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A Strategy for Maintenance of the Long-Term Performance Assessment of Immobilized Low-Activity Waste Glass

September 2016

JV Ryan
VL Freedman

U.S. DEPARTMENT OF
ENERGY

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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Executive Summary

Approximately 50 million gallons of high-level radioactive mixed waste has accumulated in 177 buried single- and double-shell tanks at the Hanford Site in southeastern Washington State as a result of the past production of nuclear materials, primarily for defense uses. The United States Department of Energy (DOE) is proceeding with plans to permanently dispose of this waste. Plans call for separating the tank waste into high-level waste (HLW) and low-activity waste (LAW) fractions, which will be vitrified at the Hanford Tank Waste Treatment and Immobilization Plant (WTP). Principal radionuclides of concern in LAW are ^{99}Tc, ^{129}I, and U, while non-radioactive contaminants of concern are Cr and nitrate/nitrite (with the latter not included in the glass). [1, 2] HLW glass will be sent off-site to an undetermined federal site for deep geological disposal while the much larger volume of immobilized low-activity waste will be placed in the on-site, near-surface Integrated Disposal Facility (IDF).

Before the immobilized low-activity waste (ILAW) can be disposed of, DOE must conduct a Performance Assessment (PA) for the IDF that describes the long-term impacts of the disposal facility on public health and environmental resources. The PA document provides an analysis of the long-term performance of the planned disposal system as a basis to set requirements for the waste form and the facility design. The PA sets these requirements such that they will protect the environment and long-term public health/safety and then demonstrates that those requirements can be met. An important provision of the PA is that as changes occur to the conceptual design and new information on elements of the disposal system becomes known, the PA will perform analyses to determine the impact of these new data on the performance of the system as a whole. Outputs of the PA include estimates of radionuclide release rates from the engineered portion of the disposal facility (source term). These estimates are expected to be based on chemical reactions that occur in the near-field and, in the case of the vitrified ILAW, are controlled by the dissolution of the vitrified matrix. Therefore, to provide credible estimates, a mechanistic understanding of the basic physical and geochemical processes that control glass dissolution and radionuclide release, must be incorporated into models to effectively simulate the glass-water reaction over the period of regulatory concern (1,000 years for compliance, 10,000 years for uncertainty analysis). The present document serves to provide a strategy and technical approach for testing programs to reduce uncertainties within the ILAW glass corrosion model.

Apart from glass composition, the dissolution rate is a function of temperature, pH, surface area of the glass exposed to the contacting solution, and composition of the solution contacting the glass. The temperature of the IDF is a known constant, 15°C. However, both the pH and the composition of the solution contacting the glass are variables that are affected by water infiltration rate, reactions with engineered and backfill materials, gas-water equilibria, secondary-phase precipitation, alkali-ion exchange, and the dissolution of the glass itself. Uncertainties are estimated and considered in the PA as a matter of course. Therefore, we have identified the following three areas to target the most potentially impactful remaining uncertainties in PA release rates due to glass. Their actual impact will be evaluated as part of the ongoing PA and the development of the PA maintenance program.

1. Improvements in secondary phase identification and geochemical parameterization

The potential acceleration of the glass reaction rate after long times at low reaction rates that is termed Stage III dissolution is one of the glass performance modeling uncertainties that has the potential to impact release concentration limits. Stage III dissolution behavior is thought to be caused by the

precipitation of zeolite phases that lower the activity of the rate-controlling orthosilicic acid ion and cause the acceleration of glass dissolution. The uncertainty lies mainly in a poor understanding of the thermodynamics and kinetics of formation, and indeed even identity, of these key crystalline phases at the low temperatures associated with the IDF. We therefore recommend the development of a testing program to identify the key secondary phases and evaluate their geochemical parameters and growth rate at low temperatures.

2. Compositional coverage for produced glasses

As glass compositions with improved performance are developed (higher waste loading, higher crystal tolerance, improved melt rate/throughput, etc.), it is important to ensure that the rate law parameter sets and uncertainties used for the PA cover any new glass compositions that are designed. Alternatively, new parameter values should be defined so that they cover the new composition space. To this end, the ILAW glass rate law parameters used to calculate glass corrosion rates (as described in this report) should be measured for a subset of new glass compositions, providing reasonable assurance that the parameter set(s) used are valid for the entire set of projected glass compositions within uncertainty and sensitivity of the PA analyses, without the need to test all glasses predicted. Glass compositions should be selected for testing with a full consultation of the formulation teams with the goal of ensuring the expanded compositions are covered under the parameter space.

3. Improvements in ion exchange modeling

Rate release calculations currently assume a constant flux from Na-ion exchange, which is a simplification of the coupling of the actual diffusive process with a constantly dissolving dissolution front. Particularly when dissolution has slowed due to a high activity of orthosilicic acid, the ion exchange mechanism has an impact on the pH of the contacting solution due to the consumption of either H^+ or H_3O^+ from solution. These pH increases affect both the glass dissolution rate and the precipitation of secondary phases (which then impacts the dissolution rate). Another reduction in uncertainty would be obtained through the adoption of a parameterized diffusive term for the ion exchange mechanism to replace the constant currently used. Presently, the constant value is measured for only one condition, with acknowledged differences in other conditions accounted for by uncertainty ranges. The use of a diffusion-controlled alkali release term would increase the versatility and accuracy of the r_{IEX} term, putting it on a solid technical basis no matter the dissolution conditions. This should be a relatively simple effort, due to the presence of models used by industry for ion-exchange strengthening applications (such as Corning Incorporated’s Gorilla Glass™) and recent connection of those formalisms to lower temperatures.

The adoption of these recommendations would further improve and define the technical basis of the glass dissolution model used as an input to the PA. Particularly with respect to a greater understanding and accounting for the secondary phases associated with Stage III dissolution behavior, the increased knowledge obtained through this program will determine the impact of recent relevant findings and improve the estimates of long-term performance, per the guidance of the PA documents.

Quality Management Program

This work was conducted with funding from Washington River Protection Solutions (WRPS) under contract 36437-161, ILAW Glass Testing for Disposal at IDF. The work was conducted as part of Pacific Northwest National Laboratory (PNNL) Project 66309 and follow-on Project 68391, ILAW Glass Testing for Disposal at IDF.

All research and development work at PNNL is performed in accordance with PNNL's laboratory-level Quality Management Program, which is based on a graded application of NQA-1-2000, *Quality Assurance Requirements for Nuclear Facility Applications*, to R&D activities. In addition to the PNNL-wide quality assurance (QA) controls, the QA controls of the WRPS Waste Form Testing Program (WWFTP) QA program were also implemented for the work. The WWFTP QA program consists of the WWFTP Quality Assurance Plan (QA-WWFTP-001) and associated QA-NSLW-numbered procedures that provide detailed instructions for implementing NQA-1 requirements for R&D work. The WWFTP QA program is based on the requirements of NQA-1-2008, *Quality Assurance Requirements for Nuclear Facility Applications*, and NQA-1a-2009, *Addenda to ASME NQA-1-2008 Quality Assurance Requirements for Nuclear Facility Applications*, and graded on the approach presented in NQA-1-2008, Part IV, Subpart 4.2, "Guidance on Graded Application of Quality Assurance (QA) for Nuclear-Related Research and Development." All staff members contributing to the work have technical expertise in the subject matter and received QA training prior to performing quality-affecting work. Use of both the PNNL-wide and WWFTP QA controls ensured that all client QA expectations were addressed in performing the work.

Acknowledgments

This work was completed as part of the ILAW Glass Testing for Disposal at IDF project. Support for this project came through Washington River Protection Solutions (WRPS). We thank James Neeway (PNNL) for his independent technical review of the document. Thanks in particular to Benjamin Parruzot (PNNL) and all the team members from ORP, SRNL, and VSL who made themselves available for valuable discussions and input. The authors also wish to acknowledge Dave Swanberg (WRPS), Steven Kelly (WRPS), Elvie Brown (WRPS), David Peeler (PNNL), Melanie Chiaradia (PNNL), and Gary L. Smith (PNNL) for programmatic guidance, direction, and support.

