PNNL-23503
RPT-66309-001 Rev. 0

Pacific Northwest
NATIONAL LABORATORY

Proudly Operated by **Battelle** *Since 1965*

A Strategy to Conduct an Analysis of the Long-Term Performance of Low-Activity Waste Glass in a Shallow Subsurface Disposal System at Hanford

September 2014

JJ Neeway
EM Pierce
VL Freedman
JV Ryan
NP Qafoku

U.S. DEPARTMENT OF
ENERGY

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

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

Printed in the United States of America

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information,
P.O. Box 62, Oak Ridge, TN 37831-0062;
ph: (865) 576-8401
fax: (865) 576-5728
email: reports@adonis.osti.gov

Available to the public from the National Technical Information Service
5301 Shawnee Rd., Alexandria, VA 22312
ph: (800) 553-NTIS (6847)
email: orders@ntis.gov <http://www.ntis.gov/about/form.aspx>
Online ordering: http://www.ntis.gov

This document was printed on recycled paper.
(8/2010)

PNNL-23503
RPT-66309-001 Rev. 0

A Strategy to Conduct an Analysis of the Long-Term Performance of Low-Activity Waste Glass in a Shallow Subsurface Disposal System at Hanford

JJ Neeway[1]
EM Pierce[2]
VL Freedman[1]
JV Ryan[1]
NP Qafoku[1]

September 2014

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

[1]Pacific Northwest National Laboratory
Richland, Washington 99352

[2]Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831

Executive Summary

Approximately 56 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 for the U.S. strategic defense arsenal. 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). Between 150,000 and 345,000 m^3 of immobilized LAW (ILAW) glass are expected to be produced at Hanford. Principal radionuclides of concern in LAW are ^{99}Tc, ^{129}I, and U, while non-radioactive contaminants of concern are Cr and nitrate/nitrite (Mann et al., 2001; Mann et al., 2003). Between 9,000 and 20,000 m^3 of HLW glass will be sent off site to an undetermined federal facility for deep geological disposal, while the much larger volume of ILAW will be placed in the on-site, near-surface Integrated Disposal Facility (IDF).

Before the ILAW can be disposed of at the IDF, a performance assessment (PA) must be conducted. The PA is a document that describes the long-term impacts of the disposal facility on public health and environmental resources. One of the major inputs to the PA is the estimate of radionuclide release rates from the engineered portion of the disposal facility into the surrounding environment. These estimates are expected to be based on chemical reactions that occur in the near-field, and to a certain extent, are controlled by the dissolution of the vitrified waste form. Once released from the vitrified matrix, the transport of the radionuclides of concern is based on chemical reactions that occur in the near- and far-field. Therefore, to provide credible estimates, a mechanistic understanding of the physical and geochemical processes that control glass dissolution, and thus radionuclide release, must be understood and incorporated into models used to predict radiation dose over the period of regulatory concern (~ 10,000 years). A cornerstone assumption for the approach to estimating the source term is that the glass matrix must dissolve for radionuclides to be released into the environment. This assumption has been demonstrated in pressurized unsaturated flow (PUF) experiments conducted with ILAW glass produced with actual radioactive low-activity waste (Pierce et al., 2006). The major parameters known to control glass dissolution are glass composition, temperature, and solution composition of the fluid contacting the glass (including pH and concentration of key ions [e.g., H_4SiO_4]). The effect of these parameters on the glass dissolution rate is essential for developing credible PA models. Though the temperature of the IDF is expected to be roughly constant at 15 °C, the pH and fluid compositions are affected by flow rate (i.e., water infiltration), reactions with near-field engineered materials, gas-water equilibria, secondary phase formation, ion exchange of alkalis in the glass with cations in solution, and the dissolution of the glass matrix. Due to the various evolving conditions expected at the site, the glass dissolution rate may vary both as a function of time and the position of the glass in the disposal system. Therefore, a fixed glass dissolution rate, and thereby radionuclide release, is not credible during PA modeling.

A major conclusion from previous PAs is that the release rate of radionuclides from the ILAW glass by reaction with water is one of the key parameters that determine the impacts of ILAW disposal on estimated dose (Mann et al., 1998a; Mann et al., 2001; Mann et al., 2003). For this reason, several ILAW testing strategies and data packages have been produced. With the use of various test methods used to study the glass corrosion process, these data packages have provided a rate law parameter estimate for a number of specific ILAW glasses that were expected to be produced at WTP at that time. Recently, however, there has been a shift in the glass compositions expected to be produced at WTP, which have a higher waste loading and are more alkali-rich.

As a result of this change, Pacific Northwest National Laboratory (PNNL) has been tasked with evaluating the corrosion behavior of the higher LAW-loaded glass formulations that are being developed by DOE Office of River Protection (ORP) to expand the range of ILAW glass compositions that can be produced at WTP. The objective of the current work is to perform testing, data collection and analysis, and modeling for the ILAW glass product to generate defensible rate laws and rate law parameters that accurately describe the glass corrosion process for use in future IDF PAs. We begin the discussion of the technical strategy with a brief overview of the history of the ILAW testing program, followed by a description of various glass corrosion mechanisms that will be studied in depth. We then give a description of the Subsurface Transport Over Multiple Phases (STOMP) simulator used to calculate contaminant release rates from the engineered components of the disposal system. Finally, we give a description of the specific areas of the glass corrosion process on which an emphasis will be placed in this study.

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).

The authors wish to acknowledge Dave Swanberg (WRPS) and Joe Westsik Jr. (PNNL) for programmatic guidance, direction, and support. We also acknowledge Fred Mann, Will Nichols (Intera Inc), Sunil Mehta (Intera, Inc.), Diana Bacon (PNNL) and Mark Rockhold (PNNL) for their technical review of the document.

The authors wish to thank John Vienna for his technical peer review and Heather Culley for editorial review and document production.

Acronyms and Abbreviations

ALK	alkali
ANL	Argonne National Laboratory
APT	atom probe tomography
AREST-CT	Analyzer for RadionuclidE Source-Term with Chemical Transport
ASTM	American Society for Testing and Materials
BNI	Bechtel National Inc.
Bq	becquerel
CMP	Configuration Management Plan
DOE	U.S. Department of Energy
EA	environmental assessment
EFTEM	energy-filtered transmission electron microscopy
EM	Environmental Management
GA	Global Arrays
GRAAL	Glass Reactivity with Allowance for the Alteration Layer
HLW	high-level waste
HRTEM	high-resolution transmission electron microscopy
ICP-OES	inductively coupled plasma optical emission spectroscopy
ICP-MS	inductively coupled plasma mass spectrometry
IDF	Integrated Disposal Facility
ILAW	immobilized low-activity waste
LAW	low-activity waste
LLW	low-level waste
ORP	Office of River Protection
PA	performance assessment
PCT	product consistency test
PRI	passivating reactive interphase
PNNL	Pacific Northwest National Laboratory
PUF	pressurized unsaturated flow
QA	quality assurance
R&D	research and development
RFP	request for proposal
SPFT	single-pass flow-through
SRNL	Savannah River National Laboratory
STOMP	Subsurface Transport Over Multiple Phases
STORM	Subsurface Transport Over Reactive Multiphases
STP	Software Test Plan

S/V	surface area-to-solution volume ratio
TEM	transmission electron microscope
TST	transition-state theory
TWRS	Tank Waste Remediation System
VHT	vapor hydration test
WRPS	Washington River Protection Solutions
WTP	Hanford Tank Waste Treatment and Immobilization Plant

Contents

Figures

Tables

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 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 (Mann et al., 2001). The DOE Office of River Protection (ORP) is proceeding with plans to immobilize and permanently dispose of the low-activity waste (LAW) fraction onsite in a shallow subsurface disposal facility (the Integrated Disposal Facility [IDF]). Pacific Northwest National Laboratory (PNNL) was contracted to provide the technical basis for estimating radionuclide release from the engineered portion of the IDF (the source term) as part of an immobilized low-activity waste (ILAW) glass testing program to support future IDF performance assessments (PAs). This work was conducted with funding from Washington River Protection Solutions under contract 36437-161, ILAW Glass Testing for Disposal at IDF. The work was conducted as part of PNNL Project 66309, ILAW Glass Testing.

1.1 Overview—ILAW Glass Disposal at Hanford

Currently, DOE plans to dispose of the glasses made from nuclear waste stored in underground tanks at Hanford at two U.S. locations: (1) the ILAW glass will be stored onsite at the IDF and (2) the high-level waste (HLW) glass will be disposed of at a federal geologic repository. The solid and liquid waste recovered from the tanks will be pre-treated to separate the low-activity fraction from the high-level and transuranic waste fractions. The LAW and HLW fractions will be separately immobilized into vitrified matrices (i.e., borosilicate glasses). Currently, vitrifying the LAW is expected to generate over 1.6×10^5 m^3 of glass (Certa et al., 2010). Once vitrified, the volume of ILAW at Hanford will be the largest in the DOE complex, and one of the largest inventories (approximately 8.9×10^{14} Bq total activity) of long-lived radionuclides—principally ^{99}Tc ($t_{1/2} = 2.1 \times 10^5$ years), ^{129}I ($t_{1/2} = 1.6 \times 10^7$ years), and U— planned for disposal in a low-level waste (LLW) facility.

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. One of the inputs to the PA is an estimate 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 ILAW glass, 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 understood and incorporated into models to effectively simulate the glass-water reaction over the period of regulatory concern (approximately 10,000 years). A cornerstone assumption for the approach to estimating the source term is that the glass matrix must dissolve for radionuclides to be released into the environment. This assumption has been demonstrated in pressurized unsaturated flow (PUF) experiments conducted with ILAW glass produced with actual radioactive low-activity waste (Pierce et al., 2006). 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 infiltration rate, reactions with other engineered materials, gas-water equilibria, secondary-phase precipitation, alkali-ion exchange, and dissolution of the glass itself. Consequently, glass dissolution rates vary both in time and as a function of position in the disposal system. There is no physical constant, such as a “leach rate” or radionuclide release rate parameter, that can credibly estimate the release of radionuclides from glass waste form in such a dynamic system.

A model based on the empirical release behavior of the glass cannot provide feedback regarding the effects of design options on the disposal-system performance. 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 dissolution rate 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), and (2) the driving force for the transformation of unstable to stable silicate materials is governed principally by the magnitude of displacement from thermodynamic equilibrium. This approach is discussed in greater detail in Section 3.2 of this report.

1.2 Purpose and Organization of the Report

The purpose of this report is to describe the strategy that will be used to evaluate higher waste loading LAW glasses in support of future IDF PAs. To this end, we have provided a brief historical perspective of LAW glass testing in support of IDF PAs (formerly ILAW PA). Section 3.0 provides an overview of the glass corrosion process, followed by a discussion of the modeling approach being used to conduct IDF source-term release calculations in Section 4.0. Lastly, we discuss the approach that will be used to fill the data gaps needed to conduct IDF PA simulations with the higher LAW loading glass formulations that are representative of ORP’s expanded compositional range.

1.3 Quality Assurance

All research and development (R&D) 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. To ensure that all client quality assurance (QA) expectations were addressed, the QA controls of the WRPS Waste Form Testing Program (WWFTP) QA program were also implemented for this work. The WWFTP QA program[1] 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 work described in this report was assigned the technology level “Applied Research” and was planned, performed, documented, and reported in accordance with Procedure QA-NSLW-1102, *Scientific*

---

[1] This QA program has been independently evaluated by Acquisition Verification Services (AVS) of Mission Support Alliance (MSA) to specified requirements of NQA-1-2004 (including NQA-1a-2005 and NQA-1b-2007 Addenda) and is operating under a WRPS-approved Supplier Quality Assurance Program Implementation Plan (SQAPIP) (QA-WWFTP-002).

Investigation for Applied Research. All staff members contributing to the work received proper technical and quality assurance training prior to performing quality-affecting work.

2.0 Historical Synopsis of ILAW Glass Performance Assessment

Provided below is a historical synopsis of the Immobilization of Low-Activity Waste (ILAW) glass PA project. Although brief, the synopsis provides context to the proposed strategy described in Section 5.0 by giving a historical perspective of the past 19 years of testing and modeling. Each of the steps taken over the past 19 years has been with the goal of improving the technical defensibility of the PA for the disposal of ILAW glass at Hanford in accordance with the regulations outlined in DOE Order 435.1 (formerly DOE Order 5820.2A) (DOE, 1988; DOE, 1998). The discussion below begins with the 1994 initial facility design evaluation (Mann, 1995b; Rawlins et al., 1994), briefly discusses 1996 interim PA and associated data packages evaluation (Mann, 1995a; Mann, 1995b; Mann, 1995c; Mann, 1995d; Mann et al., 1995; Mann et al., 1996; Mann et al., 1997), then includes a short discussion of the 1998 and 2001 PAs and associated data packages (Mann et al., 1998a; Mann et al., 1998b; Mann et al., 2001; McGrail et al., 1998b; McGrail et al., 2000a; McGrail et al., 2000b; McGrail et al., 2000c; McGrail et al., 2001b), and closes with a discussion of the glass performance data collected from 2004 through 2013.

The first Hanford ILAW glass PA activity occurred shortly after the decision was made to change the ILAW form from grout to glass. The major purpose of this initial activity, which was initiated under the Tank Waste Remediation System (TWRS) Immobilized Waste Program, was to evaluate design options for the engineered portion of the LAW disposal facility in preparation for an interim PA. This initial activity was completed in 1994 (Rawlins et al., 1994) and revised in 1995 based on review comments and the incorporation of more accurate data (Mann, 1995b). Results from the initial evaluation illustrated that various performance parameters and key assumptions can have a significant impact on the facility design and the disposal facility’s ability to achieve the required performance objectives. After completing the initial facility design evaluation (Part A), the TWRS program initiated a data collection effort in an attempt to improve the technical basis for both the performance parameters and key conservative assumptions (Part B). The performance parameters and key assumptions included the radionuclide inventory, waste form release rates, and generic information for geologic data, geochemical data, hydraulic parameters, and water infiltration rates because the facility location and design were still in the planning stages. The generic geologic data, geochemical data, and hydraulic parameters, much of which originated from other DOE sponsored projects and programs, were considered representative of the disposal area. The compiled information was documented in a series of data packages (Mann, 1995a; Mann, 1995b; Mann, 1995c; Mann, 1995d; Mann et al., 1995) that were used as part of the 1996 interim PA (Mann et al., 1996; Mann et al., 1997).

At this stage of the TWRS program, the privatization project Request for Proposal (RFP) (Wagoner, 1996) was in the bidding process and the composition of ILAW glass was not defined. Therefore, glass performance, and subsequent radionuclide release rates, in the 1996 interim PA base case scenario used a constant leach-rate that was based on a 20°C 7-day PCT limit (Stage I for glass corrosion, see Section 3.1), which was defined in the privatization project RFP (Mann et al., 1996). Because of a lack of information, it was assumed that this value represented a conservative upper bound for glass performance, and that short-term glass performance was representative of long-term behavior. In addition to the base case scenario, which used a constant leach rate, sensitivity cases were conducted with a more mechanistic approach to modeling glass performance and radionuclide release using a numerical simulator, the Analyzer for RadionuclidE Source-Term with Chemical Transport (AREST-CT) computer code (Chen et al., 1995; Chen et al., 1996). As an alternative to a constant leach rate, the AREST-CT computer code allowed the chemical environment resulting from the glass dissolution reaction to be computed as a function of time and space in the disposal system. These sensitivity analysis results illustrated that the ^{99}Tc inventory and glass performance had a significant impact on radionuclide release estimates.

The interim PA (Mann et al., 1996; Mann et al., 1997) concluded that the preliminary and final performance assessment would benefit from knowledge of the waste form, disposal facility location, and the disposal facility design, as well as from an extensive data collection activity for the generation of site specific estimates for geologic data, geochemical data, hydraulic parameters, and water infiltration rates.

The PA conducted in 1998 was to support the application for a Disposal Authorization Statement (Mann et al., 1998a), and coincided with a revision to the Radioactive Waste Management Order, which changed from DOE Order 5820.2A to DOE Order 435.1 (DOE, 1998). Prior to initiating the data collection effort with the goal of filling gaps that were identified in the 1996 PA, an ILAW testing strategy was developed to document the expected laboratory and field-scale testing, as well as model development activities required to evaluate the long-term corrosion behavior of LAW glass in the disposal facility at Hanford (McGrail et al., 1998b). This strategy was reviewed by a panel consisting of national and international glass corrosion experts prior to being adopted by the TWRS program for the 1998 PA (DOE, 1999; DOE, 2001; Grambow et al., 2000).

A major component of the testing strategy was the development of a numerical simulator at Pacific Northwest National Laboratory (PNNL) with the capability to compute time and spatial variations in the chemical environment of the unsaturated disposal systems in response to the corrosion of the glass waste forms, as well as other physical and chemical processes. Development of the numerical simulator was initiated in 1998 (Mann, 1997; Mann and Myers, 1998b; McGrail et al., 1998a). Additionally, a series of experimental techniques was outlined as part of the strategy that, when combined, provided the model parameters (i.e., rate law parameters, see Section 3.2) needed to simulate long-term glass performance. This approach was evaluated using data collected from 1996 to 1997 on the LD6-5412 glass. The LD6-5412 glass (composition provided in Table 2.1) was developed to serve as a simple reference glass during Part A of the TWRS privatization project (Wagoner, 1996) for use in high-temperature melters with double-shell slurry feed supernatant waste composition (Mann et al., 1998a; McGrail et al., 1997a). The 1998 PA also used the 7-day PCT RFP limit as the base case; the rate law parameters (Figure 2.1) derived from the LD6-5412 glass test data were used in sensitivity analyses using the AREST-CT computer code (Chen et al., 1995; Chen et al., 1996). The 1998 PA was substantially more robust than the previous iterations because of the increased understanding of waste form performance, disposal facility location, disposal facility design, and site-specific information on geologic data, geochemical data, hydraulic parameters, and water infiltration rates for the 200 Area plateau.

