Contract No:

This document was prepared in conjunction with work accomplished under Contract No. 89303321CEM000080 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

Disclaimer:

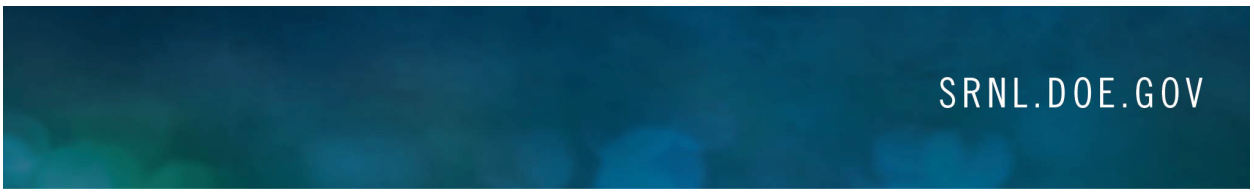
Nepheline Crystallization Studies and the Structural Integrity of the Residual (SIR) - FY22 Study Glasses

J. W. Amoroso

M. A. Page

September 2022

SRNL-STI-2022-00476, Revision 0



DISCLAIMER

Printed in the United States of America

Prepared for
U.S. Department of Energy

SRNL-STI-2022-00476
Revision 0

Keywords: *Nepheline, Durability, HLW, Glass*

Retention: *Varies*

Nepheline Crystallization Studies and the Structural Integrity of the Residual (SIR) - FY22 Study Glasses

J. W. Amoroso
M. A. Page

September 2022

Savannah River National Laboratory is operated by Battelle Savannah River Alliance for the U.S. Department of Energy under Contract No. 89303321CEM000080.

REVIEWS AND APPROVALS

AUTHORS:

J. W. Amoroso, Applied Materials Research Date

TECHNICAL REVIEW:

W. Li, Applied Materials Research, Reviewed per E7 2.60 Date

APPROVAL:

R. B. Wyrwas, Applied Materials Research Date

A. D. Cozzi, Manager Date
Applied Materials Research

J. Manna, Director Date
Materials Technology Division

ACKNOWLEDGEMENTS

The authors gratefully acknowledge Stephen P. Harris Jr. for statistical analyses and discussion. Funding for this work by the U.S. Department of Energy Office of River Protection Waste Treatment & Immobilization Plant Project through Department of Energy Work Authorization M0SRV00101 managed by Albert A. Kruger is gratefully acknowledged.

EXECUTIVE SUMMARY

In FY22 a set of 367 HLW glasses with compositions representative of the Waste Treatment and Immobilization Plant (WTP) processing region were aggregated and analyzed with the Structural Integrity of the Residual (SIR) model developed by the Savannah River National Laboratory (SRNL). An additional 12 glasses targeting 27 – 37 wt % alumina (in glass) and at waste loadings up to ~70 wt % were fabricated and added to the database. Collectively, this data set was analyzed with regression statistics and partitioning functions to reveal correlations between boron release and the chemical composition. FY22 results indicate that the SIR theoretical alkali-silicate precipitation term, Al_2O_3 and B_2O_3 concentration, and SIR computed non-bridging oxygen are significant predictors of chemical durability. A statistical model using the SIR parameters was shown to have greater overall accuracy than the nepheline discriminator model while maintaining false predictions of pour durability below 1%. In FY23, we will continue this work to focus on refining the SIR with glass compositions that challenge the SIR correlation terms, namely the theoretical crystalline precipitation and non-bridging oxygen terms.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

CCC	Canister centerline cooling
DOE	U.S. Department of Energy
EA	Environmental Assessment
EDS	Energy-Dispersive X-Ray Spectroscopy
GFC	Glass Forming Chemical
HLW	High Level Waste
ICP-AEA	Inductively Coupled Plasma-Atomic Emission Spectroscopy
LAW	Low Activity Waste
NBO	Non-Bridging Oxygen
ND	Nepheline Discriminator
NL	Normalized Mass Loss
ORP	Office of River Protection
PCT	Product Consistency Test
SEM	Scanning Electron Microscopy
SIR	Structural Integrity of Residual
SRNL	Savannah River National Laboratory
WTP	Waste Treatment and Immobilization Plant
XRD	X-Ray Diffraction