Acronyms and Abbreviations

ALTGLASS	Accelerated Leach Testing of GLASS database of glass dissolution
CEA	Commissariat à l'Énergie Atomique et aux Énergies Alternatives
CFR	Code of Federal Regulations
CMP	Configuration Management Plan
DOE	U.S. Department of Energy
ECKEChem	Equilibrium-Conservation-Kinetic Equation Chemistry
EM	U.S. Department of Energy Office of Environmental Management
eSTOMP	Subsurface Transport Over Multiple Phases (parallel computing version of computer model designated by “e”)
GA	Global Arrays
GRAAL	Glass Reactivity in Allowance for Alteration Layer
HLW	high-level waste
IDF	Integrated Disposal Facility
IEX	ion exchange
ILAW	immobilized low-activity waste
LAW	low-activity waste
LFRG	Low-Level Waste Disposal Facility Federal Review Group
NQA-1	ASME nuclear quality assurance standard
NRC	U.S. Nuclear Regulatory Commission
ORP	Office of River Protection, U.S. DOE
PA	performance assessment
PCT	product consistency test
pH(T)	pH as a function of temperature
PNNL	Pacific Northwest National Laboratory
PUF	pressurized unsaturated flow (test)
QA	Quality Assurance
SA/V	surface area to volume ratio
SPFT	single-pass flow-through test
SRNL	Savannah River National Laboratory
STOMP	Subsurface Transport Over Multiple Phases (serial version of computer model)
STP	Software Test Plan
TST	transition state theory
VSL/CUA	Vitreous State Laboratory at The Catholic University of America
WRPS	Washington River Protection Solutions
WTP	Hanford Tank Waste Treatment and Immobilization Plant
WWFTP	WRPS Waste Form Testing Program

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1.0 Introduction

The federal facilities located on the Hanford Site in southeastern Washington State have been used extensively by the U.S. government to produce nuclear materials for the U.S. strategic defense arsenal. Currently, the Hanford Site is under the stewardship of the U.S. Department of Energy (DOE) Office of Environmental Management (EM). A large inventory of radioactive and mixed waste resulting from the production of nuclear materials has accumulated, including high-level mixed waste stored in 177 underground single- and double-shell tanks located in the central plateau of the Hanford Site. [1] The DOE-EM Office of River Protection (ORP) is proceeding with plans to immobilize and permanently dispose of the low-activity waste (LAW) fraction onsite in the shallow subsurface Integrated Disposal Facility (IDF).

As strictly defined by its origin, most of the waste stored in these tanks is considered high-level radioactive waste. The U.S. Nuclear Regulatory Commission (NRC) has indicated that the low-activity fraction would be considered “incidental waste” if 1) DOE follows its program plan for separating and immobilizing the waste to the maximum extent that is technically and economically practical, 2) if the waste meets the Class C standards of Title 10 Code of Federal Regulations (CFR) Part 617, and 3) if the performance assessments (PAs) continue to indicate that public health and safety would be protected to standards comparable to those established by the NRC for the disposal of low-level waste. [3]

The purpose of this report is to update the strategy towards improving the technical basis for an immobilized low-activity waste (ILAW) glass testing program for estimating radionuclide release from the engineered portion of the IDF (the source term) as part of IDF PAs. This includes a brief historical perspective of ILAW glass testing in support of IDF PAs, including the purpose and goals of the testing programs followed by an overview of the current understanding of glass corrosion behavior. The model used to calculate that behavior is described, as are the current methods for parameterizing them. Section 5.0 outlines the ways in which these models and rate law parameters can be used to conduct IDF source-term release calculations. With these arguments, a strategy is proposed to quantify and/or reduce the most impactful remaining uncertainties in PA release rates in three areas. Within the strategy section, technical approaches to obtain information needed to execute the strategy are discussed. Per the objectives for this work, the approach is focused on reducing uncertainties in the models used to calculate performance for current and future LAW glass formulations.

2.0 ILAW Glass Performance Assessment Background

Before the ILAW can be disposed of, DOE must conduct a PA for the IDF that describes the long-term impacts of the disposal facility on public health and environmental resources. The latest full report on the Hanford Immobilized Low-Activity Waste Performance Assessment was issued in 2001 [1], along with updates issued in 2003 [4] and 2005 [5]. Those documents provide an analysis of the long-term performance of the planned disposal system as a basis to set requirements for the waste form and the facility design that will protect both the long-term public health and safety as well as the environment and then demonstrate that those requirements can be met. They showed that “a reasonable expectation exists that the disposal of the immobilized low-level fraction of tank waste from the Hanford Site can meet environmental and health performance objectives”, but this is not the end of the story. As changes occur to the conceptual design and new information on elements of the disposal system becomes known, the PA team will perform analyses to determine the impact of these new data or information collected from other programs or research institutions on the radionuclide concentrations in groundwater and dose rates. Better estimates of long-term performance will be produced and reviewed regularly, with the next update scheduled in 2017.

Outputs of the PA include estimates of radionuclide release rates from the engineered portion of the disposal facility (source term). These estimates are expected to be based on chemical reactions that occur in the near-field and, in the case of the vitrified ILAW, are controlled by the dissolution of the vitrified matrix. Therefore, to provide credible estimates, a mechanistic understanding of the basic physical and geochemical processes that control glass dissolution and radionuclide release has been incorporated into models to effectively simulate the glass-water reaction over the period of regulatory concern. Currently there is a 1000-year period for regulatory compliance, followed by a period out to 10,000 years in which sensitivity and uncertainty analyses are to be presented to evaluate whether there is any significant potential that would challenge regulatory compliance. Apart from glass composition, the dissolution rate is a function of temperature, pH, surface area of the glass exposed to the contacting solution, and composition of the solution contacting the glass. The repository design has changed over time, but the conditions experienced by the glass in any case are simply translated to the model. Currently, the temperature of the IDF is modeled as a known constant, 15°C. However, both the pH and the composition of the solution contacting the glass are variables that are affected by water infiltration rate, reactions with other engineered materials, gas-water equilibria, secondary-phase precipitation, alkali-ion exchange, and the dissolution of the glass itself. Consequently, glass dissolution rates vary both with time and as a function of the disposal system, even varying considerably based on position of the glass package in the disposal system. [6] There is no single physical constant such as a “leach rate” or radionuclide release rate parameter that can credibly estimate the release of radionuclides from glass waste forms in such a dynamic system because such an approach cannot provide feedback regarding the effects of design options on the disposal-system performance. The only way such a constant rate could be reliably used for PA calculations is if it can be shown that the waste form is robust with respect to the physical and temporal changes of the geochemical environment and the constant rate chosen is sufficiently conservative.

Therefore, the source-term analysis requires the use of a reactive-chemical transport-modeling framework that takes into account the coupled effects of fluid flow and glass-water reactions on the chemistry of liquids percolating through the disposal facility. The fluid chemistry is coupled with kinetic rate equations that describe the response of the glass corrosion rate and the precipitation of secondary phases to changes in liquid composition in the disposal facility or repository, all computed as functions of time and space. These kinetic rate equations assume that 1) the dependence of dissolution and precipitation rates on departure from equilibrium are based on arguments and assumptions of Transition State Theory (TST), [7, 8] 2) the driving force for the transformation to more stable silicate materials is governed principally by the magnitude of displacement from thermodynamic equilibrium, and 3) that pathways towards lower thermodynamic free energies can be achieved through the formation of secondary alteration phases. The rate model is discussed in detail in Section 4.0 of this report.

3.0 Review of Glass Dissolution Behavior

In general, glasses exhibit three main behavioral “stages” when dissolved in static aqueous solutions.[9] Although truly static conditions are not expected in the IDF as a whole, these stages serve to illustrate the behavior of glass in general. A conceptual schematic of these stages and the extent of alteration of the glass with reaction extent (i.e., time) is given in Figure 3.1.