Table 2.1. Composition (mass%) of LAW Reference Glass used in Waste Form Performance Tests from 1998 to 2005

Oxide	**LD6-5412**	**LAWA23***	**LAWA33**	**LAWABP1**	**LAWA44**	**LAWB45**	**LAWC22**
Al_2O_3	12.00	9.70	11.97	10.00	6.20	6.13	6.08
B_2O_3	5.00	4.23	8.85	9.25	8.90	12.34	10.06
CaO	4.00	4.46	0.00	0.00	1.99	6.63	5.12
Fe_2O_3	0.00	7.43	5.77	2.50	6.98	5.26	5.43
K_2O	1.46	2.31	3.10	2.20	0.50	0.26	0.10
La2O3	0.00	0.00	0.00	2.00	0.00	0.00	0.00
Li_2O	0.00	2.08	0.00	0.00	0.00	4.62	2.51
MgO	0.00	2.08	1.99	1.00	1.99	2.97	1.51
Na_2O	20.00	20.00	20.00	20.00	20.00	6.50	14.40
SiO_2	55.91	40.52	38.25	41.89	44.55	47.86	46.67
TiO_2	0.00	0.00	2.49	2.49	1.99	0.00	1.14
ZnO	0.00	3.43	4.27	2.60	2.96	3.15	3.07
ZrO_2	0.00	3.05	2.49	5.25	2.99	3.15	3.03
Others	1.63	0.71	0.82	0.82	0.95	1.13	0.88

*Also known as BNFL-A-98

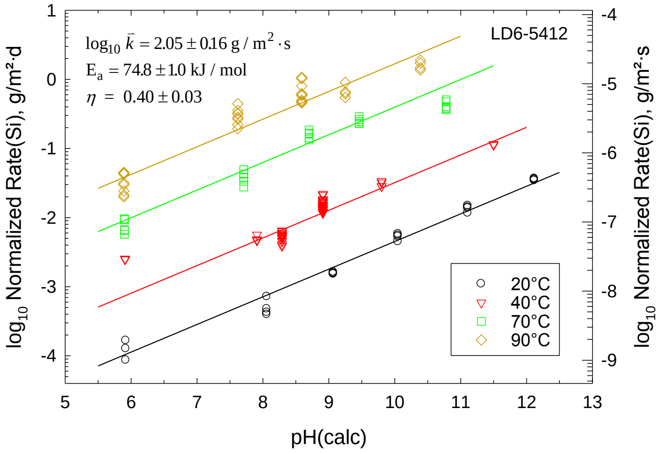


Figure 2.1. Normalized Silica Release Rate as a Function of pH and Rate Law Parameters for Reference Glass LD6-5412. The LD6-5412 glass was developed during Part A of TWRS privatization project (McGrail et al., 2000a).

During Part B of the TWRS privatization project, the DOE ORP divided the anticipated LAW into three compositional envelopes: A (highest Na^+:SO_4^- ratio), B (lowest Na^+:SO_4^- ratio), and C (significant complexant concentrations and intermediate Na^+:SO_4^- ratio). The BNFL Inc. team, which at the time was contracted to design and operate the WTP, developed a reference glass composition, LAWA23 (also known as BNFL-A-98), which met DOE contract durability requirements as defined in Wagoner (1996)[1]. The reference glass composition, along with several other preliminary glass compositions, was evaluated using PCT, a vapor hydration test (VHT), and several of the methods described in the 1998 and updated 2000 LAW glass testing strategy documents, such as the SPFT and PUF tests (McGrail et al., 1998b; McGrail et al., 2000a). The latter tests are used to derive rate law parameters that can then be used in modeling efforts. Results from the tests conducted with the slow-cooled LAWA23 glass samples indicated that this glass corroded at rates orders of magnitude higher than the quenched samples. Further evaluation of the laboratory batch glass samples with Transmission Electron Microscopy (TEM) revealed that slow-cooled LAWA23 glass samples were phase separated (Figure 2.2). This revelation caused the BNFL and TWRS project team to consider alternative glass compositions, and replaced the LAWA23 reference glass composition with LAWA33 for Envelope A. The compositions for the LAWA23 and LAWA33 glasses are provided in Table 2.1.

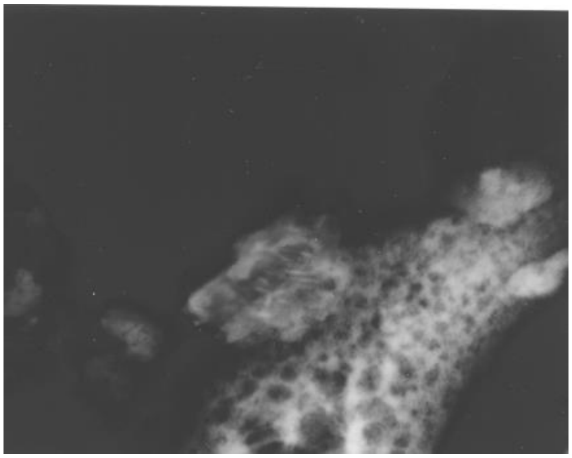


Figure 2.2. TEM Photos of LAWA23 Glass at 75,000×. Possible liquid-liquid phase separated regions are clearly evident along with a crystalline flake of unreacted Al_2O_3 (located at picture center). Image is from (McGrail et al., 1998c).

Similar to LAWA23, durability test experiments (i.e., PUF and PCT) with the LAWA33 glass demonstrated accelerated corrosion (e.g., Stage III, see Section 3.0). However, unlike LAWA23, the performance of LAWA33 was consistent for slow-cooled and quenched samples (McGrail et al., 1998b). The LAWA33 glass composition was then modified by PNNL to develop a glass with high performance and 20 wt% Na_2O by increasing the mass of ZrO_2 and adding La_2O_3. The resulting glass was known as LAWABP1 (see composition in Table 2.1) (McGrail et al., 2000c). The LAWABP1 glass was not intended to be an actual LAW glass composition produced at WTP; the purpose of producing LAWABP1 was to demonstrate that, with minor adjustments in composition, LAW glass with 20 wt% Na_2O could meet the DOE contract durability requirements, demonstrate high performance, and would not exhibit accelerated corrosion (e.g., Stage III, see Section 3.0).

Similar to the data generated for LD6-5412, LAWABP1 was used as a reference LAW glass to generate model parameters (rate law parameters and a chemical reaction network) in support of the PA (Figure 2.3) (Mann et al., 2001; McGrail et al., 2000c; McGrail et al., 2001b). In addition to being

---

[1] The BNFL Inc. contract was terminated and awarded to Bechtel National Inc. (BNI) in 2000.

documented in the 2001 PA, a journal article was published (McGrail et al., 2000b) to document the results of the experiments conducted on LAWABP1 and the Subsurface Transport Over Reactive Multi-phases (STORM) simulations used to forecast radionuclide release from the engineered portion of the disposal facility. The STORM computer code development was sponsored by the DOE and the TWRS program from 1998 through 2001 to support the base and sensitivity cases in the 2001 PA (Mann et al., 2001; McGrail et al., 2000a). The STORM computer code is a simulator that was developed by coupling Subsurface Transport Over Multiple Phases (STOMP), a non-isothermal multiphase flow simulator (White et al., 1996; White et al., 2006), with AREST-CT Version 1.1, a reactive transport and porous medium alteration simulator (Chen et al., 1995; Chen et al., 1996). The 2001 PA represents a transition to using a coupled flow and transport simulator (STORM) for both the base and sensitivity cases, whereas AREST-CT was only used to support sensitivity cases in the 1998 performance assessment (Mann et al., 1998a). More details on these computer codes are given in Section 4.0.

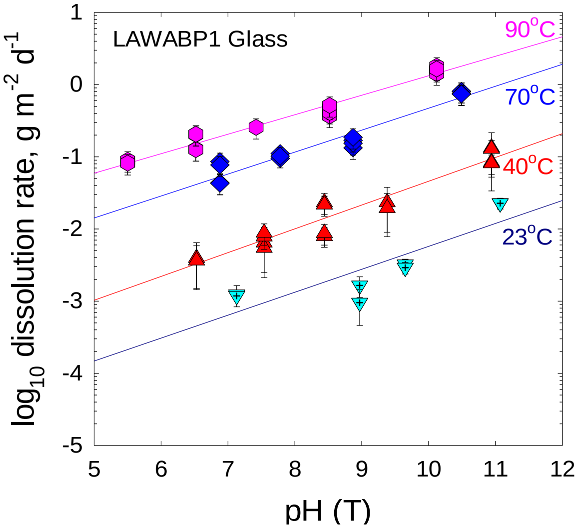


Figure 2.3. Normalized Glass Dissolution Rate, Based on Boron, as a Function of pH(T) for LAWABP1 (McGrail et al., 2000c).

As a result of the marginal performance of LAWA33, the DOE adjusted the durability specification to include a 90 °C PCT-A and 200 °C VHT (DOE, 2000; Vienna et al., 2001). Each test was required to be performed on samples that were heat treated to represent canister cooling. The PCT constraint was aimed at eliminating glasses with very low-durability secondary phases (e.g., amorphous or crystalline phase separation), and the VHT requirement was aimed at avoiding glasses prone to Stage III accelerated release of elements. The VHT contract constraint of 50 g/m^2d was set to be slightly below the measured value of LAWA33, which by testing and modeling, was determined to be a marginally performing glass. Based on the new contract specifications, the BNFL team developed three new reference glasses – LAWA44, LAWB45, and LAWC22 for envelopes A, B, and C, respectively (Table 2.1).

The three reference glasses, LAWA44, LAWB45, and LAWC22, were tested from 2001 to 2004, and the results were documented in the 2005 waste form release data package (Pierce et al., 2004; Vienna et al., 2001). The three reference glasses underwent a full set of performance tests: SPFT, PCT-B, VHT, and PUF. Two glass samples, LAWA102 and LAWAP101, prepared using actual Hanford LAW, were also tested from 2001 to 2004. The results from these glasses, where only PUF tests were performed, were also documented in the 2005 waste form release data package (Pierce et al., 2004; Vienna et al., 2001). In addition to the data package, these results were documented in a series of journal articles (Icenhower et al., 2008; Pierce et al., 2006; Pierce et al., 2011). None of the experimental results with the three new reference or radioactive glass samples saw Stage III acceleration.

In the mid 2000's, the WTP project underwent a major shift in the tank waste flow-sheet for LAW treatment under the direction of the Bechtel National Inc. (BNI) led WTP design, construction, and commissioning team. Initially, in 2003, the three LAW envelopes were split into seven sub-envelopes (A1, A2, A3, B1, B2, C1, and C2) to adjust for differences in formulations based on waste composition differences. Then, in roughly 2005, the envelope-based LAW glass formulation approach was changed to a continuum composition approach. In the continuum approach, glass is formulated based on waste composition (primarily the alkali to sulfate ratio) instead of grouping the waste into specific envelopes (Vienna, 2005). This change resulted in significant changes to the anticipated WTP glass compositions. Therefore, from 2006 to 2012, the project supported a limited number of studies to evaluate new glasses that spanned compositional ranges expected to be produced at WTP, specifically alkali:SO_3 ratios. This series of glasses was formulated and tested in various scaled melter systems up to and including the 1/3-scale Duratek pilot facility in Columbia, MD. This approach used the Na^+:SO_4^{2-} ratio of the waste to interpolate between reference glasses (Kim et al., 2012; Muller et al., 2004; Vienna, 2005). Figure 2.4 shows the waste loading for these continuum glasses on a plot of Na_2O versus SO_3 wt% in glass. The waste loading for a given glass is determined by its location on this plot (corresponding to the blue line). The concentration of all other glass components was then interpolated based on the normalized alkali concentration of the waste ($ALK = Na_2O+0.66\times K_2O$), as shown in Figure 2.5. All glass formulated along this series of lines is a direct interpolation of other glasses along a single independent composition dimension (ALK:SO_3). Each of the glasses used to form the trend met all property constraints, and were processed successfully up to pilot scale. Following this strategy significantly lowers the risk of difficulties during operations, and is currently planned to be used in WTP commissioning. The strategy is often referred to as the WTP baseline formulation approach, or the commissioning formulation approach.

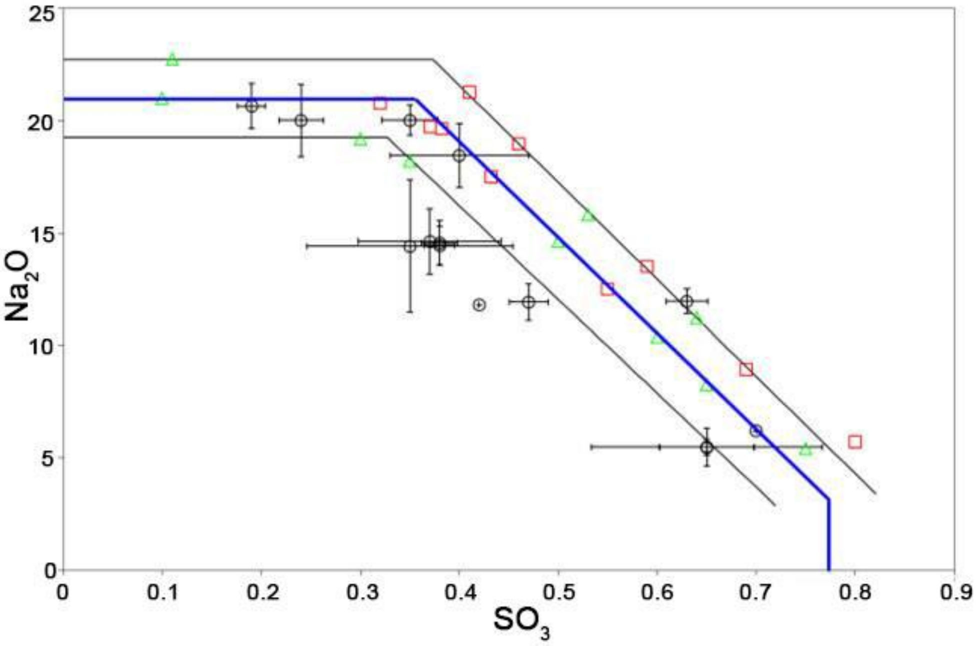


Figure 2.4. Reference ILAW Glasses Used to Develop Continuum Formulation Approach Shown in the Na_2O and SO_3 wt% Concentration Plot

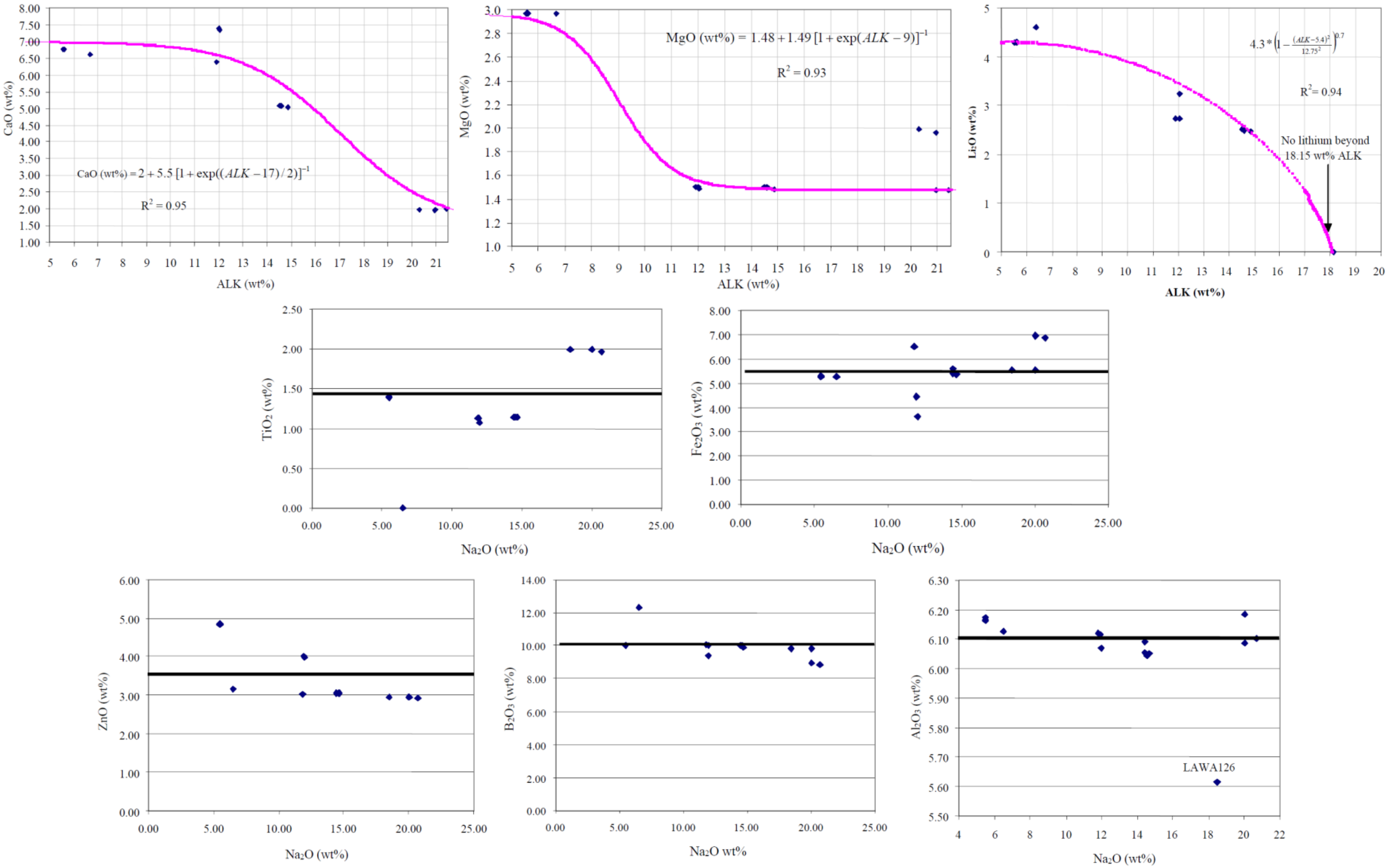


Figure 2.5. Component Concentrations as a Function of Either ALK or Na_2O (wt%) (Muller et al., 2004)

In order to further support ILAW PA efforts, further testing was then initiated on the glasses — E1A, E95A, and E290A — that fall on the correlation line (Figure 2.6). This testing augmented the previously tested glasses LAWA44, LAWB45, and LAWC22. It is important to note that LAWA44, LAWB45, and LAWC22 were part of the dataset used to develop the correlation line. Over the course of four years, a select number of experiments were conducted on the new glasses (E1A, E95A, and E290A), with the majority of the work being performed on E1A. These results were documented in a series of letter reports and one journal article (Pierce et al., 2008), which suggested the performance of the three new glasses were consistent with LAWA44, LAWB45, and LAWC22 glass formulations. For example, Pierce et al. (2008) confirmed that the dissolution rates under dilute conditions for E1A, E95A, and E290A were similar to several of the previous LAW glass formulations. Based on the data collected for these glasses, as well as the data collected in 2004 on LAWA44, LAWB45, and LAWC22, the corrosion behavior of the glass compositions that are along this continuum are considered to be well understood.