1.0 Introduction

The U.S. Department of Energy (DOE) Office of River Protection (ORP) has requested that the Savannah River National Laboratory (SRNL) support glass formulation development to support the planned vitrification of 55 million gallons of radioactive waste stored at the Hanford Site in Washington. This waste, which will be processed through the Waste Treatment and Immobilization Plant (WTP) is comprised of low-activity waste (LAW) and high-level waste (HLW). LAW accounts for ~90% of the volume as liquid supernatant and the remaining fraction of solids and heavy precipitates is HLW. Both waste feeds will ultimately be vitrified into borosilicate glass.[1]

The performance of HLW glass is quantified by its resistance to aqueous chemical degradation as measured by the ASTM Product Consistency Test (PCT).[2] The PCT response is dependent on the glass composition, and crystalline phases that form during processing, such as nepheline, are known to adversely affect the PCT response.[3, 4] One of the technical areas for glass formulation is the development of predictive models for crystallization of nepheline ($NaAlSiO_4$) in HLW glasses with high alumina concentrations. In FY20, researchers at SRNL proposed the Structural Integrity of the Residual (SIR) to predict chemical durability of HLW glass composition. The SIR is based on the concept that specific alkali-silicate phases, when precipitated from HLW glass, will affect the chemical resistance of the residual glass structure. This is because certain alkali-silicate phase remove constituents non-stoichiometrically, which disrupts the glass structure stability. HLW glass undergoes slow cooling during processing, which provides the conditions needed for crystal precipitation. The SIR uses a combination of structural parameters and alkali-silicate phase formation propensity terms to predict glass structure and durability after being subjected to slow cooling and/or devitrification. The SIR is notionally the calculated structural stability of the glass network that remains after precipitation of alkali-silicate phases, such as nepheline.

In FY21 the SIR was able to successfully screen for durable glass compositions containing 20 – 35 wt % Al_2O_3, which significantly increases the projected waste loading for glasses to be processed at WTP.[5] In FY22, additional glasses were prepared from a nominal Al and Na limited waste composition. This report summarizes work performed in FY22 to supplement development of the SIR methodology.

2.0 Approach and Methods

Nepheline crystallization studies were planned to supplement the SIR model by investigating HLW glasses specifically formulated to exhibit pour chemical durability, but that are within a favorable composition region for the Hanford WTP. Experiments consisted of heat-treating glasses and measuring chemical durability following the PCT procedure. Subsequently, statistical software was used to evaluate the effect of compositionally derived parameters on the SIR model predictions. The data set used in FY22 contained fewer glasses than the data set used in FY21, but the FY22 data set contained a significantly greater percentage of glass formulations representative of those to be processed in the Hanford WTP.

2.1 Glass Selection

Several HLW streams have been identified at Hanford based on historical processing methods and tank filling/blending operations. The Hanford HLW streams can be grouped by their limiting component, e. g. Fe, Al, Na, Zr, Cr, Bi, etc. representing the range of chemistry with respect to glass formulation.[6, 7] A series of 12 glasses were developed based on the aluminum and sodium (Al & Na) limited and the aluminum (Al) limited Hanford HLW compositions. Those HLW streams were the basis for varying glass forming chemical (GFC) additives; i.e. SiO_2, Li_2O, and B_2O_3. The test glass compositions were formulated from SIR criteria determinations that are described in detail elsewhere.[8] In summary, the SIR model screens parent glass compositions for relative ratios of B_2O_3 and Al_2O_3 as well as non-bridging oxygen (NBO) content. Subsequently, the SIR model computes theoretical residual glass compositions based on limiting precipitation of alkali-silicate phases, specifically (K, Na, Li)$AlSiO_4$ (nepheline) and (Li, Na)$_2SiO_3$. Finally, a durable glass composition region based on the *Nepheline–(Li, Na)$_2SiO_3$–Residual* ternary is parameterized from the computed molar fraction, or ratio, of (Li, Na)$_2SiO_3$,

