is treated in the abstraction as a special case of aqueous corrosion that can be described using the same rate expression used for immersion, which is given in Equation 3. The following describes the analyses done to apply this rate expression to corrosion in humid air and in dripping water.

The pH of the solution in contact with the glass during reaction in water vapor will affect the glass dissolution rate. Although the chemistry of the film of water that forms on the glass by condensation of water vapor will initially be dominated by dissolved carbon dioxide gas ($CO_2$) and may be slightly acidic, the solution pH will immediately be driven to alkaline values as the glass dissolves. The pH values of water remaining on the glass surface measured at the end of vapor hydration tests are typically pH 11 or higher when alteration phases are present. The very high pH values attained when glass reacts with the film of water is due primarily to reactions between water and alkali metals in the glass which produces hydroxide ions. The pH value of the small volume of the water film increases significantly even after very little hydroxide is produced. An upper limit to the pH is expected as ion exchange reactions approach equilibrium. The most abundant alkali metal in waste glasses is sodium, much of which is present as a modifying cation associated with silanol groups. Sodium that is present for charge compensation for trivalent cations such as aluminum, boron, and iron occupy silicon sites in the lattice is not released by ion exchange reactions to as significant an extent as sodium that is associated with silanol groups (Smets and Lommen 1982, p. 86). The reaction between glass and water to release sodium associated with silanol can be written as

$$\text{glass}{\equiv}\text{SiO-Na} + H_2O \leftrightarrow \text{glass}{\equiv}\text{SiO-H} + Na^+ + OH^- \qquad \text{(Eq. 11)}$$

The first term in the reaction in Eq. 11 represents sodium bonded to a silanol group, which includes a silicon atom bonded to three oxygen atoms in the glass (glass≡Si) and to another oxygen that is also bonded to the sodium (O-Na). The second term represents a water molecule ($H_2O$). The first term on the right side of the reaction shows the sodium atom has been replaced by a proton (H). The fourth and fifth terms represent sodium ($Na^+$) and hydroxide ($OH^-$) ions in solution, respectively. The exchange of protons from water for sodium bonded to silanol sites in the glass is sensitive to the solution concentration of sodium and the pH. The equilibrium constant for the above reaction (measured in tests with silica gel) is about $1 \times 10^{-7}$ at 50°C (Dugger et al. 1964, Table 1, p. 759). The equilibrium constant is only weakly dependent on temperature and is expected to have a similar value at 90°C. The equilibrium pH value depends on the concentration of $Na^+$. Consider the case in which the sodium concentration is 1 millimolar. Under these conditions, sodium ions bonded to the silanol groups in the glass will be replaced by protons from solution and sodium will be released from the glass at pH values below about 8. Under these conditions, sodium will be released from the glass until the solution pH reaches a value of about 12, at which point the release of sodium (and hydroxide production that occurs due to the release of sodium by ion exchange) will become negligible. At pH values above about 12, protons on the silanol groups will be replaced by sodium from solution. At higher sodium concentrations, the exchange reaction to release sodium from the glass will become negligible at even lower pH values.

That an upper limit to the solution pH will occur for reaction in water vapor is supported by the observation that upper limits to pH values have been observed in static dissolution tests at 90°C with reference waste glasses. The pH values are generally less than 12 (measured at room temperature), although higher pH values can be attained at extremely high S/V ratios (Feng and Pegg 1994, Fig. 1, p. 284; Ebert 1993, Fig. 1, p. 59). Therefore, the pH of the thin film of water is modeled to quickly attain a high value, then remain constant. Following the approach developed for corrosion of glass immersed in water, the pH term in the rate expression for corrosion in humid air and dripping water is combined with the intrinsic dissolution rate and affinity terms as an effective rate constant for dissolution in a thin film of water. In the rate expression for dissolution in a thin film of water, the separate values of the intrinsic dissolution rate, pH term, and affinity term are not specified. Instead, the combined influence of these parameters is represented by the rate coefficient, the value of which is determined from experimental results. The dissolution rate of glass exposed to a thin film of water is calculated as a function only of the temperature of the glass surface using the following expression:

$$\text{Rate}/S = k_{tf} \exp(-E_{tf}/RT) \qquad \text{(Eq. 12)}$$

where Rate/S is the glass dissolution rate divided by S, which is the surface area of glass exposed, R is the gas constant, T is absolute temperature, and $k_{tf}$ is the rate coefficient. The temperature dependence for glass dissolution in humid air and dripping water environments is represented by an Arrhenius term, where $E_{tf}$ is the activation energy for dissolution in a thin film of water on the glass surface. Besides the intrinsic dissolution rate, pH term, and affinity term, the value of $k_{tf}$ also takes into account the effects of the water condensation rate and the water drip rate.