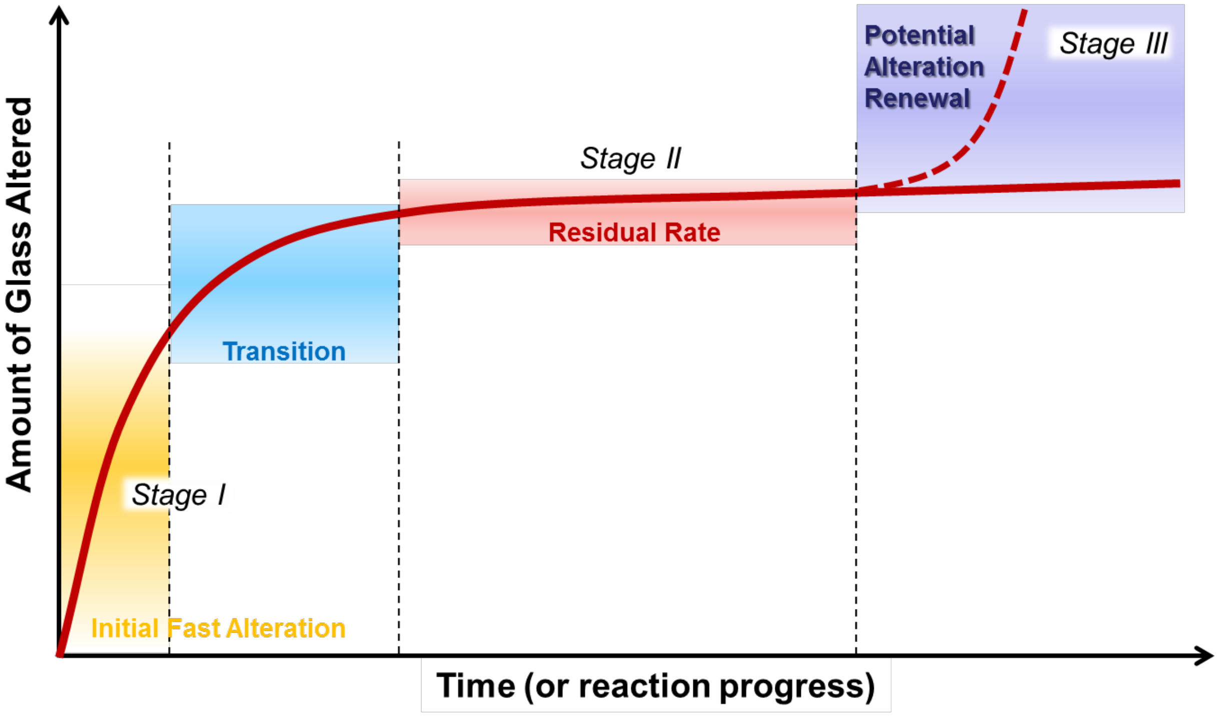

Figure 3.1. General Schematic of the Stages of the Glass-Water Reaction (from Vienna et al. 2013). [10]

Stage I dissolution behavior is characterized by the rapid breakdown of the glass network that occurs in extremely dilute solutions. In these conditions, the glass dissolves congruently as the silicon atoms that comprise the bulk of the glass network are readily dissolved into solution. Interdiffusion (also known as ion exchange) of hydrogen-containing species into the glass network leading to the release of alkalis may occur simultaneously during this period, but the dissolution rate is so rapid that this effect is largely masked by the congruent release of all glass components. Although the rate of Stage I behavior is high, the conditions of the IDF generally preclude the dissolution of glass in this manner. This is because the concentration of orthosilicic acid will always be significant in the groundwater before even coming into contact with the glass.

As the concentration of glass component ions in solution grows, the dissolution of the glass slows dramatically (more than 3 orders of magnitude). The buildup of silicon in solution and the formation of alteration layers on the glass surface correspond with a decrease in the glass dissolution rate to a relatively constant and relatively slow rate known as Stage II dissolution behavior. As seen in Section 4.0, the theory currently used for ILAW glass states that the rate decrease is due to an increase in the activity of orthosilicic acid, H_4SiO_4, in solution. Other theories suggest that the rate decrease is more strongly impacted by other factors, such as the development of a transport-limiting alteration phase [11] or a more complex affinity term that incorporates other ions in solution. [12] Although the science on whether orthosilicic acid affinity is the single most dominant mechanism that leads to Stage II dissolution behavior is not settled, it is without question that this species strongly impacts glass dissolution as all currently considered borosilicate glass dissolution models (not including constant rate approximations) include some version of this affinity term. [13] In an affinity-based model, the non-zero nature of the Stage II dissolution is due to the slow precipitation of silicon-bearing alteration phases that create a sink for orthosilicic acid and allow the continued alteration of the glass. [14] Regardless of mechanism, glasses exhibiting Stage II behavior dissolve quite slowly, with most rates well under those required to keep release rates under regulatory limits. [15] The rate of glass dissolution is so slow during Stage II behavior that the continuing ion exchange reaction may control the release of radionuclides through modifications to the local pH. [16]

In most conditions, the secondary phases that form on corroding glasses are often amorphous phyllosilicate minerals, such as smectite or chlorite [17] or amorphous polymorphs with similar compositions. These mostly form at the interface between the gel layer and solution and, as mentioned above, have a relatively small impact on the residual rate, if any. With the precipitation of certain phases, however, a marked acceleration in the reaction rate can occur [18] and this has been termed Stage III dissolution behavior. This acceleration has only been observed in extreme conditions such as static tests performed at high pH (> 10.5), high T (≥ 90 °C), and high glass-surface-area-to-solution-volume (SA/V) ratios, [19] as well as in the accelerated weathering conditions in the Pressurized Unsaturated Flow (PUF) test. [6] Additionally, a joint study between the Commissariat à l'Énergie Atomique et aux Énergies Alternatives (CEA) and the Vitreous State Laboratory at The Catholic University of America (VSL/CUA) indicated that not all glass compositions appear to create solution conditions that drive this behavior naturally in the conditions tested. [20] Certain glass compositions that do not appear to intrinsically drive Stage III behavior can be forced into it when the solution is artificially altered. [21] In any case, it appears that the range of possible Stage III rates is bounded on the high end by the Stage I dissolution rate (assuming no activity of orthosilicic acid).

4.0 Kinetic Rate Model

As already mentioned, source term calculations used in previous PA efforts [1, 22] and the 2003 risk assessment [2] have assumed that the source term for radionuclide release is controlled by the alteration of glass in water and can be calculated using a chemical affinity rate model. Coupled with that rate model are a term to represent the mechanism of ion exchange and numerous geochemical terms to represent solution modification through the precipitation of secondary phases. The rate model is based off the Transition State Theory, with the supposition that although a true reversible equilibrium may not be present, a specific species is related to a critical transition state that controls dissolution. [7] The TST equation that computes the flux of any element i released from the glass into the aqueous phase is:

$$r_i = \nu_i \vec{k} a_{H^+}^{-\eta} \exp\left(\frac{-E_a}{RT}\right)\left[1-\left(\frac{Q}{K_g}\right)\right]^{\sigma} \qquad (1)$$

where

r_i = the dissolution rate, g/(m^{2}s)
ν_i = the stoichiometric coefficient of element *i* in the glass
$\vec{k}$ = intrinsic rate constant, g/(m^2·s)
$a_{H}{}^{+}$ = hydrogen ion activity
η = pH power law coefficient
E_a = activation energy, J/mol
R = gas constant, 8.314 J/(mol·K)
T = temperature, K
Q = ion-activity product of rate controlling reaction
K_g = pseudo-equilibrium constant of rate controlling reaction
σ = Tempkin coefficient (typically taken to be $\sigma = 1$)

For ILAW glass corrosion modeling, Q is assumed to be the solution activity of orthosilicic acid, H_4SiO_4. The activity of orthosilicic acid is a function of many factors in addition to the dissolving glass and water flux. Orthosilicic acid can also be supplied by the near-field materials, and this source ensures that glass dissolution will never proceed at the forward rate predicted when Q≈0. The most impactful "sink" for orthosilicic acid is the precipitation of secondary phases, whether created directly from solution or through the growth and reactivity of other materials in the near field. Obviously, the kinetics of these processes will directly impact the dissolution of the glass. Another factor influencing the activity of orthosilicic acid is the pH. As seen in Figure 4.1, at pH values around 10, the singly ionized $H_3SiO_4^-$ species represents the majority of the soluble silicon. At higher pH values, the $H_2SiO_4^{-2}$ species becomes significant as well. The glass dissolution rate model only

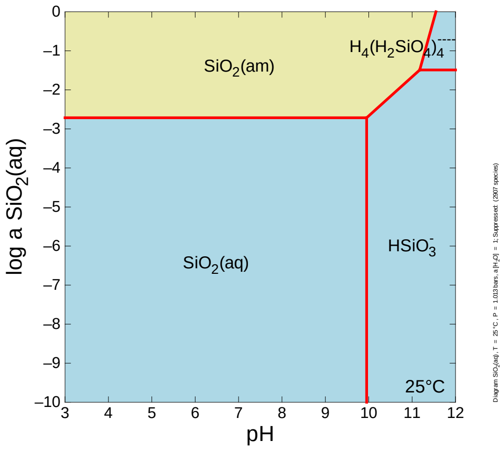

Figure 4.1 - Silicon speciation at 25°C as a function of pH calculated using Geochemist's Workbench

applies for the neutral H_4SiO_4 species, so for a given total concentration of silicon in solution, the formation of ionized silica species at high pH will drive the relative activity of orthosilicic acid lower, decreasing Q and increasing the glass dissolution rate.