$(Li, Na)_2SiO_3$ / $(Li, Na)_2SiO_3$ + Residual

The test glasses were formulated to iteratively increase the B_2O_3 content relative to the Al_2O_3 content, from a factor of 0.6 to 1.1. Nominal values for the NBO and $(Li, Na)_2SiO_3$ ratio terms were targeted when solving the formulation criteria to estimate GFC additions of SiO_2 and Li_2O. Simultaneously, the waste loading was maximized within the above constraints. Overall the test glass matrix included waste loadings between 50 and 70 wt %. The glasses represent two HLW composition regions of interest. Five of the glasses were formulated with Na_2O nominally at 17.1 wt % and the remaining seven glasses were formulated with Na_2O nominally at 4.7 wt %, corresponding to 'Al & Na' and 'Al' limited HLW streams, respectively. Table 2-1 and Table 2-2 reproduce the 'Al & Na' and 'Al' limited HLW streams and nominal waste loadings in the 12 target glasses, respectively. Figure 2-1 plots the normalized Na_2O-Al_2O_3-SiO_2 target composition from Table 2-2 for each test glass.

Table 2-1. Nominal HLW Simulant Composition Used for Glass Formulations.

Component	Al & Na Limited (wt %)	Al Limited (wt %)
Al_2O_3	45.13	52.95
B_2O_3	0.77	0.42
BaO	0.06	0.12
Bi_2O_3	2.45	2.53
CaO	1.53	2.38
CdO	0.02	0.05
Cr_2O_3	1.50	1.15
Cs_2O	0.50	0.5
F	0.48	1.47
Fe_2O_3	5.95	13.03
K_2O	1.40	0.31
Li_2O	0.16	0.38
MgO	0.46	0.26
Na_2O	26.88	7.91
NiO	0.21	0.88
P_2O_5	4.27	2.32
PbO	0.19	0.9
RuO_2	0.10	0.1
SiO_2	6.48	10.81
SO_3	0.46	0.44
TiO_2	0.36	0.02
ZnO	0.38	0.18
ZrO_2	0.26	0.87
SUM	100	100

Table 2-2. Nominal Waste Loadings and Normalized Na_2O-Al_2O_3-SiO_2 Composition of Test Glasses.

Sample ID	Waste Loading (%)	HLW Stream	Normalized Composition (wt %)		
			Na_2O	Al_2O_3	SiO_2
SIR22-01	61.0	Na & Al limited	22.0	36.9	41.1
SIR22-02	65.8	Na & Al limited	24.5	41.1	34.4
SIR22-03	64.5	Na & Al limited	24.1	40.4	35.5
SIR22-04	61.9	Na & Al limited	23.2	38.9	37.9
SIR22-05	64.2	Na & Al limited	24.6	41.2	34.2
SIR22-06	54.9	Al limited	7.4	49.2	43.4
SIR22-07	70.5	Al limited	10.5	70.5	19.0
SIR22-08	62.3	Al limited	9.0	60.5	30.5
SIR22-09	59.9	Al limited	8.6	57.6	33.8
SIR22-10	58.2	Al limited	8.3	55.7	36.0
SIR22-11	55.0	Al limited	7.8	52.0	40.3
SIR22-12	53.3	Al limited	7.5	50.3	42.2