The values of $k_{tf}$ and $E_{tf}$ are determined from the results of vapor hydration tests conducted with an amount of water in excess of the amount needed to saturate the vapor phase and form a static film of water on the sample; excess water is used in the tests to establish a reflux within the test vessel between water vapor condensing in the film and solution dripping from the sample. Under these test conditions, some of the water that condenses onto the glass sample periodically drips off the sample into the bottom of the vessel. Water that drips from the sample carries with it dissolved glass components, which collect in the liquid water at the bottom of the vessel. Fresh water continuously condenses from the vapor into the film of water on the glass, the glass continues to dissolve, and drips fall from the sample into the bottom of the vessel. The glass dissolution rate is calculated from the amounts of glass components that accumulate in the water at the vessel bottom.

There are several differences that must be considered when using test results to model the disposal system. One difference between the test conditions and the disposal system is that fresh water vapor is continuously supplied in the disposal system at a nearly constant humidity, whereas the water vapor in the test vessel is recycled by evaporation of the liquid water in the bottom of the vessel. The vapor pressure in equilibrium with the solution in the bottom of the vessel will decrease as dissolved glass components build up in the solution. This may have a minor effect on the condensation rate. The effect of the decrease in vapor pressure on the glass dissolution rate will be coupled with the glass dissolution rate and drip rate in the overall rate that is measured in the laboratory tests. Other differences include scale and configuration. Water can accumulate within cracks in the glass and within breached canisters. The difference in the configuration of the laboratory tests and the canistered glass adds conservatism to the calculated dissolution rates. That is because the rates measured in laboratory tests are for dissolution of glass at free surfaces while most of the surface of waste forms will be within tight cracks. As discussed in Section 6.1.2, the dissolution rate of glass in tight cracks is slower than the dissolution rate of free surfaces. However, the difference cannot be quantified.

The dissolution rates of two reference high level waste glasses were measured in drip tests conducted at 90°C; the dissolution rate in drip tests with a SRL 165 frit-based glass (a reference glass for DWPF waste forms) was measured to be about $5 \times 10^{-3}$ g/(m$^2$•d). The glass dissolution rate in drip tests with ATM-10 glass (a reference glass for the WVDP waste form) was measured to be about $7 \times 10^{-3}$ g/(m$^2$•d) (both rates are based on the release of boron) (Ebert 2000g). The value of $k_{tf}$ can be extracted from these results by using the same activation energy that is used for aqueous dissolution, namely, 80 kJ/mol. The same activation energy is used for the different exposure modes because the rate-limiting step for glass dissolution, namely, hydrolysis of silicon-oxygen bonds (see Section 6.1.1), is the same. The calculated values are $\log k_{tf} = 9.2$ g/(m$^2$•d) for SRL 165 glass and $\log k_{tf} = 9.4$ g/(m$^2$•d) for ATM-10 glass. These rates are used for all waste glass compositions exposed to dripping water and humid air. The use of the same parameter value for the dissolution of different glass compositions is corroborated by the finding that there was little difference in the intrinsic dissolution rates for a wide range of glass compositions in immersion tests (Section 6.2.1.2). The rate expression for dissolution of glass exposed to humid air or dripping water is:

For exposure to dripping water (at all relative humidites)

$$\log_{10}\{\text{Rate/S, g/(m}^2\bullet\text{d)}\} = 9.2 \pm 0.2 \text{ g/(m}^2\bullet\text{d)} + \log_{10}\{\exp[(-80 \pm 10\text{kJ/mol})/RT]\} \quad \text{(Eq. 13)}$$

The same rate expression and parameter values are used for exposure to relative humidities of 80% or greater.

For relative humidities less than 80% and no dripping water, the Rate = 0.