It has long been recognized that glass dissolution is impacted by Na-ion exchange. Rate release calculations assume a constant flux to represent this mechanism, which continuously introduces Na into solution, raising the pH through the process in Equation 2.

$$Na^{+}_{glass} + H_2O \rightarrow H^{+}_{glass} + Na^{+}_{aq.} + OH^{-}_{aq.} \tag{2}$$

The precise identity of the H^+ species in the glass is undetermined, as it may be a different hydrogen-containing species such as H_3O^+. [10] It is unimportant to the current discussion, however, as both represent a net consumption of protons and an increase in pH. It is understood that ion exchange is a diffusive process, [16, 23, 24] but the dual-interface problem of a continuously corroding surface and a diffusive sodium release reduces to a constant once steady state conditions are reached. [25] This is, in fact, how the r_{IEX} parameter is obtained. At sufficiently high H_4SiO_4 activities, the ion exchange rate is independent of the H_4SiO_4 activity and the Na ion exchange rate can be calculated from the rate difference for Na and B. The measurement process enlightens the conditions in which the ion exchange parameter has the greatest impact to the dissolution rate. When the orthosilicic acid activity is high and the dissolution rate is low, the influx of sodium due to ion exchange drives the pH higher, impacting the rate through both the pH power law and the decreasing percentage of orthosilicic acid as a function of total silicon in solution that occurs at high pH values. [26] The parameter reported for this mechanism is obtained by testing at a series of temperature (all at pH 9) and extrapolating a linear regression to the 15°C temperature assumed at the IDF. The ion exchange rate (r_{IEX}) is given by:

$$r_{IEX} = r_0 \exp\left(\frac{E_{IEX}}{RT}\right) \tag{3}$$

where

r_{IEX} = the ion exchange rate, mol Na/d
r_0 = intrinsic ion exchange rate constant, mol Na/d
E_{IEX} = activation energy for ion exchange, J/mol

The parameters E_a, η, $\vec{k}$, K_g, and r_{IEX} above can all be derived using the Single-Pass Flow-Through (SPFT) test method. [27-34] Briefly, the SPFT test method functions by continuously passing a fluid of known composition through a test reactor containing glass evenly dispersed on the reactor bottom. The flow rate is increased relative to the surface area of the powder tested until the dissolution becomes congruent. At that point, the ratio of flow rate to surface area (q/S) is defined as the forward rate for those conditions. Tests are designed to elucidate the various rate model parameters by independently varying conditions of the reaction. Table 4-1 gives a list of each parameter and how that parameter can be obtained during testing. These parameters are then used to populate the chemical affinity-based kinetic rate model given in Equation 1.

Table 4-1. The various rate model parameters that are measured using the Single-Pass Flow-Through method for a given glass composition.

Rate model parameter	**Symbol**	**Units**	**Description and measurement**
Intrinsic rate constant	$\vec{k}$	g/m^{2}d	The pH and temperature independent portion of the rate achieved in dilute conditions (Q≈0). This is understood to occur when the dissolution rate is independent of q/S.
Activation energy	E_a	kJ/mol	The temperature-dependent portion of the rate achieved in dilute conditions (Q≈0). Can be calculated by fitting an Arrhenius relationship of measured Q≈0 rates at various temperatures.
pH power law coefficient	η	unitless	The pH-dependent portion of the rate achieved in dilute conditions (Q≈0). Can be determined by the slope of the dissolution rate as a function of the pH. This variable differs for acidic versus alkaline conditions. The alkaline η is typically presented because the glass is expected to corrode in neutral to alkaline conditions for IDF.
Pseudo-equilibrium constant of rate-controlling reaction	K_g	unitless	Parameter quantifying the impact of orthosilicic acid on the dissolution rate. The pH and temperature are fixed and a q/S consistent with a forward rate is used. Silicon is added at several concentrations and the dissolution rate is measured at each concentration. The data can be extrapolated to calculate the value at which the activity of H_4SiO_4 should correspond to a dissolution rate of zero.
Sodium ion exchange constant	r_{IEX}	g/m^{2}d	Parameter quantifying the incongruent release of sodium due to the ion exchange process. Because the ion exchange rate is low, high silicon activity is required to see the effect: H_4SiO_4 activities that are greater than the extrapolated value calculated for K_g. The rate difference for Na and B dissolution is used as r_{IEX}.

In addition to the glass dissolution, IDF PA models must account for the formation of metastable, amorphous, and/or crystalline alteration phases during the glass-water reaction (i.e., chemical reaction network). This requires information on the glass transformation into a paragenetic assemblage of alteration products or minerals (see Table 4-2). Although the suite of weathering products that will form as a consequence of the glass-water reactions cannot be determined *a priori* at this time, as discussed by McGrail et al. [35-37] and Neeway et al., [38] the models use a representative catalog of phases to operationally include that functionality.

Table 4-2. Secondary-Phase Reaction Network for 2015 PA Data Package Input [39]

Phase	**Reaction**	**Log K (90°C)**[1]
Analcime ($Na_{0.96}Al_{0.96}Si_{2.04}O_6 \bullet H_2O$)	analcime + $3.84H^+ \leftrightarrow 0.96Al^{3+} + 0.96Na^+ + 2.04SiO_2(aq) + 2.92H_2O$	3.40
Anatase (TiO_2)	$TiO_2 + 2H_2O \leftrightarrow Ti(OH)_4(aq)$	−6.56
Baddeleyite (ZrO_2)	$ZrO_2 + 2H^+ \leftrightarrow Zr(OH)_2^{2+}$	−5.20
Calcite ($CaCO_3$)	$CaCO_3 + H^+ \leftrightarrow Ca^{2+} + HCO_3^-$	0.91
Chalcedony (SiO_2)	$SiO_2 \leftrightarrow SiO_2(aq)$	−2.65
$Fe(OH)_3(s)$	$Fe(OH)_3(am) + 3H^+ \leftrightarrow Fe^{3+} + 3H_2O$	3.04
Gibbsite [$Al(OH)_3$]	$Al(OH)_3 + 3H^+ \leftrightarrow Al^{3+} + 3H_2O$	4.46
Sepiolite [$Mg_4Si_6O_{15}(OH)_2 \bullet 6H_2O$]	sepiolite + $8H^+ \leftrightarrow 4Mg^{2+} + 6SiO_2(aq) + 11H_2O$	39.72
$Zn(OH)_2$-γ	$Zn(OH)_2$-γ + $2H^+ \leftrightarrow Zn^{2+} + 2H_2O$	11.88

[1] All Log *K* values listed in table must be temperature adjusted to 15°C before conducting IDF PA calculations.

5.0 IDF PA Source Term Model Approach

Figure 5.1 shows a simplified soil column from ground surface to the unconfined aquifer at the IDF. The yellow boxes to the left of the column generally describe the type of modeling that is conducted for the PA. Reactive transport is a key element of the modeling, as it is used to predict the evolution of the waste packages and repository components over time, and the fate of any released contaminants in the near-field. Non-reactive fate and transport models then track the far-field migration to the aquifer and any potential environmental receptors. Dose calculations are then performed and compared to toxicity levels to quantify risks to receptors.