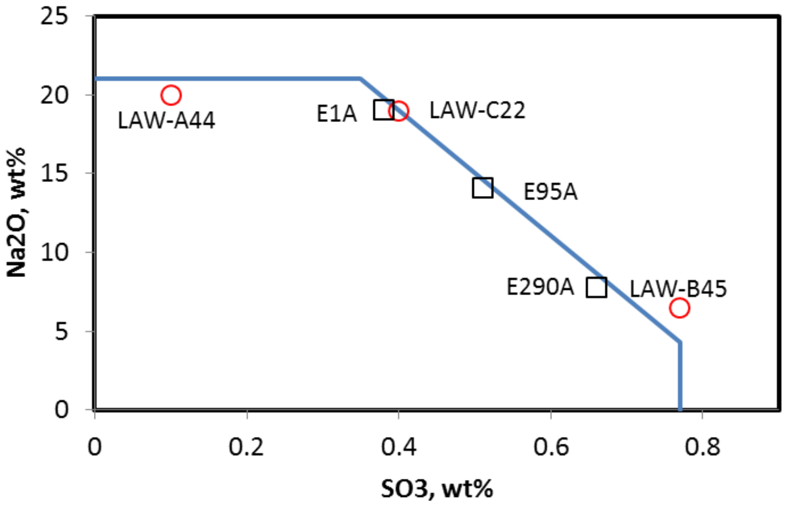


Figure 2.6. Glasses Selected for ILAW Performance Testing Shown on Na_2O wt% versus SO_3 wt% Concentration Plot

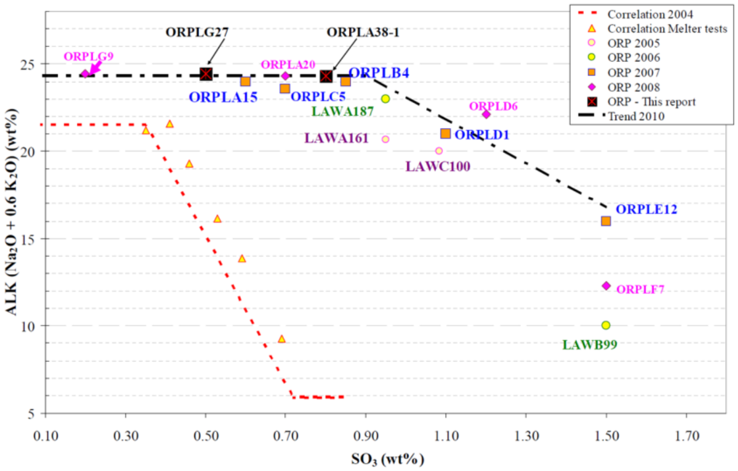


Figure 2.7. Comparison of WTP Reference Formulations with Advanced Glasses Optimized for Maximum Waste Loading (Muller et al., 2010)

Though the corrosion behavior of the glass compositions along the correlation line are assumed to be well understood, it was noted that significant cost and process flexibility gains were achievable through the optimization of waste loading in LAW glass formulations. This realization has led to an ongoing effort to optimize waste loadings, and this has significantly increased the range of various components in glass (Muller et al., 2010; Muller et al., 2012; Vienna et al., 2013a). Figure 2.7 compares the optimized glasses with the commissioning glasses described above on the ALK-SO_3 wt% concentration plot. It is clear from the figure that waste loadings for low Na^+:SO_4^{2-} ratio wastes increased by roughly 100%, and that the waste loadings for high Na^+:SO_4^{2-} ratio wastes increased by roughly 13%. When optimizing glass for maximum waste loading, it is no longer possible to simply interpolate from one successful glass to another along a single composition direction (e.g., ALK or Na^+:SO_4^{2-} ratio). A limited number of glass samples identified by Muller et al. 2010 were evaluated from 2010 until 2013. These glasses illustrated reasonable performance, and have been documented in a series of reports (Pierce et al., 2010a; Pierce et al., 2013). However, significant changes in the proportion of major glass components, which have been formulated with the goal of increasing the LAW loading, have occurred since 2010 (Vienna et al., 2013a). For example, Figure 2.8 shows the variation in major glass components as functions of ALK. For some components (e.g., CaO, Li_2O, MgO, SnO_2, and ZrO_2), there is a trend between the component concentration and ALK. For other components (e.g., Al_2O_3, B_2O_3, SiO_2, V_2O_5, and ZnO) no logical trend is formed with ALK, SO_3, or the ALK:SO_3 ratio. The composition variation for these advanced glasses can only be described in a multivariate space with a minimum of six independent composition variables. This is a fundamental difference compared to the one compositional variable that ties the WTP baseline glass formulations together. This change in formulation approach will also require a change in the strategy to evaluate the performance of glasses to be produced at WTP.

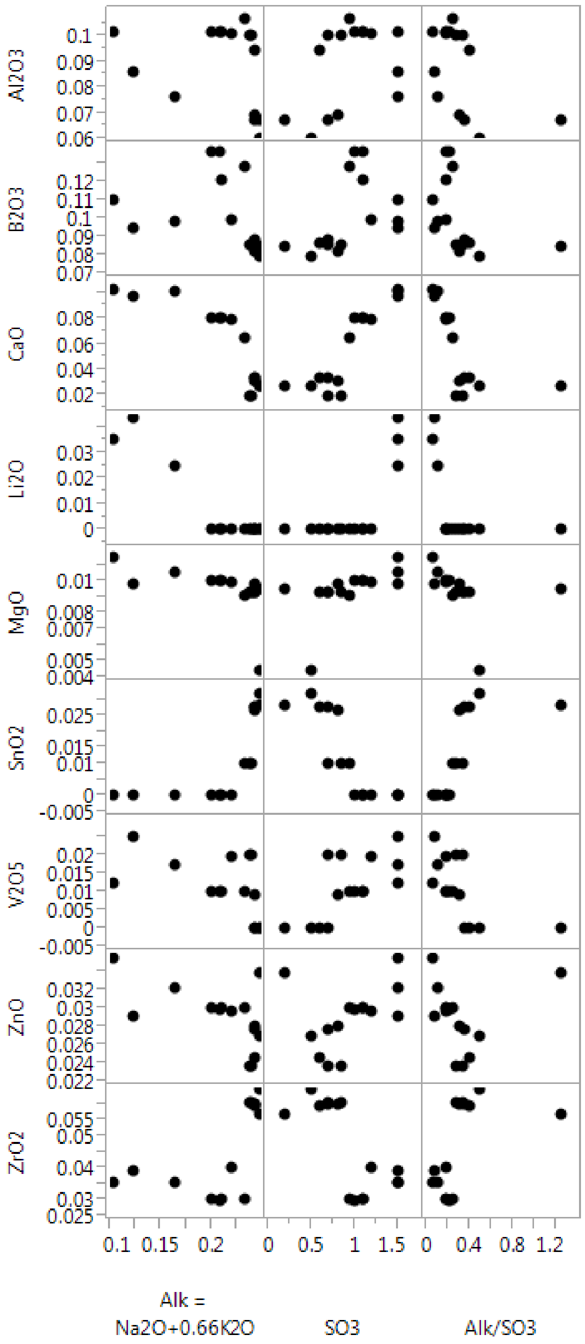


Figure 2.8. Concentration of Key Glass Components as Functions of Alkali (ALK), SO_3, and ALK/SO_3 in Mass Fraction

As a result of this change, PNNL has been tasked with studying the newer advanced glass compositions being developed to optimize waste loading to understand the impacts of the varied compositions on performance. The objective of the current strategy document is to outline performance testing, data collection, and analyses of the ILAW glass product for subsequent use in the IDF PA to show the potential environmental risk associated with long-term storage.

3.0 Review of Glass Dissolution Processes

In this section, we provide a description of the glass dissolution process, which is important for calculating radionuclide release rates in the disposal system. We begin with a brief description of the stages of glass dissolution and follow with a description of three glass corrosion mechanisms that will be studied at length in the current strategy: ion exchange, the kinetic rate law parameters, and the effects of secondary phase formation. It is important to note that throughout this document, corrosion refers to all stages of glass-water reaction, which are discussed below, and dissolution refers to the mechanism of elemental release or the rate of elemental release during the glass-water reaction.

3.1 Stages of Glass Dissolution

In general, the glass dissolution process may be divided into three main stages (Bates et al., 1994): **Stage I -** the initial interdiffusion of water into the glass network leading to the release of alkalis and the hydrolysis of the silicate network, **Stage II -** the buildup of Si in solution and the formation of alteration layers on the glass surface that correspond to a decrease in the glass dissolution rate to a relatively constant residual rate, and **Stage III -** the resumption of high elemental release rates that coincide with formation of key alteration phases on the glass surface that occur only for some glass compositions under certain conditions. Additionally, during these stages of glass alteration, the ion exchange reaction is continuing and may control the release of radionuclides, particularly under silica-saturated conditions at long time periods. A conceptual schematic of these stages as well as the extent of alteration of the glass with reaction extent (i.e., time) is given in Figure 3.1. It should be noted that different glasses have different dissolution rates, and not all glasses enter Stage III as shown for a group of representative glasses in Figure 3.2. More details on the behavior of the glass during the various alteration stages are given in Appendix B.

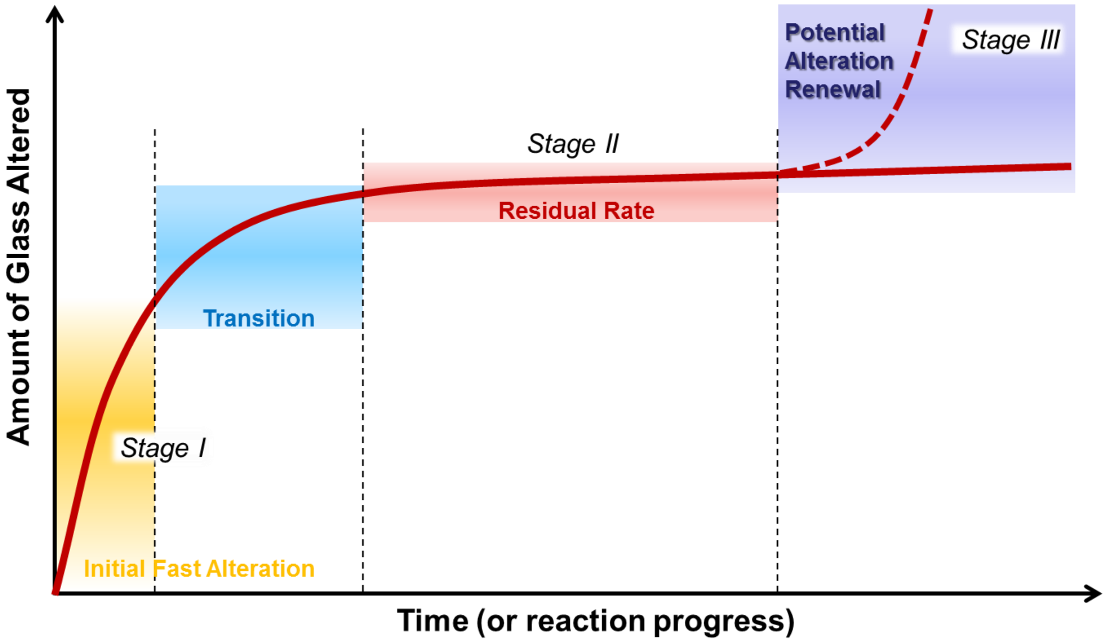


Figure 3.1. General Schematic of the Stages of the Glass-Water Reaction (Vienna et al., 2013b)

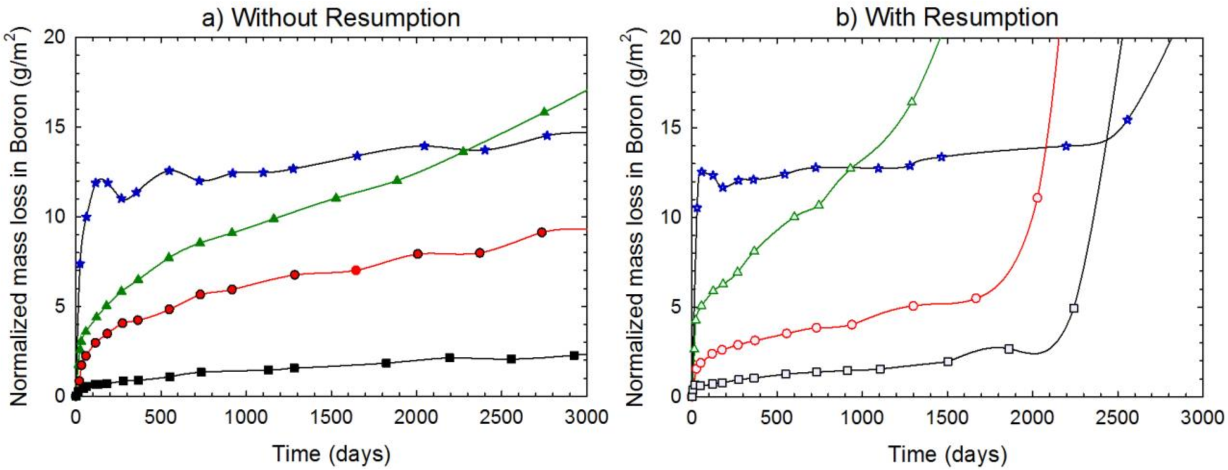


Figure 3.2. Normalized Boron Release (g/m^{-2}) by 90 °C Product Consistency Test (PCT) for Simulated HLW Glasses (Ribet et al., 2004b). The graphs have been redrawn for clarity.

3.2 Kinetic Rate Law Parameters

Previous IDF source-term calculations (Mann et al., 1998a; Mann et al., 2001), as well as the 2003 risk assessment (Mann et al., 2003), have assumed that radionuclide release (source term) from the near-field disposal system is controlled by the glass alteration rate. The approach employed uses a chemical affinity rate law to calculate the glass alteration rate. Although there are some issues regarding the applicability of the affinity rate law, it can be used to describe experimental data across a wide range of conditions (Pierce et al., 2004). This rate law is based on an irreversible reaction because glass cannot reform (i.e., precipitate from solution) under these conditions. It is important to note that a static or near-static solution becomes concentrated with components as the glass-water reaction proceeds, and numerous sparingly soluble elements (e.g., Al, Si, Zr) contained in the glass can condense at the glass-water interface after being initially dissolved. The condensed sparingly soluble elements will form a chemically and structurally distinct crystalline or amorphous alteration phase, which affects the flux calculation. How we account for this process will be discussed in greater detail below.

The equation used to compute the flux of element *i* released from the glass into the aqueous phase is given by:

$$r_i = \nu_i \vec{k} a_{H^+}^{-\eta} \exp\left(\frac{-E_a}{RT}\right)\left[1-\left(\frac{Q}{K_g}\right)\right]^{\sigma} \tag{3.1}$$

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 the rate controlling reaction
K_g = equilibrium constant of the rate controlling reaction
σ = Temkin coefficient

In the case of modeling the ILAW glass corrosion process, a dissolution reaction is used that converts glass to orthosilicic acid, H_4SiO_4, after it reacts with water. Equation (3.2) gives a simplified reaction scheme for ILAW glass corrosion using amorphous SiO_2 as a representative solid for glass.

$$\mathrm{SiO_2(am) + 2H_2O \rightarrow H_4SiO_4} \tag{3.2}$$

The rate at which this reaction occurs is a function of temperature, pH, and the aqueous concentration of H_4SiO_4, which is represented by *Q* in Equation (3.1). Equation (3.1) is used to represent Stage I of the glass-water reaction. An additional equation is used in modeling the ILAW glass corrosion process to account for aspects of Stage I (i.e., interdiffusion) and Stage II of the glass-water reaction, Equation (3.3). Equation (3.3) is used to calculate the flux of sodium, which occurs as a result of alkali ion-exchange. The ion exchange rate (r_{IEX}) is given by:

$$r_{IEX} = r_0 \exp\left(\frac{E_{IEX}}{RT}\right) \tag{3.3}$$

where
r_{IEX} = the ion exchange rate, mol of Na/(m^2·s)
r_0 = intrinsic ion exchange rate constant, mol of Na/(m^2·s)
E_{IEX} = activation energy for ion exchange, J/mol

For ILAW glass, Na is used to represent alkali-ion exchange because Na is the single most abundant alkali contained in LAW glass formulations. During Stage II of the glass-water reaction, Na is continuously introduced from the glass to solution, affecting the steady-state pH as Equation (3.1) approaches saturation (i.e., $Q/K \rightarrow 1$). This constant flux of sodium results in a continuous change in solution pH, thus affecting the long-term rate of glass corrosion.

The parameters $\vec{k}$, E_a, η, and K_g can be derived using the Single-Pass Flow-Through (SPFT) test method (see Appendix D.1) as shown in Section 5.0 (Icenhower et al., 2008; McGrail et al., 1997a; McGrail et al., 2000a; McGrail et al., 2001c; Pierce et al., 2005; Pierce et al., 2010b). Bacon and Pierce (2011) have conducted a study on the various sensitivities of these parameters as it relates to the estimated long-term radionuclide releases from glasses in unsaturated conditions. Using data from the prototypic ILAW glass composition, LAWA44, they surmised that K_g is the most sensitive variable affecting radionuclide release. To determine if this conclusion is valid for the new range of glass compositions, which have higher alkali contents, measurements of K_g as well as the other parameter will be obtained for these newer glass compositions. A detailed discussion of other rate laws available in the literature is given in Appendix C.

3.3 Ion Exchange

The interdiffusion process is defined by H^+, H_3O^+, and/or H_2O in the fluid phase being exchanged for network-modifying cations in the glass, and has been observed experimentally for decades (Doremus, 1975; Rana et al., 1961a; Rana et al., 1961b). Although ion exchange does not receive the level of attention that network hydrolysis and matrix dissolution receives, it has been the focus of some nuclear waste glass corrosion studies (Icenhower et al., 2002; McGrail et al., 2001c; McGrail et al., 2003; Neeway et al., 2014a; Ojovan et al., 2006; Pierce et al., 2005). One reason for the focus on hydrolysis and dissolution is that the ion-exchange reaction has been thought to be of short duration, and therefore had little or no bearing on the long-term radionuclide release from the glass (Vernaz et al., 1992). However, the importance of the ion-exchange process may be especially relevant at low temperature and in solutions that are near-saturated with respect to SiO_2(am). The overall chemical reaction describing the exchange of a cation, M^+, with a charged water species, given here as a proton, is written as:

$$\equiv \text{Si-O-M} + \text{H}^+ \rightarrow \equiv \text{Si-OH} + \text{M}^+ \tag{3.4}$$

It should be noted that the ion exchange rate (r_{IEX}) is used to represent the sodium release from glass independent of the matrix dissolution described in Equation (3.4). This sodium release increases pH, and thereby influences r_i for all elements. Additionally, at the high pH values, the Si in solution will distribute among charged complexes, effectively reducing the amount of H_4SiO_4 in solution, and thereby driving the reaction to a higher dissolution rate. Therefore, through the continuous release of sodium, the solution continuously deviates from a steady-state condition and glass continues to corrode.

Previously, SPFT experiments have been used to investigate the ion-exchange reaction rate (r_{IEX}) (McGrail et al., 2001c; Pierce et al., 2004; Pierce et al., 2005). The method developed by McGrail and coworkers (2001c) distinguishes between matrix dissolution and the ion-exchange reaction by subtracting the rate of matrix dissolution, calculated from the boron release, from the Na release rates, and making the proper conversion to moles of sodium per unit area per time. The method is effective in conditions where silicon is added to solution, which suppresses the matrix dissolution rate but does not affect the Na-H exchange rate. As the concentration of dissolved silicon increases, sodium release rates become faster than boron release rates. McGrail et al. (2000c) has illustrated this mechanism with the LAWABP1 glass (Figure 3.3). A decreasing trend is found for dissolution rate, based on Na and B release, as a function of silicic acid concentration. Also shown in Figure 3.3 is a divergence in the Na and B release rate at the higher silicic acid concentrations. The steady release of Na at a higher normalized rate than that of B is a result of sodium ion-exchange reactions. By running the experiment at several temperatures, the apparent activation energy of the reaction can be calculated with the use of the Arrhenius equation. McGrail et al. (2000c) calculated the apparent activation energy to be 52.7 kJ/mol for LAWABP1. This value is consistent with other LAW glass formulations, LAWA44 (65 ± 6 kJ/mol), and a sodium silicate glass (47 kJ/mol) (Pederson, 1987).