Analysis of the available information indicates that the same abstraction of the mechanistic rate expression (which is given in Equation 3) can be used for glass contacted by humid air and dripping water. This is expected since glass corrosion occurs in a thin film of water whether the glass is exposed to humid air or dripping water. In the abstraction of the rate expression for glass dissolution in a thin film of water, the intrinsic dissolution rate ($k_0$), the pH dependence, and the affinity term (1-Q/K) are combined into a single term called the thin film rate, $k_{tf}$. The use of this rate expression in performance assessment calculations will require knowledge of the surface area that is contacted by a thin film of water due to exposure to humid air or dripping water, the relative humidity, and the temperature. The use of the rate expression for glass immersed in water will require knowledge of the surface area that is immersed. In the following example, it is shown that use of the rate expression for immersion provides a conservative representation of the rate of glass dissolution under all three contact modes. Because glass dissolution will occur under alkaline conditions when contacted by humid air or dripping water (Section 6.3), the dissolution rates predicted by using Equation 12 for dissolution in a thin film are compared with the dissolution rates predicted by using Equation 5 for dissolution by immersion with the parameter values for the alkaline leg. Taking the logarithms of these expressions and substituting the parameter values results in the following rate equations.

The dissolution rate for the alkaline leg of corrosion by immersion is obtained using the mean values for Equation 8 and expressing the dissolution rate as $\mathrm{Rate}_{im}/S_{im}$, where $\mathrm{Rate}_{im}$ and $S_{im}$ give the rate of glass dissolution for immersion and the surface area that is immersed:

$$\log_{10} \mathrm{Rate}_{im}/S_{im} = 6.9 + 0.4 \bullet \mathrm{pH} + \log_{10}\{\exp(-80/RT)\} \qquad \text{(Eq. 14)}$$

The dissolution rate for glass exposed to a thin film of water is obtained using the mean values for Equation 13 and expressing the dissolution rate as $\mathrm{Rate}_{tf}/S_{tf}$, where $\mathrm{Rate}_{tf}$ and $S_{tf}$ give the rate of glass dissolution for contact by a thin film of water and the surface area that is contacted:

$$\log_{10} (\mathrm{Rate}_{tf}/S_{tf}) = 9.2 + \log_{10}\{\exp(-80/RT)\} \qquad \text{(Eq. 15)}$$

Taking the difference between Equations 14 and 15:

$$\log_{10} \mathrm{Rate}_{im}/S_{im} - \log_{10} (\mathrm{Rate}_{tf}/S_{tf}) = 0.4 \bullet \mathrm{pH} - 2.3 \qquad \text{(Eq. 16)}$$

The calculated rates are the same for glass that is immersed in water and glass contacted by a thin film of water when the pH is 5.75. Only when the pH is less than 5.75 will the dissolution rate (per unit area) predicted by the rate expression for immersion will be lower than that predicted by the rate expression for exposure to a thin film of water. At pH values equal or greater to 5.75, use of the rate expression for immersion for all contact modes will provide a conservative estimate for the glass dissolution rate. At pH values lower than 5.75, the rate expression for the acid leg for immersion should also be used for contact by humid air and dripping water. However, it is important to note that since laboratory tests results for contact by humid air and dripping water are in near neutral or alkaline solutions, no database exists to evaluate dissolution in acidic solutions under humid air or dripping conditions.

## 6.4 MODEL VALIDATION

The abstracted model in this report is designed to provide a conservative estimate of the rate (i.e., an upper bound or overestimate of the likely rate) at which waste glass will corrode when immersed in groundwater or exposed to humid air and/or dripping water in the repository.

Validation of the abstracted model involves presenting technical evidence that supports the contention that the abstracted model does provide an upper bound to the actual rate of waste glass corrosion in the repository. The general algebraic form of the proposed model is widely accepted and used in the literature of waste glass corrosion (e.g., Advocat et al. 1990; Bourcier 1994; Delage and Dussossoy 1991; Ebert 1993; Grambow et al. 1986; Knauss et al. 1990; McGrail et al. 1997a). This wide acceptance, combined with the data treatment discussed in sections 6.2 and 6.3 substantially validates the basic algebraic form of the model, namely, a forward reaction rate that depends on the glass composition, a dependence on the solution pH, an Arrhenius temperature dependence, and a term representing the feed-back effects of solutes. The approach adopted here to address model validation is to assess if the abstracted model (i.e., the general algebraic form together with the parameter values) is likely to conservatively bound the long-term rates based on the available database.