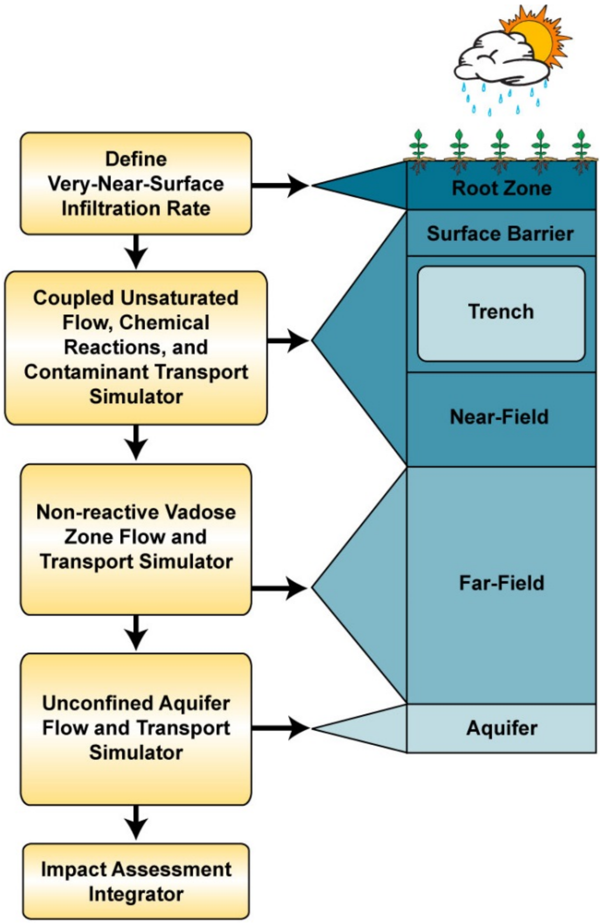

Figure 5.1. Approach to Modeling the Near-Field Environment for the IDF PA. [40]

The 1998 version of the ILAW PA showed that one of the key variables in the analysis is the waste form release rate, which must be calculated over thousands of years. [22] Evaluating the long-term behavior of the ILAW glass will therefore be a critical part of the PA. The specific rate model parameters that have been explained in Section 4.0 will be used as inputs for terms within the box in Figure 5.1 labeled Coupled Unsaturated Flow, Chemical Reactions, and Contaminant Transport Simulator. Physics-based process simulators such as STOMP/eSTOMP (serial and parallel versions of the Subsurface

Transport Over Multiple Phases computer code, respectively) will then be used for predictive analyses in the PA. STOMP [41] can simulate flow and reactive transport in three dimensions, and adheres to rigorous quality assurance (QA) procedures that are compliant with DOE Order 414.1D. Governing equations for solute mass conservation are solved sequentially, following the solution of the coupled flow equations. The ECKEChem (Equilibrium-Conservation-Kinetic Equation Chemistry) module [42] is used to simulate reactive geochemistry. Theoretical or numerical uncertainties in the input parameters or expressions for the controlling mechanisms will be treated with sensitivity and probabilistic analyses to determine a potential range of impacts. Given the complex interactions that control the degradation or weathering of system components and scenario uncertainties associated with future conditions, sensitivity and probabilistic analyses are critical to the analysis.

Modeling is a critical component of the IDF PA and requires representative input parameters to provide reliable contaminant transport predictions. Glass dissolution testing, along with knowledge of near-field phenomena, provides input rate model parameters that can be used to calculate long-term glass durability, as well as the means to validate components of the system PA. The continuing efforts to update and improve the prediction of glass dissolution will serve to reduce uncertainties. In particular, the identification, characterization, and parameterization of key secondary phases will enable the modeling of the type and quantity of minerals present in the near-field/backfill at the time of disposal, as well as the long-term weathering changes in the mineral assemblages. The secondary phases also impact the full system: chemistry, flow, and ultimately the impact on contaminant transport.

6.0 Data Needs and Strategy

Per the instructions of the 2001 Performance Assessment, [1] this document serves to identify data needs that when generated and used will reduce the uncertainties in the assessment of the long-term dissolution behavior of ILAW glasses at the IDF. The model currently used for the evaluation of ILAW glass is widely accepted among the waste glass community as representing a portion of the glass dissolution process, although it should be noted that this model is not without flaws. [43] However, the science behind it is technically defensible and appropriate for the task. Further, the approach has been reviewed and approved by the Low-Level Waste Disposal Facility Federal Review Group (LFRG). [44] Per that review, maintenance of the PA is important in order to identify, understand, and, if necessary, account for key uncertainties and unknowns that have the potential to occlude unacceptable behaviors and thus significantly under-predict radionuclide release. [45] The strategy in how to implement this maintenance has been updated several times. [30, 35, 37, 38] For the purposes of this most recent update, three main uncertainties are presented in the order of most to least potentially impactful.

6.1 Improvements in secondary phase identification and parameterization

The greatest potential uncertainty for long-term glass dissolution remains based in so-called Stage III dissolution behavior. As mentioned in Section 3.0, Stage III dissolution behavior represents a potential, delayed resumption of high ILAW glass corrosion rates that coincides with formation of key secondary phases on the outer surface of the growing alteration layers. As with Stage II, the alteration phases represent a sink for orthosilicic acid, but with much faster rates of formation in Stage III. [46] Although not all of the following need to be understood to produce an acceptable calculation of performance, the uncertainty in Stage III behavior is multifaceted, including:

- whether or not the acceleration will occur,
- whether or not there is a correlation between glass composition and susceptibility to Stage III behavior,
- which solution and environmental conditions will make Stage III more or less likely to occur,
- the precise identity of the critical phase(s) whose formation results in Stage III dissolution behavior,
- the duration at Stage II before Stage III dissolution behavior occurs, and
- the rate of alteration after the resumption.

To begin to respond to some of the points listed above, the ALTGLASS (Accelerated Leach Testing of GLASS) database can be used as a reference. The ALTGLASS database contains 98 simulated ILAW glass compositions, data first published in Papathanassiu et al., [19] that were primarily tested in fairly aggressive conditions: i.e., static solution, relatively high temperatures (90°C or higher), and high surface-area-to-volume ratios. [47] Of these, a strong majority (73%) appeared to exhibit Stage III behavior, defined here as an increase in boron release after an established period of time at Stage II. It cannot be emphasized strongly enough that **the experimental conditions experienced by these particular glasses were specifically designed to be highly aggressive and bear little resemblance to the conditions in the IDF** where low temperature, low SA/V, and slow fluid renewal can all serve to depress the likelihood, initiation, and rate of Stage III dissolution. Despite those caveats, the impact of Stage III behavior in IDF conditions is uncertain at the moment and has the potential to adversely affect the radionuclide flux. Therefore, per the provision in the PA calling for updates to reduce the amount of uncertainty in the glass rate model, [1, 45] it is important to increase the understanding of Stage III dissolution behavior in relevant environmental conditions.

In reviewing the list of uncertainties above, the first four bullets address the question of whether or not Stage III dissolution will occur. As might be imagined, answering this question conclusively is a difficult problem. The suite of secondary phases (Table 4-2) provided in the latest data package [39] includes some of the phases thought to be associated with Stage III dissolution: analcime and sepiolite. [48] Other work, however, has shown that this is not nearly an exhaustive list. The precipitation of a precursor to analcime formation, zeolite P2, has been conclusively shown to result in Stage III dissolution behavior with a rate between 1/16 and 1/32 that of the Stage I rate in equivalent conditions. [49] Additionally, when this phase was added to a system not exhibiting Stage III behavior (again in highly aggressive conditions), the dissolution immediately accelerated. [50] The result was modeled well (Figure 6.1) utilizing the geochemical parameters for zeolite P2.