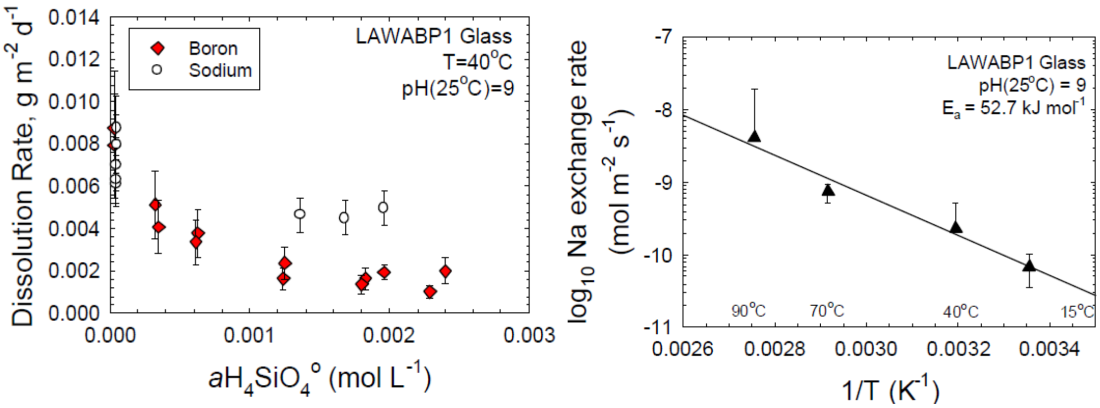


Figure 3.3. Dissolution Rate Based on B and Na Versus the Activity of Silicic Acid Concentration at 40 °C for the LAWABP1 (McGrail et al., 2000c) (left). This figure illustrates that, at high silicic acid concentrations, the Na release rates are faster than B release rates due to ion exchange. Ion-exchange rate versus reciprocal temperature for LAWABP1 Glass (right). Slope of the line through the data indicate an activation energy of 52.7 kJ/mol.

The ion-exchange process is especially important for new ORP glasses because of their high Na content. While the baseline WTP glasses had a total alkali content near 21 wt%, newer ORP glasses are envisioned to have a total alkali content near 24 wt%, making the understanding of the ion exchange mechanism even more important. The current understanding of ion exchange given by McGrail et al. (2001c), where simple Na_2O-Al_2O_3-SiO_2 glasses were examined, showed that the rate of Na ion exchange depends on the population density of non-bridging oxygen sites in the glass, the bond strength of Na atoms in Si–O^{-}Na^{+} sites, and mechanical stiffness (shear modulus) of the glass network.

A final note on the ion exchange process concerns temporal evolution of r_{IEX}. Currently, when Equation (3.3) is employed, the term r_{IEX} is a constant to account for the continuous ion exchange process. Experiments that have measured the value of r_{IEX} employed a method where the Na release rate is captured after the system is assumed to be at steady state (McGrail et al., 2001c; Pierce et al., 2004; Pierce et al., 2005). Assuming a constant value is technically imprecise, because the extent of a diffusive process, such as ion exchange, decreases as a function of time. This temporal decrease may be explained by Fick's 2nd law, given as:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x'}\left(D \frac{\partial C}{\partial x'} \right) \tag{3.5}$$

where the concentration, C, is a function of distance, x, and a diffusion coefficient, D. If the diffusion coefficient is a constant, the concentration of a species x can be solved at any point relative to the concentration of that species at distance 0, C_0:

$$C = C_0 erfc \frac{x'}{2\sqrt{(Dt)}} \tag{3.6}$$

where t is time in seconds. Thus the decrease in the rate of penetration of the diffusing species in the solid, which is directly related to its concentration, diminishes with the square root of time. Simply stated, if the interdiffusion rates of H^+ and Na^+ are constant and the interface moves slowly relative to the diffusion rate, then the flux must decrease with time at roughly the $t^{1/2}$. For this reason, the use of a constant r_{IEX} term may be inappropriate. Recent experiments performed using a HLW glass simulant, where the ion exchange mechanism has been isolated from the hydrolysis and dissolution mechanisms, have shown the rate of penetration of the diffusing alkali species diminishes with time (Neeway et al., 2014a). In short, additional research is required to better define the functional form of the ion-exchange term and parameterize the new series of glass compositions. This is critically important due to the secondary impact of ion exchange increasing pH, and thereby increasing dissolution rate.

3.4 Secondary Phase Formation and Resumption of High Elemental Release Rates

Because of the large glass volume and the low moisture and flow conditions of the disposal facility, the pore water is expected to become saturated with respect to secondary phases as the glass-water reaction proceeds with time. The secondary phases that form at the interface between the gel-layer and solution are often clay minerals (e.g., smectite, kaolinite, montmorillonite) (Buck et al., 1998; Curti et al., 2006; Pierce et al., 2007). The formation of clay phases has not been observed to change the dissolution from the residual rate. However, with the precipitation of certain phases, most often zeolitic phases, an acceleration in the reaction rate can occur (i.e., Stage III) (Van Iseghem et al., 1988). This acceleration has only been observed in static test conditions (e.g., $pH > 10.5$, $T \geq 90$ °C, high glass-surface-area-to-solution-volume (S/V) ratios), and in pressurized unsaturated flow (PUF) test conditions which have low flow, high S/V, and $T \geq 90$ °C. Furthermore, the rate acceleration has only been observed for certain glass compositions (Ebert et al., 2012; Ribet et al., 2004a), while others do not exhibit Stage III behavior under the same experimental conditions (Gin et al., 2001).

The effect of secondary phase formation on waste glass corrosion is another process that is taken into account when modeling long-term behavior in a disposal system. Generally, when glass corrodes in the presence of water, the secondary phases that form are metastable and evolve to more stable phases with time. Phases identified in laboratory experiments (Ebert et al., 2012; Fournier et al., 2014; Pierce et al., 2013; Ribet and Gin, 2004a; Strachan et al., 2000; Strachan et al., 2014; Van Iseghem and Grambow, 1988) for a given glass are used as inputs to the reactive transport model as part of its chemical reaction network. The reactive transport simulator functions by calculating the temporal evolution of the glass-water reaction in the disposal system, as a function of time and space. As a solution in contact with a dissolving glass becomes more concentrated in glass components, the solubility limit for a specific alteration phase(s) contained in the chemical reaction network is achieved. It should be noted that if a certain phase is included in the list of possible phases that may form from a given glass composition, it does not necessarily mean that the particular phase will form in a simulation. However, when a given secondary phase reaches its solubility limit, certain solution species are removed from the contacting solution to form the secondary phase, and the chemical composition of the solution responds to this change. Ultimately, the glass transforms into an assemblage of alteration products or minerals. Because the glass is expected to supply the majority of the species in the fluid in the disposal system, secondary phases that form depend primarily on the composition of the glass. If a given glass composition is relatively stable with respect to the assemblage of alteration products or minerals, the glass will corrode slowly in a solution expected to be saturated with respect to amorphous silica. This phenomenon has been demonstrated in natural glasses that have undergone only slight corrosion over geological time scales (Libourel et al., 2011; Luo et al., 1998; Techer et al., 2000). On the other hand, the glass may become unstable with the formation of these secondary phases, and the glass dissolution rate will accelerate. Consequently, the laboratory testing program is designed to determine what LAW glass compositions are prone to acceleration under IDF disposal conditions.

The Stage III rate acceleration has been attributed mostly to the precipitation of zeolitic phases (Ebert et al., 2012; Ribet and Gin, 2004a; Strachan and Croak, 2000; Strachan and Neeway, 2014; Van Iseghem and Grambow, 1988), but the process through which the effect occurs remains poorly understood. The mechanism by which phase precipitation and glass dissolution are coupled must be known to incorporate the effect into the waste glass degradation model. We note again that an increase in rate has only been observed in certain conditions and glass compositions (Ebert et al., 2012; Fournier et al., 2014). High-level waste glasses (Ribet and Gin, 2004a; Van Iseghem and Grambow, 1988) have exhibited this phenomenon, and so have a few representative LAW glasses (McGrail et al., 1998b). Static experiments have suggested that aluminum may play a significant role in Stage III behavior, with the aluminum concentration decreasing abruptly as the alteration rate increases (Barkatt et al., 1991; Gin and Mestre, 2001; Ribet and Gin, 2004a). On the other hand, the silicon concentration has been shown to increase during the same period (Barkatt et al., 1991), which was wrongly assumed to be inconsistent with the precipitation of aluminosilicate phases (see also (Vienna et al., 2013b)) and references contained therein). Strachan and Neeway (2014) recently identified an increase in the silicon concentration to be possible because of a decrease in the rate-limiting H_4SiO_4 activity that occurs near pH 9, with an increase in the negatively charged $H_3SiO_4^-$ activity causing a net increase in the silicon concentration. A recent experiment by Fournier et al. (2013) showed no effect to the alteration rate of the intermediate activity glass, CSD-B, when analcime grains were added to the experiment as a seed for nucleation, but that the rate accelerated when the silicon-rich zeolite P was added to a separate system at the same experimental conditions. The large difference in effect with small compositional difference suggests the conditions required to initiate Stage III are complex. These experiments also illustrate the importance of developing a chemical reaction network for the ILAW PA.

A final note on the effect of secondary phases on glass dissolution is that at low temperatures, a number of factors create uncertainty in the chemical reaction network.

- In most cases, the more thermodynamically stable phase is expected to form; however, because this phase precipitates at a slower rate, the amorphous or cryptocrystalline (e.g., metastable) phase is actually observed in laboratory measurements.

- The thermodynamic data required to incorporate these metastable phases into the chemical reaction network are limited and the estimates are based on an adjustment to the low-temperature stable-phase thermodynamic data. Furthermore, the thermodynamic databases do not contain measurements for phases where the chemistry has deviated from ideal as a result of elemental substitutions or phases that form solid solutions.

- The formation of the phases contained in the chemical reaction network is assumed to be instantaneous, but in reality, kinetics, specifically paragenetic sequence, plays a role in the formation of a variety of phases.

Each of the aforementioned factors can have a noticeable impact on secondary phase formation, and therefore glass corrosion and radionuclide release.

This generates some uncertainty because: (1) the phases formed in accelerated tests may not form in the timescales important to controlling glass dissolution in the disposal environment, (2) the thermodynamic data for the amorphous phases known to form first are not generally available nor are the data for the broad range of solid solutions observed, and (3) the kinetics of phase formation will likely influence the glass dissolution rate and are not well enough understood to incorporate in the models. In the case of the kinetics of phase formation, assuming instantaneous formation is conservative.

4.0 IDF PA Source Term Model Approach

The ILAW glass represents a primary barrier that minimizes radionuclide release from the near-field of the IDF LAW glass disposal cell. Thus, having a robust approach to evaluating the long-term behavior of this material is a critical component of the overall PA strategy. Our understanding of the glass corrosion process has increased significantly, especially during the last decade, because models are now able to predict glass performance based on fundamental principles of physics, chemistry, and thermodynamics. Presently, several modeling approaches are being used to predict nuclear waste glass performance for millennia. For the IDF PA, we only consider the first-order affinity model described in Equation (3.1) with adjustments due to sodium ion exchange, in Equation (3.3). Additional details describing other modeling approaches are provided in Appendix C. The affinity model and ion-exchange model can be incorporated into the physics-based process simulators, STOMP and eSTOMP. Here we give a description of STOMP/eSTOMP and how it can be used for predictive analyses in the PA.

4.1 PA Requirements

The specific parameters obtained from the proposed glass corrosion test methods that have been explained in Section 3.0 (i.e., PUF, PCT, SPFT, and VHT) can be used as inputs to STOMP/eSTOMP for predictive analyses in the PA. The parameters serve as a base for the chemical reaction network and kinetic rate law parameters used in the model. Preliminary system PA sensitivity or probabilistic calculations can alert staff as to which parameters are most sensitive in controlling the risk or impacts. This knowledge could guide additional laboratory testing to improve the accuracy, narrow the range of values for key parameters, and acquire more technically defensible supporting information before the final PA is submitted to the regulators and other stakeholders.

Figure 4.1 shows a simplified soil column from ground surface to the unconfined aquifer at the IDF site. Yellow boxes to the left of the column generally describe the type of modeling that is conducted for the PA. This strategy has already been employed in the 2001 PA (Mann et al., 2001). Reactive transport is a key element of the modeling, as it is used to predict the fate of water and gases, the evolution of the waste packages and repository components over time, and the fate of any released contaminants, the macro solutes, and reactive gases through the near-field zone and to the vadose zone. A non-reactive fate and transport model then tracks the migration to the aquifer and to any potential environmental receptors. Dose calculations are then performed and compared to toxicity levels to quantify risks to receptors. Sensitivity and probabilistic analyses are used to determine a range of doses or impacts to account for uncertainty in input parameters, limitations in the numerical algorithms (usually simplifications of controlling mechanisms) used to process the complex interactions that control the degradation or weathering of system components, and scenario uncertainties associated with future conditions.

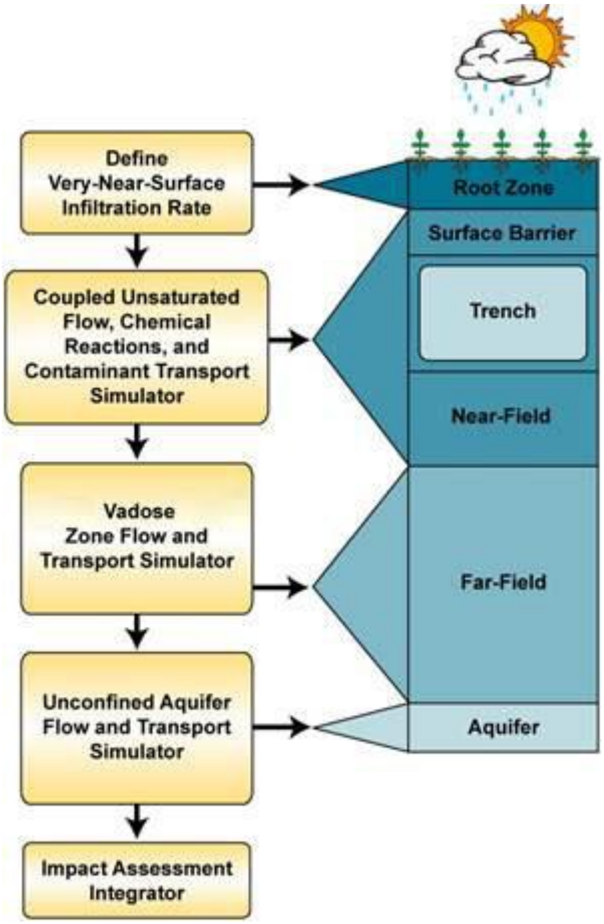


Figure 4.1. Approach to Modeling the Near-Field Environment for the IDF PA

4.2 Reactive Transport Simulators for the Waste Form Calculations

The main focus of the testing described in this strategy document fits into the box in Figure 4.1 labeled Coupled Unsaturated Flow, Chemical Reactions, and Contaminant Transport Simulator. Historically, the IDF system PA used STORM (Bacon et al., 2000; Bacon et al., 2004), a reactive transport simulator, to perform the near-field calculations of radionuclide releases from the glass. STORM was developed by coupling STOMP, a non-isothermal multiphase flow simulator (White et al., 2000; White and Oostrom, 2006), with AREST-CT Version 1.1, a reactive transport and porous medium alteration simulator (Chen et al., 1995; Chen et al., 1996). More details on STORM can be found in Bacon et al. (2000; 2004), Bacon and McGrail (2001), McGrail et al. (2001a), and Mann et al. (2001; 2003).

STORM represented subsurface flow and transport as a set of coupled, nonlinear, partial differential equations. The equations described the rate of change of pore water solute concentrations in variably water unsaturated, non-isothermal porous media. STORM capabilities included kinetic dissolution of glass (or other waste forms), kinetically controlled precipitation and dissolution of secondary phases, equilibrium aqueous solutes speciation, gas-aqueous equilibria, two-phase flow (water and air), and dynamic updates to porosity and permeability as changes in mineral volumes occurred. Most importantly, STORM simulated the waste form dissolution kinetic reaction in which equilibrium depends on silica and aluminum. Reactive transport in STORM was coupled with unsaturated flow, meaning that the unsaturated flow field could be altered by mineral dissolution and precipitation reactions. STORM was also designed to run efficiently in parallel on multi-core workstations and supercomputers, shortening execution times.

The STORM simulator, however, limits reactive transport to two dimensions, and cannot simulate three-dimensional flow and transport resulting from heterogeneities in the subsurface. Moreover, STORM is no longer under active development, and has not received a Class C Safety and Hazard Analysis and Design Software classification. Therefore, under DOE Order 414.1C, STORM cannot be used for future risk and PA analyses.

STOMP (White and Oostrom, 2006) can simulate flow and reactive transport in three dimensions, and adheres to rigorous quality assurance (QA) procedures that are compliant with DOE Order 414.1C. STOMP is a general purpose simulator that was developed at PNNL for modeling subsurface flow and transport under variably saturated conditions. The simulator uses a variable source code configuration that allows the execution memory and speed to be tailored to problem specifics. Quantitative predictions from the STOMP simulator are generated from the numerical solution of partial differential equations that describe subsurface environment transport phenomena. 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 (White et al., 2005) is used to simulate reactive geochemistry. Using the variable source code configuration of STOMP, reactive transport simulations can be implemented using an executable designated as STOMP-W-R, which simulates the governing equations for flow, solute transport, and reactive geochemistry. It is important to note that STOMP development is managed under a Configuration Management Plan (CMP) in conjunction with a Software Test Plan (STP) that details the procedures used to test, document, and archive modifications to the source code. Formal procedures for software problem reporting and corrective actions for software errors and updates are maintained and rigorously implemented. Documentation of all verification and validation testing is publicly available.

The eSTOMP simulator, the highly-scalable (parallel) version of STOMP, has been updated with the same waste form calculations that have already been incorporated into STOMP. The eSTOMP simulator was developed from STOMP using a component-based approach. The key features of this conversion were: (1) the definition of a data model to describe a grid that is distributed over multiple processors, (2) the definition of a grid component interface based on this model, and (3) the implementation of the grid component and the conversion of the remaining portions of the code using the Global Arrays toolkit (GA) (Nieplocha et al., 2006). The GA toolkit supports a one-sided communication, shared memory style programming model on both shared and distributed memory platforms. Because the eSTOMP simulator is highly scalable, it is ideally suited for running waste form calculations, since long run times can result when they are executed with a serial code.

The glass dissolution testing, along with knowledge of near-field phenomena, provides the parameters that describe temporal corrosion processes, as well as the means to validate components of the system PA. Experimental work and solid phase characterization activities identify the type and quantity of minerals present at the time of disposal, as well as the long-term paragenetic sequence in mineral assemblages. Both distribution coefficients (K_d) and solubility-precipitation constructs will be used to predict the proportions of leached contaminants between the sediments and vadose zone pore waters.