The current understanding of waste glass corrosion indicates that the predominant uncertainties in the long-term term corrosion rate in the repository are associated with the value of the $k_{eff}$ (i.e., $k_0 \bullet [1-Q/K]$ ) term in the model. The value of $k_{eff}$ is mathematically constrained to the range $k_o > k_{eff} > 0$. As discussed in Section 6.2.2 the appropriate value to use for $k_{eff}$ is uncertain. The available data show that the dissolution rate decreases monotonically over time in static or nearly static systems. However, for some compositions, after initially decreasing, the dissolution rate has been observed to increase to an apparently constant value which is referred to as $k_{III}$ in Section 6.2.3.1. Because the factors that trigger this increase in the glass corrosion rate (which is referred to as the "Stage III rate") are not well understood, the abstracted model conservatively assumes that an increase in the rate will occur for all waste glass compositions. The abstracted model also uses a conservative estimate for the value of the effective rate constant in Stage III, which is referred to as $k_{III}$. Specifically, for the high pH leg, the model uses the values of $k_{eff}$ extracted from the results of PCT-A tests (designated as $k_{PCT-A}$). The experimental evidence that the values of $k_{PCT-A}$ used in the abstracted model are likely to bound the values of $k_{III}$ is presented in Section 6.2.3.2. Also, the fact that the value of $k_{eff}$ selected for the abstracted model is close to the estimated values of $k_o$ (i.e., the intrinsic dissolution rate in the absence of solution feed-back effects) for a range of reference waste glass compositions (Table 2), and the conservative values selected for the other model parameters ($\eta$ and $E_a$) in Section 6.2.1, support the contention that the abstracted model is likely to provide a conservative upper bound to the long-term dissolution rate of waste glasses in the repository. Finally, the validity of neglecting the term $k_{long}$ in the abstracted rate expression (Equation 5) is considered. In the TSPA-VA, $k_{long}$ at 90°C was assigned a value of 0.002 $g/(m^2 \bullet d)$, so the value of $\log_{10} k_{long}$ is -2.70. The values of $\log_{10}$ rate calculated using the abstracted rate expression given in Table 6 at 90°C are greater than –2.70 and, therefore, bound the value of $\log_{10} k_{long}$. Since the temperature dependence of $\log_{10} k_{long}$ is the same as that for $\log_{10}$ rate, the rate calculated with the abstracted rate expression developed in this AMR will bound $k_{long}$ under all conditions, and neglect of $k_{long}$ in Equation 5 is justified.

The database available to validate the effective rate constant for the abstracted model only contains tests in which high pH values were attained, so only the rate expression for the high pH leg can be validated in this manner. Confidence that the expression for the low pH leg is conservative is based on the fact that the rates of all waste glasses are modeled to increase as the pH decreases. This is conservative because the rates of several reference waste glasses are known not to increase at pH values as low as 4.5.

The dissolution rates calculated using Equations 7 and 8 can be compared directly with the dissolution rate of basalts recovered from the sea bed. The dissolution rates of several basalt samples were calculated based on the thickness of the layer of palagonite that forms as an alteration phase and the age of the basalt (Grambow et al. 1996, Table 2, Fig. 3, pp. 268-269). The dissolution rates for basalts covered in sediment and exposed to Si-saturated seawater are about 0.1 μm/1000 yr, which is equivalent to $6 \times 10^{-7}$ g/(m$^2$•d). The dissolution rates calculated using Equations 7 and 8 at 3°C are $3.6 \times 10^{-6}$, $9.1 \times 10^{-6}$ and $2.3 \times 10^{-5}$ g/(m$^2$•d) at pH values of 7, 8, and 9, respectively, which is the typical pH range for seawater. Thus, the rate expression in this AMR is conservative with regard to the long-term dissolution rate of basalts.

The rate expressions for glass dissolution in acid and alkaline solutions will be compared with new information, if it becomes available, to further increase confidence in the validity of the model. If further validation of the model is needed to encompass potential composition and/or environmental conditions not specifically included in the derivation of the model, or if greater confidence in the model is required (for example, in the event that HLW glass degradation becomes a principal factor in the TSPA), this will be accomplished by confirmation testing as described in Section 17 of ASTM C1174-97 and/or by analysis of other appropriate experimental data that become available.