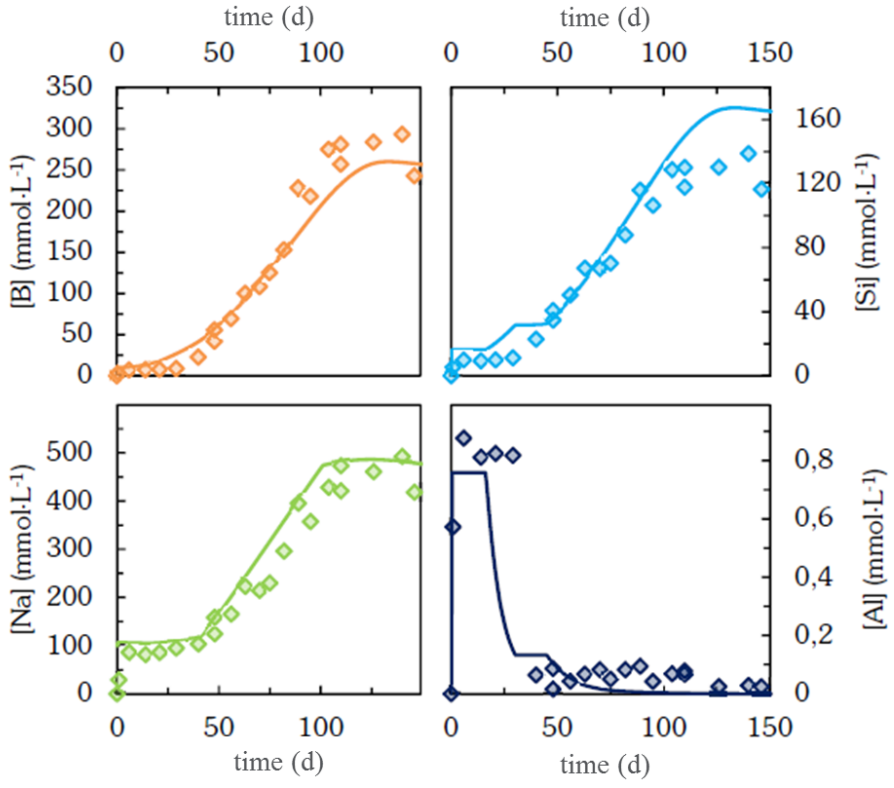

Figure 6.1 - Comparison of experimental data points and model for International Simple Glass exhibiting Stage III dissolution behavior at pH$^{(90°C)}$ 10.7, SA/V = 1362 m^{-1}, and 90°C, accounting for the precipitation of zeolite P2. [50]

It should be noted that this work was performed on glasses with simplified compositions based on high-level waste (HLW) glasses, so it would be premature to immediately apply these arguments to ILAW glasses. On the other hand, all of the components in the HLW glass studied are also present in ILAW glasses, and the difference in atomic ratios (generally more sodium and aluminum, less boron and calcium) would suggest that the ILAW glasses would be more likely rather than less to produce solution conditions that would precipitate sodium aluminosilicate zeolites such as P2. This is due to the necessity to have all ions required for the precipitation of the key phase present in solution in sufficient quantities. Once all required ions are above saturation limits, nucleation has the potential to occur and growth proceed (consuming orthosilicic acid) at kinetic rates that drive glass dissolution. The development of a more representative suite of alteration phases and their geochemical parameters would help ensure that the potential for Stage III dissolution is captured in geochemical calculations within the reactive transport and multiphysics codes used to evaluate the performance of ILAW glass in the IDF. Improvements to this suite of secondary phases are already ongoing as more and longer-duration static tests are completed and analyzed. The pressurized unsaturated flow (PUF) test may present an improved avenue for this, as it has shown the ability to reach Stage III dissolution behavior in less time than the Product Consistency Test (PCT)-B. [51] Again, the PUF conditions that showed Stage III behavior were far from the IDF conditions, but any test that can provide the phase assemblage faster should be considered.

The fifth uncertainty mentioned above is the unknown duration of delay before the commencement of Stage III dissolution behavior. It is thought [49] that the delay is due to the development of critical nuclei that then can rapidly grow in a supersaturated solution. Working with that assumption, it is unlikely that the delay could ever be accurately predicted. The random nature of most nucleation processes [52] would make the prediction of any incubation period an exercise in probability, at best. Instead, it is more appropriate to focus on whether the critical phases could form, and what the impacts would be, if they did.

In a sense, the questions of whether the phases would form and what their impacts would be are reflected in the competition between thermodynamic and kinetic controls. To that end, the risks to the PA presented by the possibility of Stage III dissolution would be reduced by a result that the formation of these phases at the low temperatures expected in the IDF is thermodynamically unfavorable. Unfortunately, a common artificial synthesis pathway for key zeolite phases is to utilize glass and some of the more innocuous alteration products such as calcium-silicate-hydrate, [53, 54] showing that those transitions are thermodynamically favored. Additionally, zeolites have been observed to form at temperatures as low as 5°C on the surfaces of basaltic glasses thousands of years old and older. [55, 56] The glasses and conditions are markedly different from the ILAW glass case, but this provides tangential evidence that the thermodynamics likely do not preclude the formation of at least some zeolites in repository conditions. It does appear that their formation is slow, however.

Therefore, the best case for uncertainty reduction lies in a determination of the kinetics of the process. In addition to their solubilities, secondary phases have associated kinetic rate constants. It is well demonstrated that some solid solution phases form at rates so slow as to not be observed in typical glass dissolution experiments. Quartz is a good example of this. By purely thermodynamic arguments, quartz should precipitate in any silicate glass/water system. Quartz is very rarely observed, however, due to its very slow kinetics of formation relative to the other silicon-bearing phases. Further, the precipitation of phases such as quartz is so slow that if it did precipitate, its impact on glass dissolution would be so low as to be unmeasurable. Per the final uncertainty mentioned at the beginning of this section, we do not have a good estimation of the kinetics of Stage III dissolution behavior or key Stage III secondary phase growth at low temperature. We therefore recommend the development of a testing program to evaluate the growth rate of what are determined to be key secondary phases. The growth rate of these phases on natural analogue glasses [57] should be included as part of these efforts, at least as a literature study. Although perhaps not to the degree of quartz, it may be that the growth rates of key zeolites will result in driven glass dissolution rates well below those needed to avoid any groundwater limits. This would provide technical confidence that the risk due to ILAW glass Stage III dissolution is low. If otherwise, then the testing program should examine methods to prevent the formation of the affecting secondary phase(s).

6.2 Compositional coverage for produced glasses

Due to the wide variety of waste compositions scheduled for immobilization, the glass compositions projected to be produced will have a wide range of compositions as well. Efforts are ongoing using actively designed compositions to improve the glass waste loading and decrease the overall mission timeframe. [58] These efforts will likely continue for the foreseeable future due to the immense benefit that optimized glass compositions bring to the entire immobilization flowsheet. It is important that (a) the rate model parameter sets and uncertainties used for the performance assessment cover any new compositions that are designed or that (b) new parameter values are defined that cover any new glass compositions. To this end, the $\vec{k}$, E_a, η, and K_g parameters used to calculate glass corrosion rates as described in Equation 1 should be measured for a subset of new glass compositions that provide a reasonable assurance that the parameter set(s) used are valid within uncertainty and sensitivity of the PA analyses. [59] The coverage of such an effort would be dramatically improved through the development of a less expensive method for obtaining the suite of rate model parameters. It is recommended that such a test be designed, such as one that removes or limits the need for solution collection and analysis. Additionally, it is possible that a subset of the rate model parameters is either not significantly dependent on composition or not sensitive to model results. In that case, it may be possible to limit the number of experiments needed to establish an operational set of parameters.

Compositions should be selected for testing with a full consultation of the formulation teams with the goal of ensuring the expanded ILAW glass compositions are covered under the parameter space. It should be noted that there is no need to understand the composition/parameter relationships at a fundamental level. If these relationships become statistically valid at some future time with the evolution of a large dataset enabled by more rapid testing, it may minimize or limit the need for expensive testing programs while increasing the statistical confidence of the covered regions. It could also assist in a materials-by-design formulation process, but that is not necessary for the PA maintenance program.

6.3 Improvements in ion exchange modeling

As described in Section 4.0, release rate calculations currently assume a constant flux from Na-ion exchange, which we understand to be a simplification of a diffusive process. Another reduction in uncertainty would be obtained through an investigation into the time-dependence of the alkali exchange reaction followed by the development of a parameterized diffusive term to replace the constant currently used. [38] The current constant value is measured for only one pH value, with acknowledged differences in other conditions accounted for by uncertainty ranges. The use of a diffusion-controlled alkali release term would increase the versatility and accuracy of the r_{IEX} term, putting it on a solid technical basis no matter the dissolution conditions. Having an accurate representation of the mechanism is important because it has a large impact on the pH of the contacting solution and, thus, both the glass dissolution rate and the precipitation of secondary phases. Due to the use of molten salt alkali ion exchange in industry [23] and recent connection of those formalisms to low temperatures, [24] this may be developed soon by other programs. The progress of external groups should be leveraged for any model development effort to ensure the state of the art model for sodium release is used.