5.0 Data Needs and Strategy

In order to provide key input parameters for near-field reactive transport modeling, well-constrained and interpretable experiments will be performed to isolate and parameterize the key mechanisms of glass corrosion. The parameters that will be measured include $\vec{k}$, E_a, η, K_g, and r_{IEX}. Another key input is the subset of secondary phases and associated thermodynamic data that must be included as part of the chemical reaction network. As the phases formed can change based on the initial glass composition and test conditions, analyses of the phases formed from a broad range of ILAW glasses and conditions is needed. Previous ILAW glass studies have provided input parameter data on WTP commissioning glasses. The corrosion behavior of a range of WTP commissioning glasses was evaluated using a variety of durability tests, which included the SPFT, PCT, PUF, and VHT methods, to obtain the required parameters for near-field reactive transport modeling. Additional details on the various test methods (SPFT, PCT, PUF, and VHT) are provided in Appendix D. Because of the wider compositional range currently being proposed for the new WTP glass formulations, and the uncertainty in how these newer glasses perform under disposal conditions, similar measurements must be conducted to develop parameter estimates in support of the near-field reactive transport modeling for the IDF PA. Because it is not possible to measure each glass due to the wide range in composition space that is proposed for the new ORP glasses, the present study will examine a subset of statistically designed samples developed using a layered design method that covers the expanded compositional range (Piepel et al., 1993). In this section we briefly describe how the parameters measured for the new glass compositions will be obtained, and propose some new experiments that will provide a more robust understanding of the glasses in the new compositional space.

As part of the strategy, a set of static screening tests will be used to guide the design of the more intensive parameter testing (i.e., SPFT and PUF). The screening tests methods that will be used include PCT-A, PCT-B, and VHT. Each of these test methods allows for a large set of glasses to be evaluated relatively quickly. The PCT-A consists of placing glass of a known particle size into a solution of deionized water in a stainless steel reactor at a glass-mass-to-solution-volume ratio (S/V) of 1:10. The reactor containing the glass is then sealed and placed in an oven at 90 °C for 7 days. The PCT-B method, which is similar to PCT-A, can be performed at a variety of S/V ratios to examine the behavior of the glass at varying time periods and temperatures. Performing the test for longer time periods, up to several years, gives invaluable information, such as the tendency of certain glass compositions to undergo Stage III alteration. Furthermore, solid-state analyses may be performed to obtain further information on secondary phases that form as a result of the aqueous alteration. The VHT qualifying test involves suspending a glass coupon in a sealed reactor with 0.25 mL of water. The reactor is then placed in an oven at 200 °C for a minimum of 7 days (typically 24 days has been used in glass development efforts). Upon termination of the experiment, the sample is removed and the altered thickness of the glass is measured. From the altered thickness, the rate of glass corrosion can be calculated. The results collected from the PCT-A, PCT-B, and VHT will be used to gain insight on the impact of glass composition on the rate of glass corrosion, as well as the propensity of particular glasses to exhibit Stage III corrosion behavior by analyzing the surface alteration products observed for each glass.

As mentioned earlier, several key parameters for the rate law ($\vec{k}$, E_a, η, and K_g) can be derived using the SPFT test method (Icenhower et al., 2008; McGrail et al., 1997a; McGrail et al., 2000a; McGrail et al., 2001c; Pierce et al., 2005; Pierce et al., 2010b) (see Appendix D.1). The SPFT tests are designed to elucidate various parameters by independently varying experimental conditions. Table 5.1 gives a list of each parameter and how that parameter can be obtained during testing. Although a particular experiment is called out, each parameter value is obtained through a regression analysis of the entire dataset. These parameters are then used to populate the chemical affinity-based kinetic rate law given in Equation (3.1).

Table 5.1. The Various Parameters that are Obtained Using the Single-Pass Flow-Through Method for a Given Glass Composition

Parameter	Symbol	Units	Measurement
Forward rate	$\vec{k}$	g/m^2d	The pH (7, 8, 9, 10, 11, and 12) and temperature (23, 40, 70, and 90 °C) are fixed and the flow rate is varied. The forward rate is given when the dissolution rate is independent of flow rate.
Activation energy	E_a	kJ/mol	The pH is fixed, the temperature is varied, and a flow rate consistent with a forward rate is used at each temperature (23, 40, 70, and 90 °C) and pH (7, 8, 9, 10. 11, and 12).
pH power law coefficient	η	unitless	The temperature (23, 40, 70, and 90 °C) is fixed, the pH (7, 8, 9, 10, 11, and 12) is varied, and a flow rate consistent with a forward rate is used.
Equilibrium constant of rate controlling reaction	K_g	unitless	The pH (9) and temperature (23, 40, 70, and 90 °C) are fixed and a flow rate constant 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 activity of H_4SiO_4 should correspond to a dissolution rate of zero.
Ion exchange constant	r_{IEX}	g/m^2d	The same conditions are used as for measuring K_g. The dissolution rate is measured at H_4SiO_4 activities that are greater than extrapolated value calculated for K_g. For increasingly greater H_4SiO_4 activities, the rate is independent of the H_4SiO_4 activity. The rate difference for Na and B is used as r_{IEX}.

The last test method that is commonly used to supply information for ILAW data packages is the PUF test (Appendix D.4). The test is performed under hydraulically unsaturated conditions, thus simulating the open flow and transport conditions expected in the IDF. The results from the PUF experiment provide data on the secondary phases expected to form as a result of glass corrosion. This is obtained by characterizing the reacted glass at the end of the PUF experiment to determine the alteration layer thickness and reaction products that have formed on the surface of the glass. The data collected from the PUF experiments have also been used to validate model parameters derived from SPFT experiments (Pierce and Bacon, 2011).

Each of the aforementioned test methods have been used extensively in the past to provide the data needed to generate the model parameters used in a reactive transport simulator. In the present strategy document, we will use a similar approach for the wider compositional range currently being proposed for the new WTP glass formulations. Provided below is a list of the various tests that will be performed. The list includes methods that have previously been employed, and highlights newer experimental techniques that are now available.

- As in previous data packages, the various parameters that will be used to model the glass corrosion process as described in Equation (3.1) will be derived using the SPFT method. Once these parameters have been estimated, they will be compared to previous values measured for the baseline WTP glasses (Bacon et al., 2010). For experiments designed to measure the forward rate of reaction, an advanced version of the SPFT method will be employed. This technique is designed to measure the retreat of the glass surface by masking the subsection of the glass surface with insoluble epoxy prior to starting the experiment. The initial marker allows for the surface retreat depth to be measured, and a dissolution rate can be calculated as a function of height. This experimental approach is advantageous because it eliminates the need for solution concentration measurements.

- Because alkali elements are the principal component involved in the ion-exchange reaction with water, it is theorized that an increase in the total alkali content in the new WTP glass formulations may have a direct effect on the importance of this reaction in terms of the long-term performance of the glass. An investigation of the time dependence on the alkali exchange reaction will be performed. The use of a diffusion-controlled alkali release term will increase the versatility and accuracy of the r_{IEX} term. This will be measured using the advanced SPFT.

- At present, the chance for a glass sample to enter Stage III of the glass corrosion process is poorly understood. The onset of this acceleration has been found to be correlated with the appearance of certain alteration phases on the glass surface and that these phases are mainly zeolitic. Experiments that identify the phases, and perhaps find solutions to mitigate their effect, are needed. One experimental method that will be used to investigate the types of zeolites that are formed is the PUF method. However, to canvas a larger number of glasses than are practical to test in PUF, a set of static tests will be performed with high S/V at 90 °C. These tests will include instrumentation to either continuously or periodically measure parameters that indicate acceleration (e.g., electrical conductivity or pH). This approach will allow for the identification of certain glasses in a compositional range are determined to be particularly susceptible to Stage III alteration.

- The variation in each measured parameter ($\vec{k}$, E_a, η, and $K_{g,}$ r_{IEX}) will be evaluated to determine compositional trends that can ultimately be used to either assign different parameters to different waste forms in the model or to form a performance weighted set of average parameters considering the amount of each glass composition to be produced. Boundaries between glass compositions that are prone to Stage III acceleration and glasses that do not accelerate will be defined.

6.0 Conclusion

An overall strategy for evaluating the long-term performance of the advanced ORP LAW glasses being considered for treatment of Hanford LAW has been presented. Laboratory testing is recommended to parameterize the dissolution models for the increased compositional space. Various testing to be performed includes single-pass flow-through (SPFT), product consistency test (PCT), vapor hydration test (VHT), and pressurized unsaturated flow (PUF) tests. Due to the new, high-Na compositional space, extra effort is recommended to understand the effect of ion exchange and secondary phase formation (including propensity for Stage III dissolution behavior) on the long-term performance of glass in the IDF. The tests will also allow an understanding of the chemical reaction network that can then be used to constrain the calculations that will be used in the chemical transport model, STOMP.

7.0 References

ASTM (2008) Standard Test Method for Determining the Chemical Durability of Nuclear Waste Glasses: The Product Consistency Test (PCT). ASTM C1285-02, ASTM International, West Conshohocken, PA.

ASTM (2009) Standard Test Method for Measuring Waste Glass or Glass Ceramic Durability by Vapor Hydration Test. ASTM C1663-09, ASTM International, West Conshohocken, PA.

ASTM (2010) Standard Practice for Measurement of the Glass Dissolution Rate Using the Single-Pass Flow-Through Test Method. ASTM C1662-10, ASTM International, West Conshohocken, PA.

Bacon, DH, White, MD, McGrail, BP (2000) Subsurface Transport Over Reactive Multiphases (STORM): A General, Coupled, Nonisothermal Multiphase Flow, Reactive Transport, and Porous Medium Alteration Simulator, Version 2, User's Guide. PNNL-13108, Pacific Northwest National Laboratory, Richland, WA.

Bacon, DH, McGrail, BP (2001) Waste Form Release Calculations for the 2001 Immobilized Low-Activity Waste Performance Assessment. PNNL-13369, Pacific Northwest National Laboratory.

Bacon, DH, White, MD, McGrail, BP (2004) Subsurface Transport Over Reactive Multiphases (STORM): A Parallel, Coupled, Nonisothermal Multiphase Flow, Reactive Transport, and Porous Medium Alteration Simulator, Version 3.0, User's Guide. PNNL-14783, Pacific Northwest National Laboratory, Richland, WA.

Bacon, DH, Pierce, EM (2010) Sensitivity Analysis of Kinetic Rate-Law Parameters Used to Simulate Long-Term Weathering of ILAW Glass. PNNL-19472, Pacific Northwest National Laboratory, Richland, WA.

Bacon, DH, Pierce, EM (2011) Development of Long-Term Behavior Models for Radioactive Waste Forms. In: M.I. Ojovan (Ed.), Handbook of advanced radioactive waste conditioning technologies. Woodhead Publishing Limited, Cambridge, UK, pp. 448.

Barkatt, A, Olszowka, A, Sousanpour, W, Adel-Hadadi, MA, Adiga, R, Baraktt, A, Marbury, GS, Li, S (1991) Leach Rate Excursions in Borosilicate Glasses: Effects of Glass and Leachant Composition. In: T.A. Abrajano, L.H. Johnson (Eds.), *Scientific Basis for Nuclear Waste Management XIV*. Materials Research Society, Boston, MA, **212** 65-76.

Bates, JK, Bradley, CR, Buck, EC, Cunnane, JC, Ebert, WL, Feng, X, Mazer, JJ, Wronkiewicz, DJ, Sproull, J, Bourcier, WL, McGrail, BP, Altenhofen, MK (1994) High-Level Waste Borosilicate Glass: A Compendium of Corrosion Characteristics. DOE-EM-0177, U.S. Department of Energy, Washington, D.C.

Boksay, ZG, Bouquet, G, Dobos, S (1968) The Kinetics of the Formation of Leached Layers on Glass Surfaces. *Physics and Chemistry of Glasses*, **9(2)**, 69-71.

Bourcier, WL, Peiffer, DW, Knauss, KG, McKeegan, KD, Smith, DK (1990) A Kinetic Model for Borosilicate Glass Dissolution Based on the Dissolution Affinity of a Surface Layer. In: V. Oversby, M., P.W. Brown (Eds.), *Scientific Basis for Nuclear Waste Management XIII*. Materials Research Society, Boston, MA, **176** 209-216.

Bourcier, WL (1994) Critical Review of Glass Performance Modeling. ANL-94/17, Argonne National Laboratory, Argonne, Illinois.

Buck, EC, Chamberlain, DB, Giere, R (1998) Intergrowth Structures in Synthetic Pyrochlores: Implications for Radiation Damage Effects and Waste Form Formulation. In: D. Wronkiewicz, J. Lee (Eds.), *Scientific Basis for Nuclear Waste Management XXII*. Materials Research Society, Boston, MA, **556** 19-26.

Bunker, BC, Arnold, GW, Beauchamp, EK, Day, DE (1983) Mechanisms for Alkali Leaching in Mixed Na-K-Silicate Glasses. *Journal of Non-Crystalline Solids*, **58**, 295-322.

Cailleteau, C, Angeli, F, Devreux, F, Gin, S, Jestin, J, Jollivet, P, Spalla, O (2008) Insight into silicate-glass corrosion mechanisms. *Nature Materials*, **7**, 978-983.

Certa, PJ, Wells, MN (2010) River Protection Project System Plan. ORP-11242, Rev. 5, US Department of Energy, Office of River Protection (ORP), Richland, WA.

Chave, T, Frugier, P, Ayral, A, Gin, S (2007) Solid state diffusion during nuclear glass residual alteration in solution. *Journal of Nuclear Materials*, **362**, 466-473.

Chen, Y, Engel, DW, McGrail, BP, Lessor, KS (1995) *AREST-CT V1.0* Software Verification. PNNL-10692, Pacific Northwest National Laboratory, Richland, WA.

Chen, Y, McGrail, BP, Engel, DW (1996) Source-Term Analysis for Hanford Low-Activity Tank Waste Using the Reaction-Transport Code AREST-CT. In: W. Gray, I. Triay (Eds.), *Scientific Basis for Nuclear Waste Management XX*. Materials Research Society, Pittsburgh, PA, **465** 1051-1058.

Curti, E, Crovisier, JL, Morvan, G, Karpoff, AM (2006) Long-Term Corrosion of Two Nuclear Waste Reference Glasses (MW and SON68): A Kinetic and Mineral Alteration Study. *Applied Geochemistry*, **21**, 1152-1168.

Daval, D, Hellmann, R, Saldi, GD, Wirth, R, Knauss, KG (2013) Linking nm-scale measurements of the anisotropy of silicate surface reactivity to macroscopic dissolution rate laws: New insights based on diopside. *Geochimica et Cosmochimica Acta*, **107**, 121-134.

DOE, 1988. Radioactive Waste Management, DOE Order 5820.2A. US Department of Energy, Washington, D.C.

DOE, 1998. Radioactive Waste Management, DOE Order 435.1. US Department of Energy, Washington, D.C.

DOE (1999) Final Report for the Hanford Site 200 Area Plateau Composite Analysis and the Immobilized Low-Activity Tank Waste, US Department of Energy, Richland, WA.

DOE (2000) Design, Construction, and Commissioning of the Hanford Tank Waste Treatment and Immobilization Plant, US Department of Energy, Office of River Protection, Richland, WA.

DOE (2001) Final Review Team Report for the March 2001 Revision of the Hanford Immobilized Low-Activity Waste Performance Assessment, US Department of Energy, Richland, WA.

Doremus, RH (1975) Interdiffusion of Hydrogen and Alkali Ions in a Glass Surface. *Journal of Non-Crystalline Solids*, **19**, 137.

Doremus, RH (1977) Diffusion in Glasses and Melts. *Journal of Non-Crystalline Solids*, **25**, 261.

Ebert, WL, Fortner, JA, Crawford, CL, Marra, JC (2012) Stage 3 Dissolution Tests with AFCI Glass. FCRD-SWF-2012-000204, U.S. Department of Energy, Washington, D.C.

Fournier, M, Frugier, P, Gin, S (2013) Effect of Zeolite Formation on Borosilicate Glass Dissolution Kinetics. *Procedia Earth and Planetary Science*, **7**, 264-267.

Fournier, M, Gin, S, Frugier, P (2014) Resumption of Nuclear Glass Alteration: State of the Art. *Journal of Nuclear Materials*, **448**, 348-363.

Frugier, P, Gin, S, Minet, Y, Chave, T, Bonin, B, Godon, N, Lartigue, JE, Jollivet, P, Ayral, A, De Windt, L, Santarini, G (2008) SON68 Nuclear Glass Dissolution Kinetics: Current State of Knowledge and Basis of the New GRAAL Model. *Journal of Nuclear Materials*, **380**, 8-21.

Frugier, P, Chave, T, Gin, S, Lartigue, JE (2009) Application of the GRAAL Model to Leaching Experiments with SON68 Nuclear Glass in Initially Pure Water. *Journal of Nuclear Materials*, **392**, 552-567.

Geisler, T, Janssen, A, Scheiter, D, Stephan, T, Berndt, J, Putnis, A (2010) Aqueous corrosion of borosilicate glass under acidic conditions: A new corrosion mechanism. *Journal of Non-Crystalline Solids*, **356**, 1458-1465.

Gin, S, Mestre, JP (2001) SON 68 Nuclear Glass Alteration Kinetics between pH 7 and pH 11.5. *Journal of Nuclear Materials*, **295**, 83-96.

Gin, S, Beaudoux, X, Angéli, F, Jégou, C, Godon, N (2012) Effect of Composition on the Short-Term and Long-Term Dissolution Rates of Ten Borosilicate Glasses of Increasing Complexity from 3 to 30 Oxides. *Journal of Non-Crystalline Solids*, **358**, 2559-2570.

Grambow, B (1981) The Role of Metal Ion Solubility in Leaching of Nuclear Waste Glasses. In: W. Lutze (Ed.), *Scientific Basis for Nuclear Waste Management V*. Materials Research Society, Berlin, Germany, **11**.

Grambow, B (1985) A General Rate Equation for Nuclear Waste Glass Corrosion. In: C.M. Jantzen, J.A. Stone, R.C. Ewing (Eds.), *Scientific Basis for Nuclear Waste Management VIII*. Materials Research Society, Pittsburgh, PA, **44**.

Grambow, B, Lutze, W, Vernaz, EY, Wicks, GG (2000) Final Report - Peer Review Committee (PRC) Assessment of the Proposed Long-Term Performance Strategy for Hanford Immobilized Low Activity Waste (ILAW). WSRC-RP-2000-00876, Westinghouse Savannah River Company, Aiken, SC.

Grambow, B, Müller, R (2001) First-Order Dissolution Rate Law and the Role of Surface Layers in Glass Performance Assessment. *Journal of Nuclear Materials*, **298**, 112-124.

Guittonneau, C, Gin, S, Godon, N, Mestre, JP, Dugne, O, Allegri, P (2011) A 25-Year Laboratory Experiment on French SON68 Nuclear Glass Leached in a Granitic Environment - First Investigations. *Journal of Nuclear Materials*, **408**, 73-89.

Hellmann, R, Wirth, R, Daval, D, Barnes, J-P, Penisson, J-M, Tisserand, D, Epicier, T, Florin, B, Hervig, RL (2012) Unifying Natural and Laboratory Chemical Weathering with Interfacial Dissolution–Reprecipitation: A Study Based on the Nanometer-Scale Chemistry of Fluid–Silicate Interfaces. *Chemical Geology*, **294–295**, 203-216.