# 7. CONCLUSIONS

From the analyses described above, abstracted models were developed and parameter values were determined that can be used to calculate bounding values of the dissolution rates of waste glasses that are contacted by humid air or dripping water or are immersed in water. The parameter values were determined based on analysis of experimental results for reference waste glasses. The mechanistically-based rate expression for dissolution of glass in aqueous solutions can be abstracted as a simplified rate expression that includes terms that take into account the effects of pH and temperature explicitly and combines the effects of the glass composition and solution composition in a single parameter, $k_{eff}$. The value of $k_{eff}$ is selected so as to bound the dissolution rates of the full range of waste glass compositions over the service life of the disposal system, including the possible increase in the rate when alteration phases form. The bounding rate for the immersion of glass in water, the abstracted rate expression is:

$$\text{Rate} = S \bullet k_{eff} \bullet 10^{\eta \bullet pH} \bullet \exp(-E_a/RT) \qquad \text{(Eq. 17)}$$

where S is the surface area of glass that is exposed to humid air or dripping water, or is immersed. The initial surface area is estimated using the geometric surface area of each glass log and a cracking factor to account for surface area generated by fracturing (see Equation 4).

$$S_0 = f_{cracking} \bullet (2\pi r_o^2 + 2\pi r_o \bullet L_o) \qquad \text{(Eq. 4)}$$

An initial surface area of 94.6 m$^2$ is calculated based on the dimensions of the DWPF canister and weight of the glass waste form using a cracking factor of 20. The specific surface area is calculated by dividing the initial surface area by the initial weight of the glass log. The surface area that remains as the glass degrades is calculated as the product of the specific surface area and the mass of glass that remains. For the DWPF glass log, the specific surface area is 5.62 x $10^{-2}$ $m^2/kg$. Since the effective rate constant, $k_{eff}$, is expressed in units of $g/(m^2 \bullet d)$ (see below) and the surface area in units of $m^2$, the rate calculated with Equation 18 has units of g/d. The other terms in Equation 18 are dimensionless. Different parameter values are used for dissolution under conditions that are acidic or basic relative to the value of $pH_m$. The term $pH_m$ is used to identify the pH value at which the rate at a particular temperature is a minimum and to distinguish between the low pH and high pH legs. Equation 9 is used to calculate $pH_m$

$$pH_m = 2.1 + 1149/T \qquad \text{(Eq. 9)}$$

where T is absolute temperature (Kelvin). The bounding parameter values for the low pH and high pH legs are:

For the low pH leg ($pH < pH_m$)

$\log_{10} k_{eff} = 9 \pm 1$ $g/(m^2 \bullet d)$
$\eta = -0.6 \pm 0.1$
$E_a = 58 \pm 15$ kJ/mol

For the high pH leg ($pH \geq pH_m$)

$\log_{10} k_{eff} = 6.9 \pm 0.5$ $g/(m^2 \bullet d)$
$\eta = 0.4 \pm 0.1$
$E_a = 80 \pm 10$ kJ/mol

The value of $pH_m$ at a particular temperature can be calculated as the intersection of the high and low pH legs using the mean values of the parameters. The expression determined using the mean parameter values and the rate expression in Equation 18 is:

$$pH_m = 2.1 + 1149/T \qquad \text{(Eq. 9)}$$

where T is the absolute temperature (Kelvin). The value of $pH_m$ is used to determine which set of parameter values should be used for the temperature and pH conditions of interest. If the pH of interest is less than $pH_m$, then the parameters for the low pH leg should be used in the rate expression. If the pH of interest is greater than or equal to $pH_m$, then the parameters for the high pH leg should be used in the rate expression. The abstracted model parameters are listed in Table 7.