7.0 Conclusions

The PA for the IDF provides an analysis of the long-term performance as a basis to set requirements for the waste form and the facility design, and then demonstrates that those requirements can be met. An important provision of the PA is that it is updated regularly to account for design changes and scientific advancements that impact this analysis and demonstration. The preceding document serves to provide an updated strategy and technical approach for glass performance testing programs to reduce uncertainties within the model that represents the source term from ILAW glass waste forms.

The radionuclide release rate is directly correlated to the glass dissolution rate, which is itself a function of glass composition, temperature, pH, surface area of the glass exposed to the contacting solution, and composition of the solution contacting the glass. This solution is, in turn, impacted by such variables as infiltration rate, reactions with engineered and backfill materials, gas-water equilibria, secondary-phase precipitation, alkali-ion exchange, and, of course, the dissolution of the glass itself. Uncertainties are estimated and considered in the PA as a matter of course, but we have identified three main areas to target the more tractable and/or impactful uncertainties to PA-calculated release rates from glass.

The most impactful of these is the potential acceleration of the glass reaction rate after long times at low reaction rates that is termed Stage III dissolution. Currently, Stage III dissolution behavior is modeled as being caused by the precipitation of zeolite phases that lower the activity of the rate-controlling orthosilicic acid ion and cause the acceleration of glass dissolution. The uncertainty lies mainly in a poor understanding of the thermodynamics and kinetics of formation of key phases at the low temperatures associated with the IDF. A testing program is needed to evaluate the geochemical parameters and, more importantly, the growth rate of key secondary phases at low temperatures.

Changes in glass composition will be a perennial focus area for ILAW glasses due to the high variability of tank waste and the desire for glasses with higher waste loading, higher solubility for key waste components, and improved melt rate/throughput. There must be confidence that the rate model parameters described in this report are applicable to any new glass compositions that are designed. If the models do not represent the glass performance within a reasonable sensitivity and uncertainty analysis, new parameter values should be determined and assigned. To this end, the parameters used to calculate glass corrosion rates should be determined for a subset of new glass compositions, providing a reasonable assurance that the rate model parameter set(s) that are used are valid within uncertainty and sensitivity of the PA analyses. ILAW glass compositions should be selected for testing following a full consultation with the formulation teams with the goal of ensuring the expanded compositions are covered under the parameter space.

Ion exchange is the final of the three identified potential uncertainty areas, with the uncertainty mainly due to the simplistic assumptions currently used to describe the mechanism. Rate release calculations currently assume a constant flux from Na-ion exchange. However, ion exchange is, in actuality, a diffusive process. The mechanism impacts the dissolution rate through modifications of the solution pH. Due to the consumption of either H^+ or H_3O^+ from solution, the mechanism increases pH in solution over time, impacting both the glass dissolution rate and the precipitation of secondary phases (which then impacts the dissolution rate). A reduction in uncertainty would be obtained through the adoption of a parameterized diffusive term for the ion exchange mechanism to replace the constant currently used.

In general, the adoption of these recommendations would further improve and define the technical basis of the glass dissolution model used as an input to the PA. Particularly with respect to a greater understanding and accounting for the secondary phases associated with Stage III dissolution behavior, the increased knowledge obtained through this program will determine the impact of recent relevant findings and improve the estimates of long-term performance, per the guidance of the PA documents.

8.0 References

1. Mann, F.M., et al., (2001), *Hanford Immobilization Low-Activity Tank Waste Performance Assessment: 2001 Version*: Department of Energy Office of River Protection, DOE/ORP-2000-24.
2. Mann, F.M., et al., (2003), *Integrated Disposal Facility Risk Assessment*: CH2M Hill Hanford Group, Inc., RPP-15834, Rev. 0.
3. C.J. Paperiello, D., Office of Nuclear Material Safety and Safeguards, U.S. Nuclear Regulatory Commission, (June 9, 1997), *Classification of Hanford Low-Activity Tank Waste Fraction*: letter to Jackson Kinzer, Assistant Manager, Office of Tank Waste Remediation System.
4. Mann, F.M., (2003), *Annual Summary of the Immobilized Low-Activity Waste Performance Assessment for 2003, Incorporating the Integrated Disposal Facility Concept*: US DOE, DOE/ORP-2000-19, Rev. 3.
5. Mann, F.M., (2005), *Annual Summary of the Integrated Disposal Facility Performance Assessment for 2004*: US DOE, DOE/ORP-2000-19, Rev. 4.
6. Bacon, D. and E.M. Pierce, (2005), *Sensitivity Analysis of Kinetic Rate-Law Parameters Used to Simulate Long-Term Weathering of ILAW Glass*: Pacific Northwest National Laboratory, PNNL-19472.
7. Grambow, B. *A general rate equation for nuclear waste glass corrosion*. in *Scientific Basis for Nuclear Waste Management VIII*. 1985. 44, p. 15.
8. (1982), *Workshop on the Leaching Mechanisms of Nuclear Waste Forms, May 19-21*: Materials Characterization Center, PNL-4382.
9. Bates, J.K., et al., (1994), *High-Level Waste Borosilicate Glass: A Compendium of Corrosion Characteristics.*: U.S. Department of Energy, DOE-EM-0177.
10. Vienna, J.D., et al., *Current Understanding and Remaining Challenges in Modeling Long-Term Degradation of Borosilicate Nuclear Waste Glasses.* International Journal of Applied Glass Science, 2013. **4**(4): p. 283-294.
11. Frugier, P., et al., *SON68 nuclear glass dissolution kinetics: Current state of knowledge and basis of the new GRAAL model.* Journal of Nuclear Materials, 2008. **380**(1–3): p. 8-21.
12. Bourcier, W.L. *Affinity Functions for Modeling Dissolution Rates*. in *CEA Summer Session Proceedings*. 1997. p. 318-28.
13. Gin, S., et al., *An international initiative on long-term behavior of high-level nuclear waste glass.* Materials Today, 2013. **16**(6): p. 243-248.
14. Pierce, E., et al., (2013), *Integrated Disposal Facility FY 2012 Glass Testing Summary Report*: Pacific Northwest National Laboratory, PNNL-21812, Rev. 1.
15. Burandt, M.B., (2012), *Final Tank Closure and Waste Management Environmental Impact Statement for the Hanford Site, Richland, Washington*: US Department of Energy, DOE/EIS-0391.
16. McGrail, B.P., et al., (2001), *Ion-Exchange Processes and Mechanisms in Glasses*: Pacific Northwest National Laboratory, EMSP-60362.
17. Pierce, E.M., et al., *Accelerated weathering of high-level and plutonium-bearing lanthanide borosilicate waste glasses under hydraulically unsaturated conditions.* App. Geo., 2007. **22**(9): p. 1841-1859.
18. Van Iseghem, P. and B. Grambow. *The Long-Term Corrosion and Modelling of Two Simulated Belgian Reference High-Level Waste Glasses*. in *Scientific Basis for Nuclear Waste Management XI*. 1988. 112, p. 631-639, Pittsburgh, Pennsylvania: Materials Research Society.
19. Papathanassiu, A., et al., (2011), *ILAW Glass Testing for Disposal at IDF: Phase 1 Testing*: Vitreous State Laboratory, The Catholic University of America, VSL-11R2270-1.
20. Ribet, S., et al., *Compositional Effects on the Long-Term Durability of Nuclear Waste Glasses: A Statistical Approach.* MRS Online Proceedings Library Archive, 2004. **824**: p. CC5.3 (6 pages).