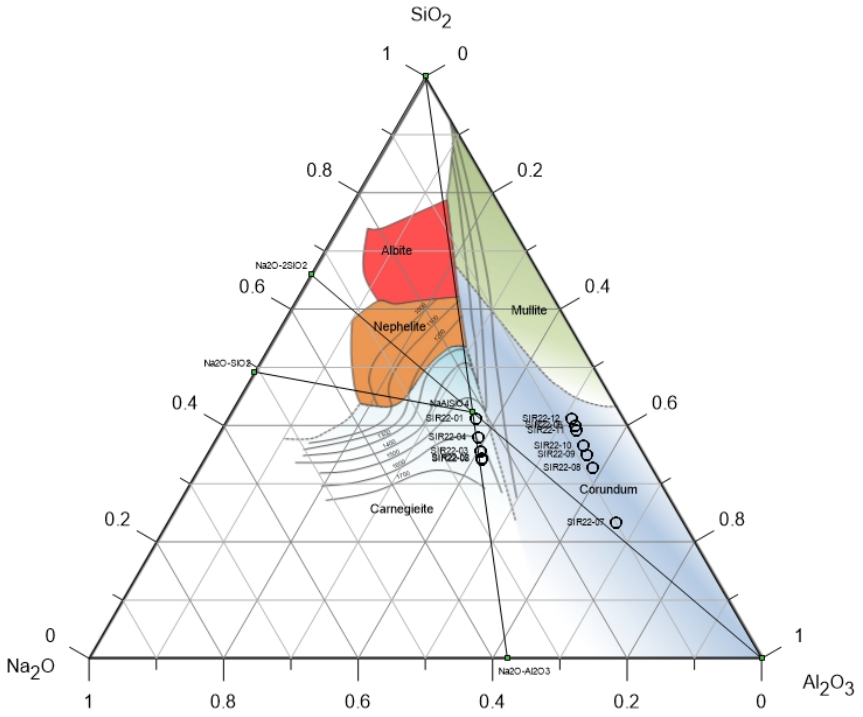


Figure 2-1. Na_2O-Al_2O_3-SiO_2 normalized ternary (wt %) showing relationships among the target glass compositions. Composition SIR22-2 and SIR22-5 overlap in this plot.

2.2 Sample Preparation

2.2.1 Glass Fabrication

Each glass was prepared from a dry batch of stoichiometric quantities of reagent grade oxides, carbonates, sulphates, and phosphates mixed to yield approximately 50g of melted glass. The batch was hand mixed to ensure uniform consistency of the powder and transferred to a Pt/Au alloy crucible fitted with a lid. The

batch was heated from ambient temperature to 1200°C using the furnace ramp rate of ~10 K/min. After 2 hours at 1200°C, the glass was poured form the crucible into water to quench the glass. The resulting glass was collected and dried to be used as feedstock for subsequent heat treatment and characterization.

2.2.2 Glass Heat Treatment

Figure 2-2 shows the canister centerline cooling (CCC) profile that was used to heat treat (slow cool) the glasses prior to performing the PCT. The CCC profile was based on that reported WTP HLW glass.[6] Twenty-five grams of fabricated glass (2.2.1) was combined into a Pt/Au alloy crucible and fitted with a lid. The crucible and glass were placed into a furnace preheated to 1200°C. After 1 hour, a pre-programmed furnace ramp profile matching the WTP HLW CCC was initiated to control the cooling of the glass. Temperature was monitored during the CCC heat treatment and the cooled glass was retained as feedstock for subsequent testing and characterization.

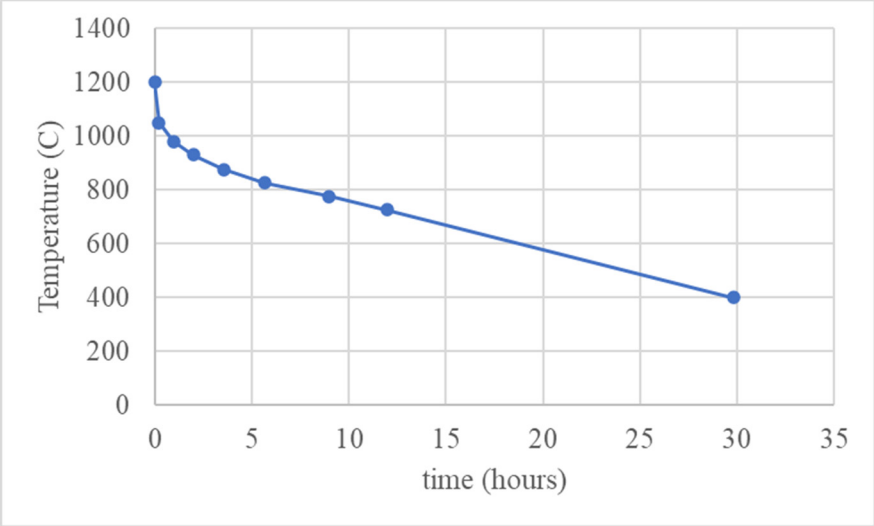


Figure 2-2. Programmed CCC profile used to heat treat glass samples.

2.3 Characterization

2.3.1 Chemical Composition

Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) was used to measure elemental concentrations in solid samples and leachate solutions. Elemental compositions were measured by preparing a representative sample via a sodium peroxide fusion method or a lithium-metaborate fusion method depending on concentration and element. Samples were prepared in duplicate and analyzed twice for each element of interest, with the instrumentation being re-calibrated between duplicate analyses. Standards were intermittently measured to ensure the performance of the instruments over the course of the analyses. Elemental composition measurements were converted to an oxide basis based on expected cation valence in the glass. Leachate samples were received acidified and diluted prior to measuring elemental concentrations.