Table 7: Summary of HLW Degradation Model Parameters

| Parameter | Distribution Type | Mean | Minimum | Maximum | Units | Source | Section |
|---|---|---|---|---|---|---|---|
| Rate expression<br>Rate = $S \bullet k_{eff} \bullet 10^{\eta \bullet pH} \bullet \exp(-E_a/RT)$ | Calculated | | | | $g/(m^2 \bullet d)$ | ANL-EBS-MD-000016 REV00D | 6.2.3; 7 |
| $pH_m = 2.1 + 1149/T$ | Calculated | | | | none | ANL-EBS-MD-000016 REV00D | 6.2.3.3; 7 |
| for $pH < pH_m$; | | | | | | | |
| Rate coefficient $k_{eff,\ low}$ | Uniform | 9 | 8 | 10 | $g/(m^2 \bullet d)$ | ANL-EBS-MD-000016 REV00D | 6.2.3.3; 7 |
| pH dependence factor $\eta_{low}$ | Uniform | -0.6 | -0.5 | -0.7 | none | ANL-EBS-MD-000016 REV00D | 6.2.1.3; 7 |
| Temperature dependence factor $E_{a,\ low}$ | Uniform | 58 | 43 | 73 | kJ/mol | ANL-EBS-MD-000016 REV00D | 6.2.1.3; 7 |
| for pH   $pH_m$: | | | | | | | |
| Rate coefficient $k_{eff,\ high}$ | Uniform | 6.9 | 6.4 | 7.4 | $g/(m^2 \bullet d)$ | ANL-EBS-MD-000016 REV00D | 6.2.3.3; 7 |
| pH dependence factor $\eta_{high}$ | Uniform | 0.40 | 0.3 | 0.5 | none | ANL-EBS-MD-000016 REV00D | 6.2.1.2; 7 |
| Temperature dependence factor $E_{a,\ high}$ | Uniform | 80 | 70 | 90 | kJ/mol | ANL-EBS-MD-000016 REV00D | 6.2.1.2; 7 |
| Exposed Surface Area (initial)<br>$S_0 = f_{cracking} \bullet (2\pi r_o^2 + 2\pi r_o \bullet L_o)$ | Calculated | 100 | 95 | 105 | $m^2$ | ANL-EBS-MD-000016 REV00D | 6.2.1; 7 |
| Exposed Surface Area<br>$S = S_{sp}$ * mass of glass log | Calculated | | | | $m^2$ | ANL-EBS-MD-000016 REV00D | 6.2.1; 7 |
| Initial radius of glass log $r_o$ | Calculated | 0.30 | 0.30[a] | 0.30[a] | m | Stout and Leider 1998; Table 2.2.2.1-1 | 6.2.1; 7 |
| Initial length of glass log $L_o$ | Calculated | 2.35 | 2.21[b] | 2.49[c] | m | Stout and Leider 1998; Table 2.2.2.1-1 | 6.2.1; 7 |
| Mass of glass log | Calculated | 1775 | 1650[d, e] | 1900[c, e] | kg | Stout and Leider 1998; Table 2.2.2.1-1 | 6.2.1; 7 |
| Cracking factor: $f_{cracking}$ | Constant | 20 | 20 | 20 | none | ANL-EBS-MD-000016 REV00D | 6.2.1; 7 |
| Specific surface area<br>$S_{sp}$ = S/mass of glass log | Calculated | $5.63 \times 10^{-2}$ | $5.53 \times 10^{-2}$[c] | $5.73 \times 10^{-2}$[d] | $m^2/g$ | Readily Available | 6.2.1; 7 |
| Gas constant: R | Constant | 8.314 | 8.314 | 8.314 | $J/(mol \bullet K)$ | Readily Available | 6; 7 |

NOTES:
[a] Estimated based on DWPF, WVDP, and Hanford glass waste forms.
[b] Estimated based on DWPF and Hanford glass waste forms.
[c] Estimated based on WVDP glass waste forms.
[d] Estimated based on Hanford glass waste forms.
[e] Estimated initial mass based on DWPF, WVDP, and Hanford glass waste forms.

The abstractions of the rate expression for glass dissolution that are described in this AMR are intended to be applicable to waste glasses that meet the requirements for vitrified high-level waste forms (DOE 1996). The models and conclusions described in this document may be affected by technical product input information that requires confirmation. Any changes to the models and conclusions that may occur as a result of completing the confirmation activities will be reflected in subsequent revisions of this document. The status of the input information quality may be confirmed by review of the Document Input Reference System (DIRS) database.

The TBVs (to be verified) associated with this AMR and its related DIRS are the following: the experimental data used to provide regressed fitting constants for the rate expression in the degradation models; the form of the temperature dependence of the degradation rate; and the estimate of the accessible surface area of the HLW glass waste form to be used in calculating release in the TSPA-SR. Although testing of HLW glass remains in progress, it is expected that the TSPA-SR will not be sensitive to variations in the glass composition as long as the composition of the HLW glass conforms to the requirements in DOE (1996). The data that have been collected for glasses that conform to those requirements indicate that the TBVs on the degradation data and the assumptions for the temperature dependence will be satisfied through acceptance via publications in the peer-reviewed literature and/or data qualification process. The estimate of the surface area of glass exposed to water used in this AMR , namely, 20 times the geometric surface area of a glass log, is conservative. Further experiments and analyses are likely to support use of a multiplicative factor that is less than. Therefore, the impact of the surface area TBV on the TSPA-SR is considered to be small.

This document may be affected by technical product input information that requires confirmation. Any changes to the document that may occur as a result of completing the confirmation activities will be reflected in subsequent revisions. The status of the input information quality may be confirmed by review of the Document Input Reference System database.

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