21. Ribet, S. and S. Gin, *Role of neoformed phases on the mechanisms controlling the resumption of SON68 glass alteration in alkaline media.* Journal of Nuclear Materials, 2004. **324**(2–3): p. 152-164.
22. Mann, F.M., et al., (1998), *Hanford Low-Activity Tank Waste Performance Assessment*: DOE/RL-97-69, Rev. 0.
23. Varshneya, A.K., *The physics of chemical strengthening of glass: Room for a new view.* Journal of Non-Crystalline Solids, 2010. **356**(44–49): p. 2289-2294.
24. Neeway, J.J., et al., *Ion-Exchange Interdiffusion Model with Potential Application to Long-Term Nuclear Waste Glass Performance.* The Journal of Physical Chemistry C, 2016. **120**(17): p. 9374-9384.
25. Boksay, Z., G. Bouquet, and S. Dobos, *The kinetics of the formation of leached layers on glass surfaces.* Physics and Chemistry of Glasses, 1969. **9**: p. 69.
26. Feng, X. and I.L. Pegg, *A glass dissolution model for the effects of S/V on leachate pH.* Journal of Non-Crystalline Solids, 1994. **175**(2): p. 281-293.
27. ASTM, *C1662-10, Standard Practice for Measurement of the Glass Dissolution Rate Using the Single-Pass Flow-Through Test Method*. 2010, ASTM International: West Conshohocken, PA, 2010,.
28. McGrail, B.P., et al., *Measurement of Kinetic Rate Law Parameters on a Na-Ca-Al Borosilicate Glass for Low-Activity Waste.* Journal of Nuclear Materials, 1997. **249**: p. 175-189.
29. McGrail, B.P., et al., *The structure of* Na_2O-Al_2O_3-SiO_2 *glass: impact on sodium ion exchange in* H_2O *and* D_2O*.* Journal of Non-Crystalline Solids, 2001. **296**(1-2): p. 10-26.
30. McGrail, B.P., et al., (2000), *A Strategy to Conduct an Analysis of the Long-Term Performance of Low-Activity Waste Glass in a Shallow Subsurface Disposal System at Hanford*: Pacific Northwest National Laboratory, PNNL-11834 Rev. 1.
31. Pierce, E.M., et al., *Experimental determination of the effect of the ratio of B/Al on glass dissolution along the nepheline (NaAlSiO4)-malinkoite (NaBSiO4) join.* Geochimica et Cosmochimica Acta, 2010. **74**(9): p. 2634-2654.
32. Pierce, E.M., et al., *Effect of Al/B ratio on the dissolution of nepheline glass,* $Na_3(Al, B)_{1\text{-}4}Si_4O_{16}$*.* Geochimica et Cosmochimica Acta, 2005. **69**(10): p. A781.
33. Pierce, E.M., et al., *An experimental study of the dissolution rates of simulated aluminoborosilicate waste glasses as a function of pH and temperature under dilute conditions.* Applied Geochemistry, 2008. **23**(9): p. 2559-2573.
34. Icenhower, J.P., et al., *Experimentally determined dissolution kinetics of Na-rich borosilicate glass at far from equilibrium conditions: Implications for Transition State Theory.* Geochimica et Cosmochimica Acta, 2008. **72**(12): p. 2767-2788.
35. McGrail, B., et al., (1998), *A Strategy to Conduct an Analysis of the Long-Term Performance of Low-Activity Waste Glass in a Shallow Subsurface Disposal System at Hanford*: Pacific Northwest National Laboratory, PNNL-11834.
36. McGrail, B., et al., (2000), *A Strategy to Conduct an Analysis of the Long-Term Performance of Low-Activity Waste Glass in a Shallow Subsurface Disposal System at Hanford*: Pacific Northwest National Laboratory,
37. McGrail, B., et al., (2003), *A Strategy to Assess Performance of Selected Low-Activity Waste Forms in an Integrated Disposal Facility*: Pacific Northwest National Laboratory, PNNL-14362.
38. Neeway, J.J., et al., (2014), *A Strategy to Conduct an Analysis of the Long-Term Performance of Low-Activity Waste Glass in a Shallow Subsurface Disposal System at Hanford*: Pacific Northwest National Laboratory, PNNL-23503; RPT-66309-001, Rev.0.
39. Freedman, V.L., J.V. Ryan, and D.H. Bacon, (2015), *Immobilized Low-Activity Waste Glass Release Data Package for the Integrated Disposal Facility Performance Assessment*: Pacific Northwest National Laboratory, PNNL-24615.

40. Bacon, D. and E. Pierce, *Development of long-term behavior models for radioactive waste forms*, in *Handbook of advanced radioactive waste conditioning technologies*. 2011, Woodhead Publishing Limited: Cambridge, UK. p. 488.
41. White, M.D. and M. Oostrom, (2006), *STOMP: Subsurface Transport Over Multiple Phases, Version 4.0, User's Guide*: Pacific Northwest National Laboratory, PNNL-15782.
42. White, M.D. and M. B.P., (2005), *STOMP Subsurface Transport Over Multiple Phases, Version 1.0, Addendum: ECKEChem Equilibrium-Conservation-Kinetic Equation Chemistry and Reactive Transport,*: Pacific Northwest National Laboratory, PNL-15482.
43. Gin, S., et al., *Theoretical consideration on the application of the Aagaard–Helgeson rate law to the dissolution of silicate minerals and glasses.* Chemical Geology, 2008. **255**(1–2): p. 14-24.
44. DOE, (2000), *Immobilized Low-Activity Tank Waste Disposal Facility Performance Assessment Condition in the Disposal Authorization Statement*: memorandum from Jay E. Roderick and William E. Murphie, co-chairs of the Low-Level Waste Disposal Facility Federal Review Group, U.S. Department of Energy, Washington, D.C., June 2, 2000.
45. Mann, F.M., (2000), *Maintenance Plan for the Hanford Immobilized Low-Activity Tank Waste Performance Assessment* U.S. Department of Energy, DOE/ORP-2000-01.
46. Ebert, W.L., et al., (2011), *Glass Testing Activities at ANL and SRNL: FY11 Progress Report*: Fuel Cycle Research and Development Program, FCRD-WAST-2011-000404.
47. Ebert, W.L., (2014), *An Evaluation of the ALTGLASS Database for Insights into Modeling Stage 3 Behavior*: FCRD-SWF-2014-000616.
48. Inagaki, Y., et al., *Corrosion Behavior of a Powdered Simulated Nuclear Waste Glass in the Presence of Bentonite.* Journal of Nuclear Science and Technology, 1994. **31**(9): p. 948-959.
49. Fournier, M., P. Frugier, and S. Gin, *Effect of Zeolite Formation on Borosilicate Glass Dissolution Kinetics.* Procedia Earth and Planetary Science, 2013. **7**: p. 264-267.
50. Fournier, M., *Etude des mécanismes à l'origine des reprises d'altération: Modélisation et impact sur les verres de confinement [Study of the mechanisms underlying resumptions of alteration: Modeling and evaluation of the impact on nuclear waste glasses]*. 2015, Université Montpellier.
51. McGrail, B.P., P.F. Martin, and C.W. Lindenmeier, *Accelerated Testing of Waste forms using a Novel Pressurized Unsaturated flow (PUF) Method.* MRS Online Proceedings Library Archive, 1996. **465**: p. 253.
52. Van Siclen, C.D., *Random nucleation and growth kinetics.* Physical Review B, 1996. **54**(17): p. 11845-11848.
53. Y, M.N., et al., *Synthesis of pure zeolite P2 from calcium silicate hydrate tobermorite.* Orient J Chem, 2015. **31**(2).
54. Ghobarkar, H., et al., *The Reconstruction of Natural Zeolites*. 2003, Boston: Kluwer Academic Publishers.
55. Parruzot, B., *Altération des verres basaltiques dans des environnements confinés : analogie avec le stockage géologique des verres nucléaires [Basaltic glass alteration in confined environments: analogy to nuclear waste glass geological repository]*. 2014, Université Montpellier 2.
56. Crovisier, J.L., T. Advocat, and J.L. Dussossoy, *Nature and role of natural alteration gels formed on the surface of ancient volcanic glasses (Natural analogs of waste containment glasses).* Journal of Nuclear Materials, 2003. **321**(1): p. 91-109.
57. Dibble Jr, W. and W. Tiller, *Kinetic model of zeolite paragenesis in tuffaceous sediments.* Clays and Clay Minerals, 1981. **29**(5): p. 323-330.
58. Peeler, D., et al., (2015), *Office of River Protection Advanced Low-Activity Waste Glass Research and Development Plan*: Pacific Northwest National Laboratory, PNNL-24883; EWG-RPT-008.
59. Bacon, D.H. and E.M. Pierce, (2010), *Sensitivity Analysis of Kinetic Rate-Law Parameters Used to Simulate Long-Term Weathering of ILAW Glass*: Pacific Northwest National Laboratory, PNNL-19472.

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