2.3.2 Phase Identification

Powder x-ray diffraction (XRD) was used as the primary means to identify phases after heat treatment. Samples were initially ground in an automatic Spex mill for 4 minutes. Subsequently, the powders were hand ground in agate with alcohol and mounted to a glass slide using a collidion/Amyl Acetate solution. XRD was performed under conditions to allow a qualitative determination of the type of crystalline phases present in concentration ≥ 0.5 wt%. Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray spectroscopy (EDS) were performed to characterize the chemical distribution and morphology of precipitated phases in the glasses.

2.3.3 Product Consistency Test

The product consistency test (PCT), ASTM Standard C1285,[2] was performed to evaluate the chemical durability of heat treated glasses. The Approved Reference Material (ARM) standard was included in the experimental test matrices. The PCT was performed in triplicate according to Method A; approximately 15 ml of water were added to approximately 1.5 g of sample or standard in stainless steel vessels. Two blanks containing Approximately 15 ml of water were also tested alongside the sample glasses. Sample glasses and standards were ground, washed, and prepared according to the standard PCT procedure. The stainless steel vessels were closed, sealed, and heated in an oven at 90 ± 2 °C for 7 days. Once cooled, the solutions were sampled (filtered and acidified), and analyzed using the chemical analysis methods previously described (Section 2.3.1). Multi-element standard solutions were included as a check on the accuracy of the ICP instruments used for these measurements.

Elemental release was calculated and reported as normalized elemental mass loss (NL_i) using the expression,

$$NL_i = \frac{C_i}{(f_i) \cdot (SA/V)}$$

where NL_i is the normalized release mass loss for element "*i*" (g/m^2), c_i is the concentration of element "*i*" in solution (g/L), f_i is the mass fraction of element "*i*" in the unleached sample[1] (unitless), SA/*V* is the surface area of the sample divided by the leachate volume (m^2/L). Values are reported as NL_i to enable comparison of the glasses tested in this study with the existing database of glasses, which report PCT in g/m^2. The computed geometric surface area of 1.99 x10^{-2} m^2/g, equivalent to the averaged spherical particle size in the PCT-A sieve fraction, was used to calculate the SA/V term.[2]

2.4 Data Set and Statistical Analyses

A data set of glass compositions compiled from a number of sources and that have been previously used to support Hanford HLW vitrification was used to assess the applicability of the SIR methodology.[9] The data set contained 367 historical glass compositions for which normalized boron mass loss (NL_B) after CCC heat treatment was reported in the literature. The data set represents a range of glasses that were intentionally developed to understand the impact of composition on HLW glass behavior, with approximately 70% of the glass compositions developed explicitly for Hanford HLW. The glasses fabricated in FY22 and reported here were added to that data set of 367 compositions. This combined data set (378 compositions) was used in combination with statistical methods to explore correlations within the data set related to the SIR. Although a model based on the SIR methodology has been proposed,[5, 8] the purpose of this analysis was to elucidate correlations among variables relevant to the SIR.

Statistical analyses were performed using the JMP Pro 16.2.0 software package.[10] One of the primary tools used was the partition platform, which recursively splits (*partitions*) data according to a relationship between the predictors and response values, creating a decision tree. The partition algorithm searches all possible splits of predictors to best predict the response until the desired fit is achieved. The technique is considered as a data mining technique because it is useful for exploring relationships without having a good prior model, can handle large problems easily, and the results are interpretable. In this case, the response value was NL_B, and the predictors included each component oxide, as well as the SIR parameters which included computed non-bridging oxygen, theoretical alkali-silicate phase concentration, and the ratio of Li_2SiO_3 to the computed residual glass composition.[5]

2.5 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

[1] In all cases, measured elemental concentrations were used as opposed to target concentrations.

3.0 Results and Discussion

3.1 Glass Fabrication and Composition

One composition, SIR22-07, could not be poured from the crucible after initial melting and further testing was not performed on that glass. The remaining 11 glasses were heat treated, characterized, and measured for chemical durability. The target and measured glass compositions (converted to oxides) for each of the 11 glasses are summarized in **Error! Reference source not found.**. In general, the measured compositions agree with the target values. When the measured compositions are normalized to account for Cs and F, the major components Al_2O_3, B_2O_3, Fe_2O_3, and SiO_2 are within 10 percent of the target values,[2] except the measured Na_2O concentrations.[3] For the 'Al limited' glasses (SIR22- 06-12) the percent differences between measured and target were nominally 70% whereas the absolute difference was 2-3 wt %. For the 'Al & Na limited' glasses (SIR22- 01-05) the percent differences between measured and target were nominally 14% whereas the absolute difference was also 2-3 wt %. This suggest a systematic error, and would account for the large relative differences observed in the 'Al' limited glass formulations compared to the 'Al & Na" limited glass formulations."