Icenhower, JP, McGrail, BP, Luttge, A (2002) Origins of Deviations from Transition-State Theory: Effects of Ion-Exchange Kinetics in gGlass. *Geochimica et Cosmochimica Acta*, **66**, A351.

Icenhower, JP, Samson, SD, Lüttge, A, McGrail, BP (2004) Towards a Consistent Rate Law: Glass Corrosion Kinetics Near Saturation. In: R. Gieré, P. Stille (Eds.), *Energy, Waste, and the Environment – A geochemical Perspective*. Geological Society of London, London, UK.

Icenhower, JP, McGrail, BP, Shaw, WJ, Pierce, EM, Nachimuthu, P, Shuh, DK, Rodriguez, EA, Steele, JL (2008) Experimentally Determined Dissolution Kinetics of Na-rich Borosilicate Glass at Far From Equilibrium Conditions: Implications for Transition State Theory. *Geochimica et Cosmochimica Acta*, **72**, 2767-2788.

Jantzen, CM, Bibler, NE, Beam, DC, Pickett, MA (1994) Development and Characterization of the Defense Waste Processing Facility (DWPF) Environmental Assessment (EA) Glass Standard Reference Material, Ceramic Transactions. American Ceramic Society, Westerville, OH, pp. 313-322.

Jantzen, CM, Brown, KG, Pickett, JB (2010) Durable glass for thousands of years. *International Journal of Applied Glass Science*, **1**, 38-62.

Kerisit, S, Pierce, EM (2012) Monte Carlo simulations of the dissolution of borosilicate glasses in near-equilibrium conditions. *Journal of Non-Crystalline Solids*, **358**, 1324-1332.

Kerisit, S, Ryan, JV, Pierce, EM (2013) Monte Carlo simulations of the corrosion of aluminoborosilicate glasses. *Journal of Non-Crystalline Solids*, **378**, 273-281.

Kim, DS, Vienna, JD (2012) Preliminary ILAW Formulation Algorithm Description. 24590-LAW-RPT-RT-04-0003, Rev.1 and ORP-56321, River Protection Project, Hanford Tank Waste Treatment and Immobilization Plant, Richland, WA.

Libourel, G, Verney-Carron, A, Morlok, A, Gin, S, Sterpenich, J, Michelin, A, Neff, D, Dillmann, P (2011) The use of natural and archeological analogues for understanding the long-term behavior of nuclear glasses. *Comptes Rendus Geoscience*, **343**, 237-245.

Luo, JS, Abrajano, TA, Ebert, WL (1998) Natural analogues of nuclear waste glass corrosion. ANL-98/22, Argonne National Laboratory, Argonne, IL.

Machiels, AJ, Pescatore, C (1981) The Influence of Surface Processes in Waste Form Leaching. In: J.G. Moore (Ed.), *Scientific Basis for Nuclear Waste Management III*. Materials Research Society, New York, NY, **3**.

Mann, FM (1995a) Data Packages for the Hanford Low-Level Tank Waste Interim Performance Assessment. WHC-SD-WM-RPT-166, Rev. 0, Richland, WA.

Mann, FM (1995b) Computer Code Selection Criteria and Considerations for the Hanford Low-Level Waste Interim Performance Assessment. WHC-SD-WM-CSWD-073, Richland, WA.

Mann, FM (1995c) Scenarios of the TWRS Low-Level Waste Disposal Program. WHC-EP-0828, Rev. 1, Richland, WA.

Mann, FM (1995d) Performance Objectives of the Tank Waste Remediation System Low-Level Waste Disposal Program. WHC-EP-0826, Rev. 1, Richland, WA.

Mann, FM, Eiholzer, CR, Khaleel, R, Kline, NW, Lu, AH, McGrail, BP, Rittmann, PD, Schmittroth, F (1995) Definition of the Base Analysis Case of the Interim Performance Assessment. WHC-SD-WM-RPT-200, Rev. 0, Richland, WA.

Mann, FM, Eiholzer, CR, Lu, AH, Rittmann, PD, Kline, NW, Chen, Y, McGrail, BP (1996) Hanford Low-Level Tank Waste Interim Performance Assessment. WHC-EP-0884, Rev. 0, Richland, WA.

Mann, FM (1997) Statements of Work for FY 1998 to 2003 for the Hanford Low-Level Tank Waste Performance Assessment Project. HNF-SD-WM-PAP-062, Rev. 2, Richland, WA.

Mann, FM, Eiholzer, CR, Lu, AH, Rittmann, PD, Kline, NW, Chen, Y, McGrail, BP (1997) Hanford Low-Level Tank Waste Interim Performance Assessment. HNF-EP-0884, Rev. 1, Richland, WA.

Mann, FM, Eiholzer, CR, Lu, AH, Rittmann, PD, Kline, NW, Chen, Y, McGrail, BP (1998a) Hanford Low-Activity Tank Waste Performance Assessment. DOE/RL-97-69, Rev. 0, Richland, WA.

Mann, FM, Myers, DA (1998b) Computer Code Selection Criteria for Flow and Transport Code(s) to Be Used in Undisturbed Vadose Zone Calculations for TWRS Environmental Analyses. HNF-1839, Rev. 0, Richland, WA.

Mann, FM, Burgard, KC, Root, WR, Puigh, RP, Finfrock, SH, Khaleel, R, Bacon, DH, Freeman, EJ, McGrail, BP, Wurstner, SK, LaMont, PE (2001) Hanford Immobilization Low-Activity Tank Waste Performance Assessment: 2001 Version. DOE/ORP-2000-24, US Department of Energy, Office of River Protection, Richland, WA.

Mann, FM, Puigh, RJ, Finfrock, SH, Khaleel, R, Wood, MI (2003) Integrated Disposal Facility Risk Assessment. RPP-15834, Rev. 0, CH2M Hill Hanford Group, Inc., Richland, WA.

McGrail, BP, Ebert, WL, Bakel, AJ, Peeler, DK (1997a) Measurement of Kinetic Rate Law Parameters on a Na-Ca-Al Borosilicate Glass for Low-Activity Waste. *Journal of Nuclear Materials*, **249**, 175-189.

McGrail, BP, Martin, PF, Lindenmeier, CW (1997b) Accelerated Testing of Waste Forms Using a Novel Pressurized Unsaturated Flow (PUF) Method. In: W. Gray, I. Triay (Eds.), *Scientific Basis for Nuclear Waste Management XX*. Materials Research Society, Boston, MA, **465** 253-260.

McGrail, BP, Bacon, DH (1998a) Selection of a Computer Code for Hanford Low-Level Waste Engineered Performance Assessment. PNNL-10830, Rev. 1, Pacific Northwest National Laboratory, Richland, WA.

McGrail, BP, Ebert, WL, Bacon, DH, Strachen, DM (1998b) A Strategy to Conduct an Analysis of the Long-term Performance of Low-Activity Waste Glass in a Shallow Subsurface Disposal System at Hanford. PNNL-11834, Richland, WA.

McGrail, BP, Martin, PF, Lindenmeier, CW, Schaef, HT (1998c) Corrosion Testing of Low-Activity Waste Glasses Fiscal Year 1998 Summary Report. PNNL-12014, Pacific Northwest National Laboratory, Richland, WA.

McGrail, BP, Martin, PF, Lindenmeier, CW, Schaef, HT (1999) Application of the Pressurized Unsaturated Flow (PUF) Test for Accelerated Ageing of Waste Forms. In: L.G. Malilinson (Ed.), Ageing Studies and Lifetime Extension of Materials. Kluwer Academic/Plenum Publishers, New York, NY, pp. 313-320.

McGrail, BP, Bacon, DH, Ebert, WL, Saripalli, KP (2000a) A Strategy to Conduct an Analysis of the Long-Term Performance of Low-Activity Waste Glass in a Shallow Subsurface Disposal System at Hanford. PNNL-11834 Rev. 1, Pacific Northwest National Laboratory, Richland, WA.

McGrail, BP, Bacon, DH, Icenhower, JP, Mann, FM, Puigh, RP, Schaef, HT, Mattigod, SV (2000b) Near-Field Performance Assessment for a Low-Activity Waste Glass Disposal System: Laboratory Testing to Modeling Results. *Journal of Nuclear Materials*, **298**, 95-111.

McGrail, BP, Icenhower, J, Martin, PF, Rector, D, Schaef, HT, Rodriguez, EA, Steele, JL (2000c) Low-Activity Waste Glass Studies: FY2000 Summary Report. PNNL-13381, Pacific Northwest National Laboratory, Richland, WA.

McGrail, BP, Bacon, DH, Icenhower, JP, Mann, FM, Puigh, RJ, Schaef, HT, Mattigod, SV (2001a) Near-Field Performance Assessment for a Low-Activity Waste Glass Disposal System: Laboratory Testing to Modeling Results. *Journal of Nuclear Materials*, **298**, 95-111.

McGrail, BP, Icenhower, JP, Martin, PF, Schaef, HT, O'Hara, MJ, Rodriguez, EA, Steele, JL (2001b) Waste Form Release Data Package for the 2001 Immobilized Low-Activity Waste Performance Assessment. PNNL-13043 Rev. 2, Pacific Northwest National Laboratory, Richland, WA.

McGrail, BP, Icenhower, JP, Shuh, DK, Liu, P, Darab, JG, Baer, DR, Thevuthasen, S, Shutthanandan, V, Engelhard, MH, Booth, CH, Nachimuthu, P (2001c) 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*, **296**, 10-26.

McGrail, BP, Bacon, DH, Meyer, PD, Ojovan, MI, Strachan, DM, Ojovan, NV, Startceva, IV (2003) New Developments in Field Studies of Low-Activity Waste Glass Corrosion and Contamination Transport. In: R. Finch, D. Bullen (Eds.), *Scientific Basis for Nuclear Waste Management XXVI*. Materials Research Society, Boston, MA, **757** 83-95.

Mendel, JE (1984) Final Report of the Defense High-Level Waste Leaching Mechanisms Program. PNL-5157, Pacific Northwest Laboratory, Richland, WA.

Minet, Y, Bonin, B, Gin, S, Frugier, P (2010) Analytic Implementation of the GRAAL Model: Application to a R7T7-type Glass Package in a Geological Disposal Environment. *Journal of Nuclear Materials,* **404**, 178-202.

Muller, IS, Diener, G, Joseph, I, Pegg, IL (2004) Proposed Approach for Development of LAW Glass Formulation Correlation. VSL-04L4460-1 and ORP-56326, Vitreous State Laboratory, The Catholic University of America, Washington, DC.

Muller, IS, Joseph, I, Pegg, IL (2010) Selection of Bounding Low Activity Waste Glasses for Leach Testing. VSL-10L2000-1, Vitreous State Laboratory, Washington, D.C.

Muller, IS, Kot, W, Pasieka, H, Gilbo, K, Perez-Cardenas, F, Joseph, I, Pegg, IL (2012) Compilation and Management of ORP Glass Formulation Databases. VSL-12R2470-1 and ORP-53934, Vitreous State Laboratory, The Catholic University of America, Washington, DC.

Neeway, JJ, Abdelouas, A, Grambow, B, Schumacher, S (2011) Dissolution Mechanism of the SON68 Reference Nuclear Waste Glass: New Data in dynamic System in Silica Saturation Conditions. *Journal of Nuclear Materials*, **415**, 31-37.

Neeway, JJ, Kerisit, S, Gin, S, Wang, Z, Zhu, Z, Ryan, JV (2014a) Low-Temperature Lithium Diffusion in Boroaluminosilicate Glasses. *Journal of Non-Crystalline Solids*, **405**, 83-90.

Neeway, JJ, Qafoku, NP, Williams, BD, Rod, K, Bowden, ME, Brown, CF, Pierce, EM (2014b) Performance of the Fluidized Bed Steam Reforming Product under Hydraulically Unsaturated Conditions. *Journal of Environmental Radioactivity*, **313**, 119-128.

Nieplocha, J, Palmer, B, Tipparaju, V, Krishnan, M, Trease, H, Aprà, E (2006) Advances, Applications and Performance of the Global Arrays Shared Memory Programming Toolkit. *International Journal of High Performance Computing Applications*, **20**, 203-231.

O'Neil, JR, Taylor, HPJ (1967) The Oxygen Isotope and Cation Exchange Chemistry of Feldspars. *American Mineralogist,* **52**, 1414-1437.

Ojovan, MI, Pankov, A, Lee, WE (2006) The Ion Exchange Phase in Corrosion of Nuclear Waste Glasses. *Journal of Nuclear Materials,* **358**, 57-68.

Pederson, LR (1987) Comparison of Sodium Leaching Rates from a $Na_2O \cdot 3SiO_2$ Glass in H_2O and D_2O. *Physics and Chemistry of Glasses*, **28(1)**, 17-21.

Pescatore, C, Machiels, AJ (1982) Effects of Wurfaces on Glass Waste Form Leaching. *Journal of Non-Crystalline Solids*, **49**, 379-388.

Piepel, GF, Anderson, CM, Redgate, PE (1993) Response Surface Designs for Irregularly-Shaped Regions; Parts 1, 2, and 3, *1993 Proceedings of the Section on Physical and Engineering Sciences*, Alexandra, VA 205-227.

Pierce, EM, McGrail, BP, Rodriguez, EA, Schaef, HT, Saripalli, KP, Serne, RJ, Martin, PF, Baum, SR, Geizler, KN, Reed, LR, Shaw, WJ (2004) Waste Form Release Data Package for the 2005 Integrated Disposal Facility Performance Assessment. PNNL-14805, Pacific Northwest National Laboratory, Richland, WA.

Pierce, EM, McGrail, BP, Bagaasen, LM, Rodriguez, EA, Wellman, DM, Geiszler, KN, Baum, SR, Reed, LR, Crum, JV, Schaef, HT (2005) Laboratory Testing of Bulk Vitrified Low-Activity Waste Forms to Support the 2005 Integrated Disposal Facility Performance Assessment. PNNL-15126 Rev. 1, Pacific Northwest National Laboratory, Richland, WA.

Pierce, EM, McGrail, BP, Valenta, MM, Strachan, DM (2006) The Accelerated Weathering of a Radioactive Low-Activity Waste Glass under Hydraulically Unsaturated Conditions: Experimental Results from a Pressurized Unsaturated Flow Test. *Nuclear Technology*, **155**, 149-165.

Pierce, EM, McGrail, BP, Martin, PF, Marra, J, Arey, BW, Geiszler, KN (2007) Accelerated Weathering of High-Level and Plutonium-Bearing Lanthanide Borosilicate Waste Glasses under Hydraulically Unsaturated Conditions. *Applied Geochemistry*, **22**, 1841-1859.

Pierce, EM, Richards, EL, Davis, AM, Reed, LR, Rodriguez, EA (2008) Aluminoborosilicate waste glass dissolution under alkaline conditions at 40 °C: Implications for a chemical affinity-based rate equation. *Environmental Chemistry*, **5**, 73-85.

Pierce, EM, Bacon, DH, Kerisit, S, Windisch, C, Cantrell, KJ, Valenta, MM, Burton, SD, Serne, RJ, Mattigod, SV (2010a) Integrated Disposal Facility FY2010 Glass Testing Summary Report. PNNL-19736, Pacific Northwest National Laboratory, Richland, WA.

Pierce, EM, Reed, LR, Shaw, WJ, McGrail, BP, Icenhower, JP, Windisch, CF, Cordova, EA, Broady, J (2010b) Experimental determination of the effect of the ratio of B/Al on glass dissolution along the nepheline ($NaAlSiO_4$)-malinkoite ($NaBSiO_4$) join. *Geochimica et Cosmochimica Acta*, **74**, 2634-2654.

Pierce, EM, Bacon, DH (2011) Combined Experimental and Computational Approach to Predict the Glass-Water Reaction. *Nuclear Technology*, **176**, 22-39.

Pierce, EM, Kerisit, S, Krogstad, EJ, Burton, SD, Bjornstad, BN, Freedman, VL, Cantrell, KJ, Valenta, MM, Crum, JV, Westsik Jr, JH (2013) Integrated Disposal Facility FY 2012 Glass Testing Summary Report. PNNL-21812, Rev. 1, Pacific Northwest National Laboratory, Richland, WA.

Pierce, EM, Lukens, WW, Fitts, JP, Jantzen, CM, Tang, G (2014) Experimental Determination of the Speciation, Partitioning, and Release of Perrhenate as a Chemical Surrogate for Pertechnetate from a Sodalite-Bearing Multiphase Ceramic Waste Form. *Applied Geochemistry*, **42**, 47-59.

Poinssot, C, Gin, S (2012) Long-term Behavior Science: The Cornerstone Approach for Reliably Assessing the Long-Term Performance of Nuclear Waste. *Journal of Nuclear Materials*, **420**, 182-192.

Rana, MA, Douglas, RW (1961a) The Reaction Between Glass and Water. Part I. Experimental Methods and Observations. *Physics and Chemistry of Glasses*, **2**, 179-195.

Rana, MA, Douglas, RW (1961b) The Reaction Between Glass and Water. Part 2. Discussion for the Results. *Physics and Chemistry of Glasses*, **2**, 196-204.

Rawlins, JA, Karnesky, RA, Khaleel, R, Mann, FM, McGrail, BP, McMahon, WJ, Piepho, MG, Rittmann, PD, Schmittroth, F (1994) Impacts of Disposal System Design Options on Low-Level Glass Waste Disposal System Performance. WHC-EP-0810, Rev. 0, Richland, WA.

Ribet, S, Gin, S (2004a) Role of Neoformed Phases on the Mechanisms Controlling the Resumption of SON68 Glass Alteration in Alkaline Media. *Journal of Nuclear Materials*, **324**, 152-164.

Ribet, S, Muller, IS, Pegg, IL, Gin, S, Frugier, P (2004b) Compositional Effects on the Long-Term Durability of Nuclear Waste Glasses: A Statistical Approach. In: V.M. Oversby, L.O. Werme (Eds.), *Scientific Basis for Nuclear Waste Management XXVIII*. Materials Research Society, **824** 309-314.

Ryan, JV, Mitroshkov, AV, Zhu, Z, Neeway, JJ (2012) Initial Isotope Tracer Test Results to Improve the Mechanistic Understanding of Glass Corrosion. FCRD-SWF-2012-000074, Pacific Northwest National Laboratory, Richland, WA.

Strachan, DM, Croak, TL (2000) Compositional Effects on Long-Term Dissolution of Borosilicate Glass. *Journal of Non-Crystalline Solids*, **272**, 22-33.

Strachan, DM, Neeway, JJ (2014) Effects of Alteration Product Precipitation on Glass Dissolution. *Applied Geochemistry*, **45**, 144-157.

Techer, I, Advocat, T, Lancelot, J, Liotard, JM (2000) Basaltic Glass: Alteration Mechanisms and Analogy with Nuclear Waste Glasses. *Journal of Nuclear Materials*, **282**, 40-46.

Van Iseghem, P, Grambow, B (1988) The Long-Term Corrosion and Modelling of Two Simulated Belgian Reference High-Level Waste Glasses. In: M.J. Apted, R.E. Westerman (Eds.), *Scientific Basis for Nuclear Waste Management XI*. Materials Research Society, Pittsburgh, Pennsylvania, **112** 631-639.

Van Iseghem, P, Aertsens, M, Gin, S, Deneele, D, Grambow, B, McGrail, BP, Strachan, D, Wicks, GG (2006a) A Critical Evaluation of the Dissolution Mechanisms of High-level Waste Glasses in Conditions of Relevance for Geological Disposal (GLAMOR). Contract FIKW-CT-2001-20140, European Commission,.

Van Iseghem, P, Lemmens, K, Aertsens, M, Gin, S, Ribet, IS, Grambow, B, Crovisier, JL, Del Nero, M, Curti, E, Schwyn, B, Luckscheiter, B, McMenamin, T (2006b) Chemical Durability of High-Level Waste Glass in Repository Environment: Main Conclusions and Remaining Uncertainties from the GLASTAB and GLAMOR Projects. In: P. Van Iseghem (Ed.), *Scientific Basis for Nuclear Waste Management XXIX*. Materials Research Society, Ghent, Belgium, **932** 293-304.

Vernaz, EY, Dussossoy, JL (1992) Current state of knowledge of nuclear waste glass corrosion mechanisms: the case of R7T7 glass. *Applied Geochemistry*, **1**, 13-22.

Vernaz, EY, Gin, S, Jegou, C, Ribet, I (2001) Present understanding of R7T7 glass alteration kinetics and their impact on long-term behavior modeling. *Journal of Nuclear Materials*, **298**, 27-36.

Vienna, JD, Jiricka, A, Hrma, PR, Smith, DE, Lorier, TH, Schulz, RL, Reamer, IA (2001) Hanford Immobilized LAW Product Acceptance Testing: Tanks Focus Area Results. PNNL-13744, Pacific Northwest National Laboratory, Richland, WA.

Vienna, JD (2005) Preliminary ILAW Formulation Algorithm Description. 24590-LAW-RPT-RT-04-0003, Rev.0, River Protection Project, Hanford Tank Waste Treatment and Immobilization Plant, Richland, WA.

Vienna, JD, Kim, DS, Skorski, DC, Matyas, J (2013a) Glass Property Models and Constraints for Estimating the Glass to Be Produced at Hanford by Implementing Current Advanced Glass Formulation Efforts. PNNL-22631, Pacific Northwest National Laboratory, Richland, WA.

Vienna, JD, Ryan, JV, Gin, S, Inagaki, Y (2013b) Current Understanding and Remaining Challenges in Modeling Long-Term Degradation of Borosilicate Nuclear Waste Glasses. *International Journal of Applied Glass Science*, **4**, 283-294.

Wagoner, JD (1996) Letter from JD Wagoner to Prospective Offerors, Request for Proposal (RFP) No. DE-WO6-96RL-3308, US Department of Energy, Richland, WA.

Wallace, RM, Wicks, GG (1983) Leaching chemistry of defense borosilicate glass. *Materials Research Society Symposium Proceedings*, **15**, 23-28.

Werme, L, Bjorner, IK, Bart, G, Zwicky, U, Grambow, B, Lutze, W, Ewing, R, Magrabi, C (1990) Chemical corrosion of highly radioactive borosilicate waste glass under simulated repository conditions. *Journal of Materials Research*, **5**, 1130-1146.

White, MD, Oostrom, M (1996) STOMP: Subsurface Transport Over Multiple Phases, Theory Guide. PNNL-11217, Pacific Northwest National Laboratory, Richland, WA.

White, MD, Oostrom, M (2000) STOMP Subsurface Transport Over Multiple Phases Version 2.0 Theory Guide. PNNL-12030, Pacific Northwest National Laboratory, Richland, WA.

White, MD, McGrail, BP (2005) STOMP Subsurface Transport Over Multiple Phases, Version 1.0, Addendum: ECKEChem Equilibrium-Conservation-Kinetic Equation Chemistry and Reactive Transport,. PNL-15482, Pacific Northwest National Laboratory, Richland, WA.

White, MD, Oostrom, M (2006) STOMP: Subsurface Transport Over Multiple Phases, Version 4.0, User's Guide. PNNL-15782, Pacific Northwest National Laboratory, Richland, WA.

Appendix A

Disposal System Description

Appendix A

Disposal System Description

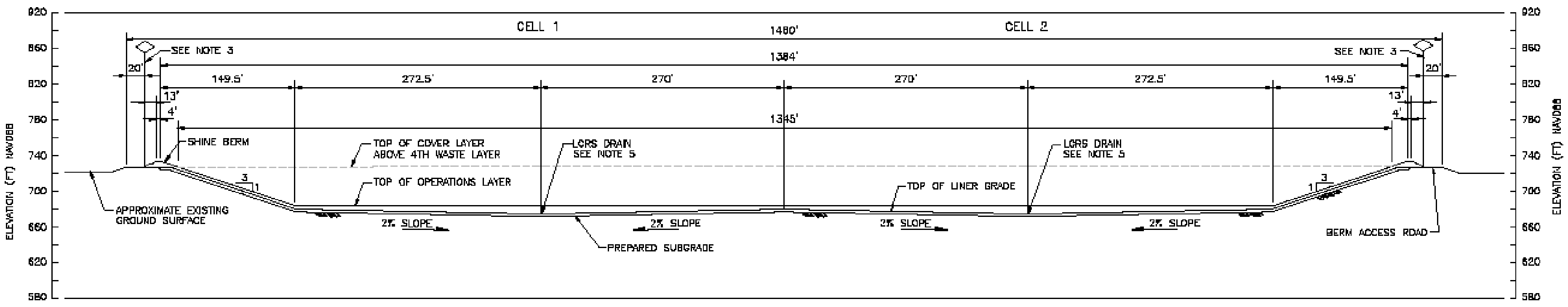
Plans call for the IDF system to include a protective surface barrier with design elements to minimize root intrusion, animal intrusion, and water infiltration. The site is not near any existing or past waste disposal sites. A conceptual design has been described by Mann et al. (2003) and is shown in Figure A.1. The use of silt-loam soils when combined with a representative community of shrub-steppe vegetation has been shown to cause most precipitation falling on the region to be lost through evapotranspiration. Consequently, the disposal facility is to be located in relatively dry, unsaturated soil, and performance assessment models must be applicable to the specific physics and chemistry of this type of system.

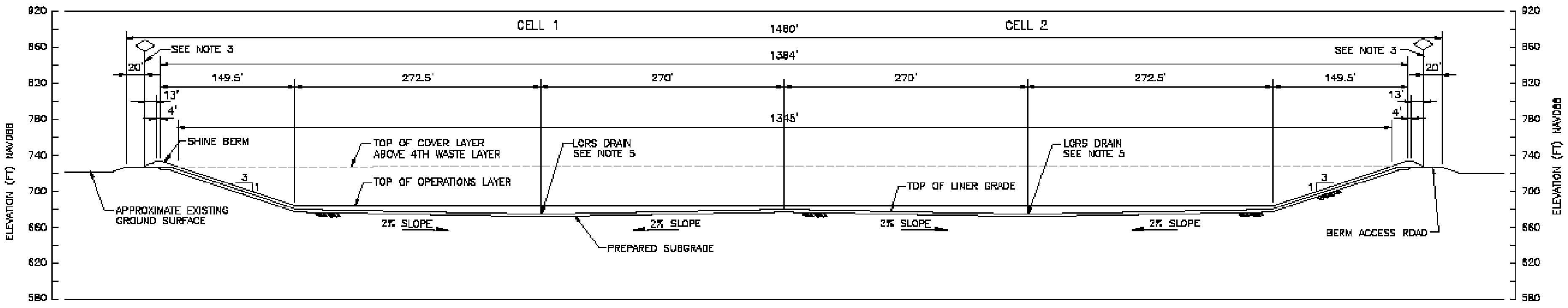
An important input for reactive transport modelling is water flow. Water flow in the near-surface unsaturated zone is transient due to infrequent precipitation events. Transient water flow begins when water enters at the ground surface and infiltrates downward into the soil column. At some point along the column depth, the transient effects will dampen out, and the downward flowing water will reach a steady infiltration rate. Thus, the unsaturated zone essentially comprises two regions: one where water flow is transient and one where water flow is stable until it reaches the aquifer. The IDF will be situated in the region of steady flow. However, plans call for a protective surface barrier to be engineered to minimize water infiltration.

ILAW glass canisters produced at WTP are to be right circular cylinders (1.22 m diameter by 2.29 m tall), made of 304L stainless steel and at least 85% filled with LAW glass (2 m high). These waste packages are stacked, at a maximum, 4 layers high in the IDF trench corresponding to a maximum glass height of 8 meters. The remaining fill material into the trench is assumed to be backfill soil. Each cell in the IDF trench consists of a contiguous group of waste packages in a given layer.

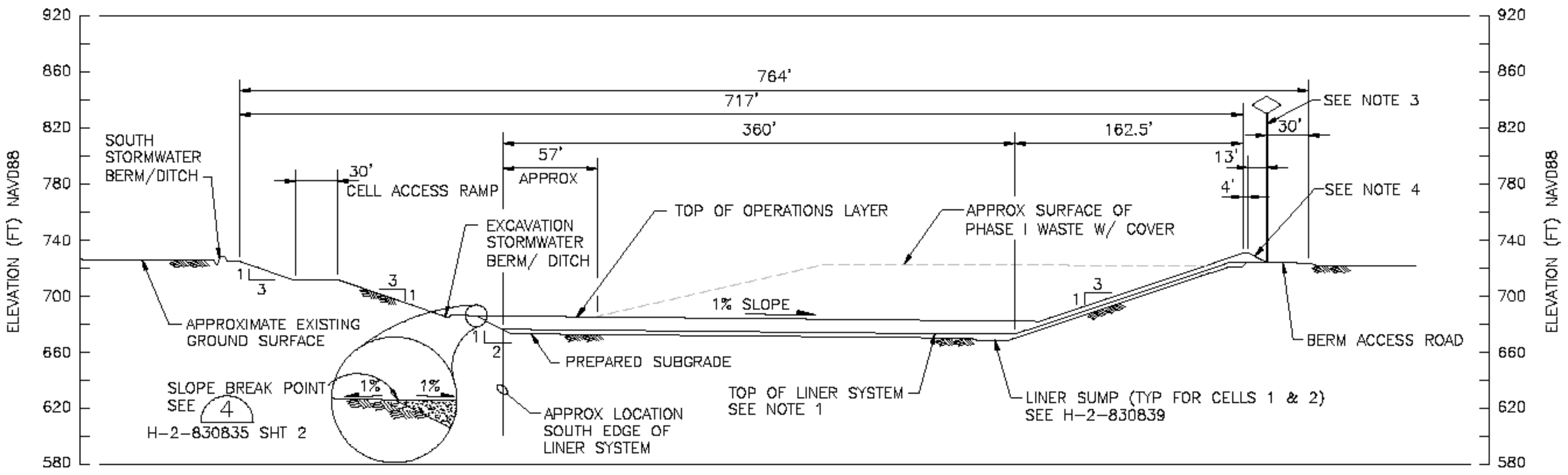
Backfilled soil is included around and on top of the waste containers in the facility. The soil was included in these concepts: 1) for structural support, 2) to wick moisture away from the waste containers, and 3) to provide radiation shielding for the facility workers. The waste packages are to be located approximately 15 m below the top of the surface barrier. At this depth, the ambient temperature is approximately 15 °C, and temperature fluctuations are less than 2 °C.

East – West Cross-Section





North – South Cross Section



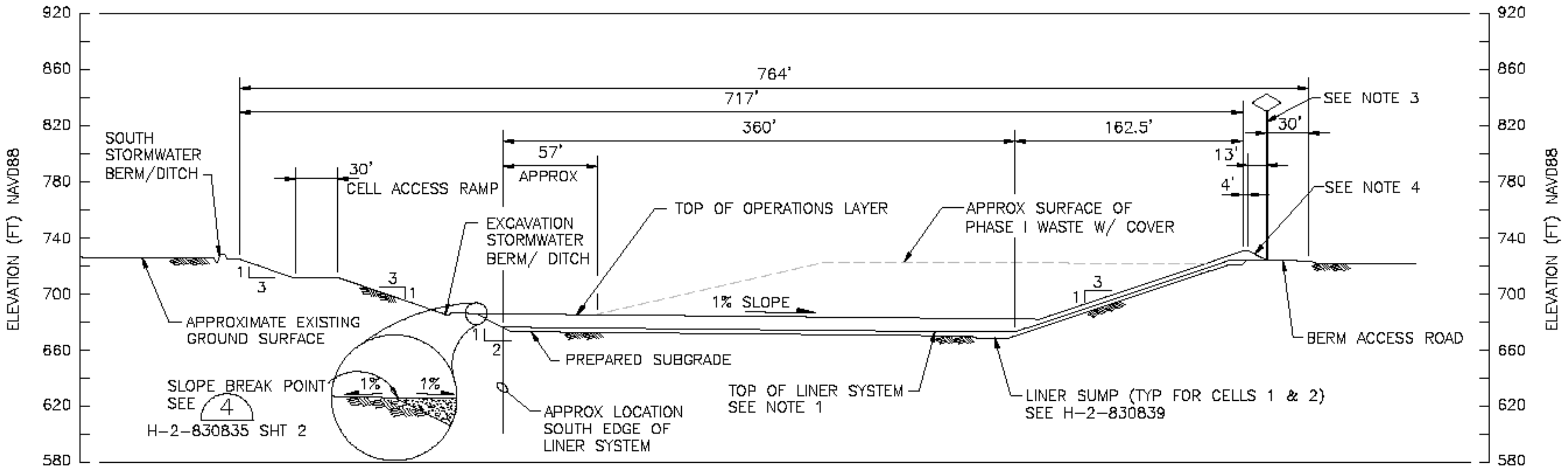


Figure A.1 IDF Trench Conceptual Model

Appendix B

Glass Dissolution Process

Appendix B

Glass Dissolution Process

Although the glass dissolution process is summarized in Section 3.0, this section goes into more detail on the mechanisms that control glass dissolution and the variety of models that have been utilized to model corrosion. The corrosion of silicate glass is a complex process that is dependent on parameters such as glass composition, the glass surface area-to-leachate volume ratio (in static conditions) or leachant flow rate (in flowing conditions), and time, as well as environmental parameters such as pH, temperature, and the chemical composition of the leachate. The transformation of the pristine glass material to a complex corrosion product containing amorphous surface layers and crystalline alteration phases is a result of several concurrent mechanisms such as water diffusion, ion-exchange, and hydrolysis of network-forming species, and release soluble glass components into the surrounding solution. Much of this work relevant to silicate waste glasses has been compiled and critically reviewed (Bates et al., 1994; Bourcier, 1994; Frugier et al., 2009; Icenhower et al., 2004; Jantzen et al., 2010; Mendel, 1984; Poinssot et al., 2012; Van Iseghem et al., 2006a; Vernaz et al., 2001; Vienna et al., 2013b; Werme et al., 1990). As mentioned earlier, the glass dissolution process in static conditions may be divided into three main behavioral stages (Bates et al., 1994), explained in more detail below.

The initial (**Stage I**) period of relatively rapid dissolution is characterized by nearly congruent release due to the hydrolysis of the silicate network, along with diffusion of water into the glass network, and ion exchange of hydrogen-containing species with alkalis (Doremus, 1975; Rana and Douglas, 1961a; Rana and Douglas, 1961b). In a static solution with sufficiently high surface-area/volume ratio, this stage is relatively short-lived. Largely due to alkali ion exchange, static solutions exhibit an increase in pH. The hydrolysis of the silicate network and the release of Si into solution results in an increase in the concentration of dissolved components. With this, a porous, silica-rich, cation-depleted, amorphous phase commonly referred to as the gel begins to form. This hydrated gel is composed primarily of insoluble glass components (i.e., Al, Fe, and Si) that either restructure from the glass network, or dissolve and re-condense (i.e., the back reaction in the dissolution step) at the glass-water interface.

The net effect is that the glass dissolution slows from the initial rate to a much slower residual rate that defines **Stage II** behavior. In the transition to this second stage, the matrix dissolution rate becomes dependent on the solution saturation state (concentration of elements in solution) and the alteration layers become thicker and an effective barrier to transport. Although the relative importance of the two mechanisms is still a matter for debate, the community has reached consensus that both the build-up of solution species and the alteration layers must be accounted for in models of the glass-water reaction. The underlying mechanism controlling these process is still being debated (Van Iseghem et al., 2006a). The slow reaction rate that is measured when the solution is saturated with respect to amorphous silica is often referred to as the “residual rate” or “steady state” and has been the focus of many recent studies (Cailleteau et al., 2008; Chave et al., 2007; Frugier et al., 2008; Gin et al., 2012; Guittonneau et al., 2011; Neeway et al., 2011; Poinssot and Gin, 2012).

Eventually, in static conditions, the solution becomes saturated with respect to secondary phases. These phases are most often clay minerals, such as smectite or chlorite (Pierce et al., 2007), that form at the interface between the gel layer and solution and 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 (Van Iseghem and Grambow, 1988) and this has been termed **Stage III** behavior. This acceleration has only been observed in extreme conditions such as high pH (> 10.5), high T (> 90 °C), high glass-surface-to-solution-volume (S/V) ratios, and in the accelerated dissolution conditions in the Pressurized Unsaturated Flow (PUF) test. Additionally, only certain glass compositions appear to create solution conditions that drive this behavior naturally (Ribet et al., 2004b), while other glass compositions can be made to exhibit Stage III behavior when the solution is artificially altered (Ribet and Gin, 2004a).

Appendix C

Published Modeling Techniques

Appendix C

Published Modeling Techniques

This section presents a brief summary of the various conceptual/mechanistic models that have been employed historically by various groups to describe glass dissolution behavior.

C.1 Diffusion Models

One traditional method of discussing the selective removal of alkali ions from glasses involves the basic mechanism of ion exchange in which H^+, $H3O^+$, and/or H_2O exchanges for an M+ ion in the glass. The displacement of M^+ from the glass results in the formation of a hydrated surface that is depleted of alkali ions (Doremus, 1975; Doremus, 1977; Rana and Douglas, 1961a; Rana and Douglas, 1961b). This reaction occurs at all stages of glass dissolution and may become the dominant reaction under certain conditions (e.g., solution saturated conditions and/or long time scales). The rate-limiting step in this model is the counter-diffusion or interdiffusion of M^+ and H^+ (or H_3O^+, H_2O). Models eventually evolved to take into account the effects caused by diffusion through the hydrated glass (i.e., opening the surface structure through hydrolysis and dissolution) (Boksay et al., 1968). The mechanism, however, could not explain the behavior of mixed-alkali glasses where interdiffusion coefficients were 2 to 7 orders of magnitude greater than the measured solid-state diffusion coefficients (Bunker et al., 1983). Despite this, the concept of diffusion is still included in some of the current models being developed today.

C.2 Surface (“Passivating”) Layer Models

Another type of model is based on the concept of a "passivating" layer that builds up on the surface of a glass and reduces the element release rate. This model was first proposed in the early 1980s (Machiels et al., 1981; Pescatore et al., 1982; Wallace et al., 1983) and efforts are still being made to develop model based on this concept. In fact, the passivating-layer model is being developed to describe the behavior of French HLW glass (Frugier et al., 2008; Frugier et al., 2009; Minet et al., 2010). The passivating layer theory is based on the development of a layer that limits the diffusion of a species between the pristine glass and solution. Physical evidence of the phenomenon has been demonstrated by Cailleteau et al. (2008), who demonstrated a sharp drop in the elemental release rate for silicate glasses with the buildup of a dense outer layer on the corroded glass surface. This layer, however, seemed to be a surface layer and not a layer between the pristine glass and gel as is hypothesized to be controlling the dissolution rate of glass in passivating layer models. Recent work by Ryan et al. (2012) has used Atom Probe Tomography (APT) with nanometer-scale resolution to locate the existence of a small layer between the pristine glass and the gel; however, it is unknown if this layer is responsible for limiting the glass corrosion rate. Monte Carlo modelling of simple glasses has also shown the appearance of a blocking layer, which upon formation, is responsible for slowing the rate of glass dissolution (Kerisit et al., 2012; Kerisit et al., 2013). This concept is the basis behind one of the more mature glass dissolution models in use today, which is described in more detail below.

C.3 Dissolution/Precipitation Models

Another theory for mineral or glass dissolution is based on an interfacial dissolution reprecipitation method where the pristine material dissolves on contact with water and reforms at the interface to form the alteration layer. The theory assumes congruent dissolution of the surface that is spatially and temporally coupled to a precipitating phase at an inward-moving reaction front. The idea was first theorized in the 1960s by O'Neil and Taylor (1967), and has again garnered attention with the use of new instrumentation with better depth resolution, including high resolution and energy filtered transmission electron microscopy (HRTEM, EFTEM) (Daval et al., 2013; Hellmann et al., 2012). The theory has been used to describe alteration layer striations observed in nuclear waste glasses corroded in hydrothermal, acidic environments (Geisler et al., 2010).

C.4 Solution Chemistry Models

One of the shortcomings of most of the work mentioned above is the absence of a description of the solution chemistry, both before and after contact with the glass. To resolve this, Grambow (1981) was able to demonstrate that the solution chemistry could be modelled using the solubility of various minerals that precipitate during the reaction, and that these could be explained using a geochemical modelling code. Grambow was also able to determine that the rate of glass dissolution was dependent on the concentration of orthosilicic acid, H_4SiO_4, where the rate limiting reaction is the hydrolysis and removal of $Si(OH)_4$ groups. This resulted in a first-order rate law (Grambow, 1985), a variant of which is given in Equation (3.1). The model has been successfully applied to several types of glass. Attempts were also made to extend the solubility of the alteration layer (Bourcier et al., 1990). Modelling glass dissolution by this method has gained international approval, and has been recommended for use in performance assessments for Hanford LLW glass (McGrail et al., 1998b).

C.5 Calculation of Glass Dissolution Using GRAAL and the GM Model

Several conceptual models have been discussed in the previous section. Implementation of these concepts using credible mathematical models is necessary to be able to defend the science behind the mechanisms controlling the glass dissolution rate. The outputs from these models will be used as the radionuclide source term for modelling of the performance of the entire disposal system. These models are best when they are simple, robust, and can reproduce experimental data through the various stages of the glass corrosion process. In this section, we introduce two models that have been proposed in the last decade. The first, GRAAL (Frugier et al., 2008), was produced explicitly to describe the behavior of the French HLW glass, SON68, and is based on the creation of a diffusion limiting layer that controls glass dissolution. The second is the GM2004 model (Grambow et al., 2001), which is based on an affinity-controlled mechanism with the allowance of water diffusion in glass that leads to continued glass dissolution even in saturated conditions. Both models address the following processes: build-up of a gel layer, description of the gel layer (which may have protective properties) by transport limitations of dissolved silica, accumulation of dissolved silica in the bulk solution, retention of silica in the gel and incongruent release of soluble glass constituents, and the use of a limiting solution concentration of dissolved silica at the glass surface. The GM2004 and a predecessor of the GRAAL model, known as r(t), were examined in detail by a team of international experts as part of the GLAMOR project (Van Iseghem et al., 2006b). In describing these models, we are not attempting to replace the current model (Equation

(3.1)) used for ILAW, but rather to describe other concepts through which experts model the glass corrosion process.

C.5.1 GRAAL Model

The GRAAL[1] (Glass Reactivity with Allowance for the Alteration Layer) model has been proposed by Frugier and coworkers (Frugier et al., 2008; Frugier et al., 2009; Minet et al., 2010) explicitly to reproduce experimental data from SON68 glass corrosion studies. In general, the model proposes that transport through a thin, dense layer is the rate-limiting step in the overall glass dissolution kinetics. This layer, called the passivating reactive interphase (PRI), is a sparingly soluble phase whose stability is directly dependent on the nature of the secondary phases and the flow rate. The model takes the sum of the rate law for gel dissolution and the rate law for diffusion through this layer.

The diffusion rate law corresponds to the mathematical formalism of ion diffusion in a semi-infinite 1- D medium, and follows a square-root time-dependent rate law, which can be seen in the following equation giving the dissolution rate of the PRI:

$$\frac{dE}{dt} = r_{disso}\left(1 - \frac{C_{Si}(t)}{C_{sat}}\right) \tag{C.1}$$

where E is the dissolved PRI thickness at time t, r_{disso} is the PRI dissolution rate in pure water, and C_{sat} is the corresponding H_4SiO_4 concentration at which dissolution ceases.

The formation of the PRI is given by:

$$\frac{de}{dt} = \frac{r_{hydr}}{1 + \frac{e \cdot r_{hydr}}{D_{PRI}}} - \frac{dE}{dt} \tag{C.2}$$

where r_{hydr} is the hydrolysis rate of soluble glass constituents (boron, alkali ions) during the creation of the PRI, e is the PRI thickness at time t, and D_{PRI} is the water diffusion coefficient in the PRI. The model also involves a silica model sink term.

Something that is readily apparent from the model is that, although it is considered a transport-limiting model based on the formation of a passivating layer, it still considers an affinity-driven rate law where the concentration of Si in solution is tracked. A geochemical version of this model combining the chemical equilibria in solution, ion transport by convection of diffusion, and element diffusion through the PRI has been released (Frugier et al., 2009), as well as a simplified version of the model that only considers the silica saturation concentration and the precipitation of neophormed phases by an affinity relation for silicon above a precipitation threshold C_{sat} (Minet et al., 2010). It should be noted that the species that is assumed to control the reaction via transport through the PRI remains undefined.

---

[1] The translation of “graal” from French to English is “grail”.

C.5.2 GM Model

The GM2004 model is a 1-D model where diffusion coefficients, rate constants, surface layer porosities, and solubility constants are considered to be constant (Grambow and Müller, 2001). This dissolution is the sum of two parallel reactions— water diffusion/ion exchange and the congruent dissolution of glass elements at the gel/diffusion layer. In general terms, the evolution of the glass corrosion process, as described from the model, is the growth of an altered layer as a function of time. This layer grows at the interface between the gel and solution, and the rate of glass dissolution is tracked. The time-dependent concentration of water in the glass can be described using an equation that considers the advection, dispersion, and reaction of water in the glass and is typically used for mass transfer calculation of reactive contaminant transport in porous media.

The equation focuses on the transport of water through the gel layer and also considers the silica saturation effect as mentioned previously. The protective effect of the gel layer may be explained by the buildup and hindering of dissolved silica in the gel layer, which gives a high local silica concentration and thus slows glass dissolution. A resulting mass balance constraint requires that the mass flux of dissolved material from the glass surface equals the mass transfer across the transport barrier.

Due to the complexity of the equations used in the model, they will not be presented here. In summary, transport is controlled by the surface layer and/or through transport control in the porous media surrounding the glass. The slower of these processes will be the rate controlling step. This model does not account for geochemical constraints, such as the pH dependency of the affinity controlled reactions or of solubility-controlled secondary phase formation, and it does not account for the effects of pH evolution during the preceding reaction.

Appendix D

Laboratory Testing

Appendix D

Laboratory Testing

This appendix describes various laboratory testing methods.

D.1 Single-Pass Flow-Through (SPFT) Test

The Single-Pass Flow Through (SPFT) test method involves dissolving a solid material by continuously flowing the solution through a container (ASTM, 2010). A schematic apparatus of the SPFT system is presented in Figure D.1. The system functions through the use of syringe pumps (Kloehn) that draw the chemically controlled solution (i.e., pH, [H_4SiO_4]) from the input reservoirs and transfer it to the reactor vessels through Teflon tubing. The oven is maintained at a desired temperature for the entire test duration. The reactors contain one influent and one effluent port with the solid sample dispersed at the bottom of the reactor. The SPFT system design ensures adequate mixing of the solids with influent. Effluent solutions are analyzed for elements that can trace the extent of glass dissolution. The steady-state rate of reaction is assumed when effluent concentrations of the analyte of interest differed by less than 10%.

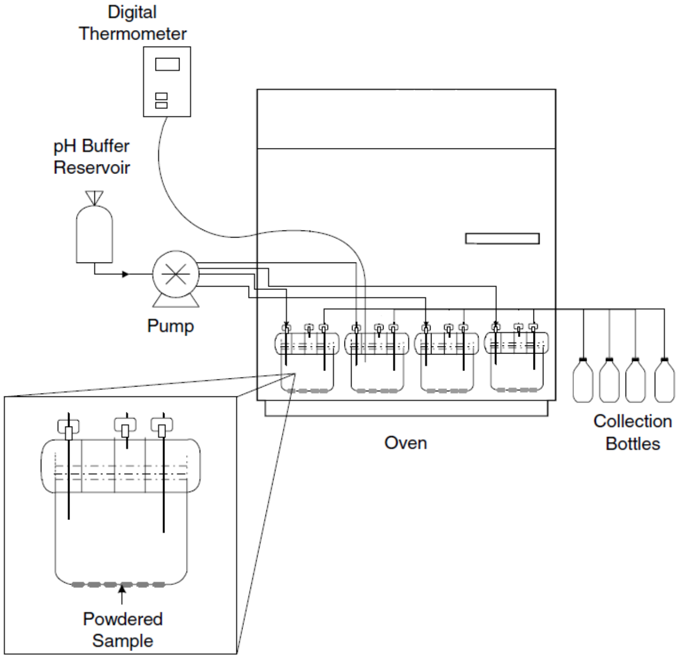


Figure D.1 Schematic of the Single-Pass Flow-Through (SPFT) Apparatus for Determining Reaction Rates in Continuous Flow Solution.

D.2 Product Consistency Test (PCT)

The Product Consistency Test (PCT) method is generally used "to evaluate whether the chemical durability and elemental release characteristics of nuclear, hazardous, and mixed glass waste forms have been consistently controlled during production" (ASTM, 2008). The PCT can be run in two methods designated A and B. Method A is a more stringent test with all variables being constrained. The test is run with a glass waste form that is crushed and sieved to – 100 to + 200 mesh (0.149-0.074 mm). At least 1 g of the sieved material is placed in a Type 304L stainless steel vessel. An amount of ASTM Type I water equal to 10 ± 0.5 cm^3/g of sample mass is added, giving an S/V ratio of approximately 20000 m^{-1}. The vessel is sealed and placed in an oven at 90 °C for seven days. The solution concentration and pH are then measured to give an indication of glass performance. Generally, to be considered an acceptable waste form, a glass should demonstrate higher chemical durability in the PCT-A than the Environmental Assessment (EA) glass (NL_{Na}= 6.81 +- 0.95 g/m^2) (Jantzen et al., 1994). The PCT-B method allows more variation in the test method, including varying experimental duration, temperature, S/V ratio, and the ability to use a Teflon vessel. In general, the PCT-B method is a well-constrained static test.

D.3 Vapor Hydration Test (VHT)

For the vapor hydration tests (ASTM, 2009), glass is suspended from a support rod inside the test vessel with platinum wire (Figure D.2). A volume of water determined by the volume of the test vessel and the test temperature is added to the vessel. For a 22 mL test vessel with testing conducted between 5 and 300 °C, the volume of water varies from 0.05 to 1.39 g. The vessel is then sealed and placed in an oven at the desired test temperature and left undisturbed. After the desired test duration, the vessel is removed from the oven and the bottom of the vessel is cooled to condense the vapor in the vessel. The extent of glass dissolution is quantified by measuring the alteration thickness of the sample coupon. To comply with current regulations, the alteration rate at 200 °C should be less than 50 g/m^2d (DOE, 2000; Vienna et al., 2001). Samples may also be examined with optical microscopy, XRD, SEM, and other analytical methods.

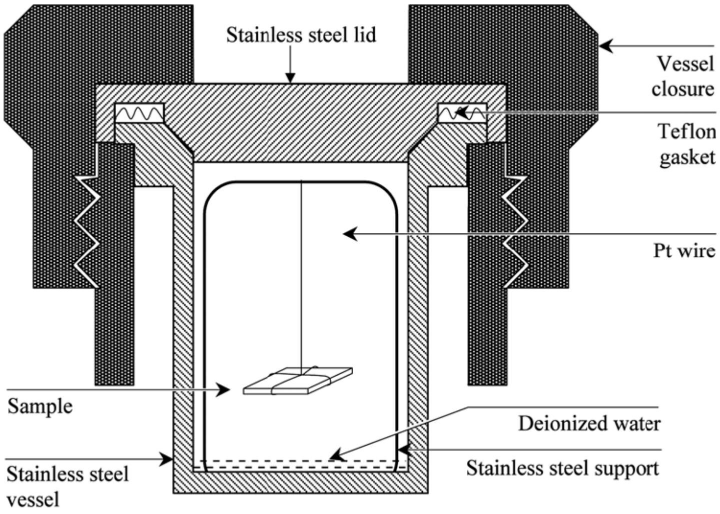


Figure D.2 Apparatus for Conducting Vapor Hydration Tests (ASTM, 2009)

D.4 Pressurized Unsaturated Flow (PUF) Test

The PUF apparatus is used to mimic hydraulically unsaturated flow in vadose zone environments, such as the IDF, while allowing the corroding waste form to achieve a final reaction state. A schematic picture of the apparatus is depicted in Figure D.3. The PUF column operates under a hydraulically unsaturated condition by creating a constant-pressure, steady-state vertical water flow, while maintaining uniform water content throughout the column using gravity to induce flow. Hydraulically unsaturated porous media are characterized by the presence of a continuous air phase along with a continuous water phase. A constant pressure is achieved with monitored gas pressure, and a porous stainless steel plate (0.2-μm pores) at the effluent end of the column wicks water from the material, which then transports to the sample vial.

The columns are constructed from polyether ether ketone (PEEK) materials and are 7.62-cm long and 1.91-cm wide with a porous plate placed at the bottom between the material and the effluent port. The porous plate is water saturated before packing, and stays saturated throughout the experiment to maintain water flow. Gravity transports water from the influent port to the plate, and the positive gas (air) pressure applied keeps the material uniformly water unsaturated at the constant flow rate supplied by programmable syringe pumps (2.0 mL day^{-1}). All system parameters are monitored using LabVIEW™ (National Instruments Corporation), which logs test data from several thermocouples, pressure sensors, inline sensors for effluent pH and electrical conductivity, and an electronic strain gauge that measures column mass. The mass was used along with measurements at the start and end of the experiment to calculate the relative hydraulic saturation (% saturation). Periodic gas venting involves the control of solenoid valves by LabVIEW™.

Columns are dry packed with the material of interest. After packing, the column is mounted on the apparatus and a heating coil with thermocouples is attached to the column. The column is then vacuum-saturated with 18.2 MΩ DI H_2O at ambient temperature. The column initially is allowed to desaturate by gravity drainage, with the gas pressure being brought up to the desired level. A temperature controller is then programmed to heat the column to an approximate desired temperature and this temperature is maintained throughout the experiment. After reaching the desired temperature, the influent valve is opened, and influent is set to a low flow rate of ~2 mL/d. Effluent samples are collected and acidified for elemental analysis with inductively coupled plasma-optical emission spectroscopy (ICP-OES) or -mass spectrometry (ICP-MS). After termination of the experiment, the solid samples can be collected from the column at depths of 0.5 cm to characterize the evolution of phases along the depth of the column.

More details of the system and test procedure have been described previously by McGrail and coworkers (McGrail et al., 1997b; McGrail et al., 1999) and Pierce and coworkers (Neeway et al., 2014b; Pierce et al., 2006; Pierce et al., 2007; Pierce et al., 2014).

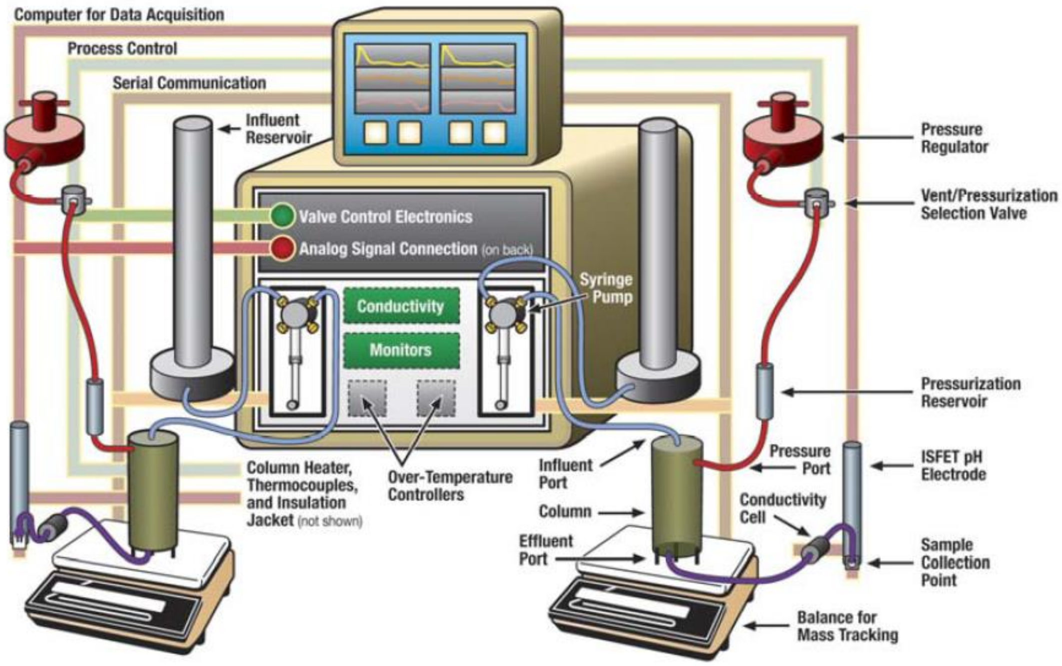


Figure D.3 Schematic of the Pressurized Unsaturated Flow Apparatus (Pierce et al., 2007)

Distribution

No. of
Copies

2 Washington River Protection Solutions
Dave Swanberg
WRPS Documents – TOCVND@rl.gov

1 Oak Ridge National Laboratory
Eric Pierce

No. of
Copies

8 Pacific Northwest National Laboratory
VL Freedman
JJ Neeway
NP Qafoku
JV Ryan
JD Vienna
JH Westsik, Jr
Project File
Information Release (pdf)

Pacific Northwest
NATIONAL LABORATORY

U.S. DEPARTMENT OF
ENERGY

Proudly Operated by **Battelle** *Since 1965*

902 Battelle Boulevard
P.O. Box 999
Richland, WA 99352
1-888-375-PNNL (7665)

www.pnnl.gov