[2] The Fe_2O_3 value reported for SIR22-02 is greater than 10 percent of the target value.
[3] The normalized compositions are not shown in **Error! Reference source not found.**. The normalized compositions are obtained by dividing each component by the sum of the total oxides, less the target Cs_2O and F concentrations.

Table 3-1. Target and Measured Composition (wt %) of Test Glasses.

ID/ Oxide	SIR22-01		SIR22-02		SIR22-03		SIR22-04		SIR22-05		SIR22-06	
	TARGET	MEAS	TARGET	MEAS	TARGET	MEAS	TARGET	MEAS	TARGET	MEAS	TARGET	MEAS
Al_2O_3	27.53	26.92	29.68	28.15	29.11	27.11	27.95	26.36	28.96	27.59	29.08	28.81
B_2O_3	11.28	10.93	14.19	13.56	13.91	12.72	13.36	11.77	15.82	14.96	17.87	17.82
BaO	0.04	<0.06	0.04	<0.06	0.04	<0.06	0.04	<0.06	0.04	<0.06	0.07	0.07
Bi_2O_3	1.49	1.44	1.61	1.52	1.58	1.42	1.52	1.43	1.57	1.45	1.39	1.32
CaO	0.93	0.79	1.01	0.84	0.99	0.79	0.95	0.80	0.98	0.82	1.31	1.12
CdO	0.01	<0.06	0.01	<0.06	0.01	<0.06	0.01	<0.06	0.01	<0.06	0.03	<0.06
Cr_2O_3	0.92	0.60	0.99	0.47	0.97	0.62	0.93	0.64	0.96	0.66	0.63	0.39
Cs_2O	0.31	n.m.	0.33	n.m.	0.32	n.m.	0.31	n.m.	0.32	n.m.	0.27	n.m.
F	0.29	n.m.	0.32	n.m.	0.31	n.m.	0.30	n.m.	0.31	n.m.	0.81	n.m.
Fe_2O_3	3.63	3.47	3.91	3.24	3.84	3.37	3.68	3.50	3.82	3.53	7.16	6.73
K_2O	0.85	0.79	0.92	0.81	0.90	0.76	0.87	0.78	0.90	0.78	0.17	0.16
Li_2O	1.53	1.56	0.13	0.14	0.76	0.75	2.06	1.95	0.72	0.72	7.96	8.12
MgO	0.28	0.22	0.30	0.24	0.30	0.22	0.28	0.23	0.30	0.23	0.14	0.11
Na_2O	16.40	18.60	17.68	20.29	17.34	19.01	16.65	19.21	17.25	19.82	4.34	7.40
NiO	0.13	0.12	0.14	0.12	0.14	0.12	0.13	0.12	0.13	0.12	0.48	0.38
P_2O_5	2.61	1.35	2.81	2.24	2.75	2.09	2.64	2.11	2.74	2.21	1.27	0.96
PbO	0.12	0.10	0.12	0.11	0.12	0.11	0.12	0.11	0.12	0.12	0.49	0.44
RuO_2	0.06	<0.07	0.07	<0.07	0.06	<0.07	0.06	<0.07	0.06	<0.07	0.05	<0.07
SiO_2	30.70	30.91	24.80	23.96	25.60	24.39	27.24	26.21	24.05	23.00	25.64	26.10
SO_3	0.28	0.22	0.30	0.24	0.30	0.21	0.28	0.21	0.30	0.21	0.24	0.13
TiO_2	0.22	0.13	0.24	0.15	0.23	0.21	0.22	0.22	0.23	0.17	0.01	<0.08
ZnO	0.23	0.24	0.25	0.25	0.25	0.23	0.24	0.23	0.24	0.24	0.10	0.10
ZrO_2	0.16	0.08	0.17	0.06	0.17	0.08	0.16	0.07	0.17	0.06	0.48	0.19
	100.00	**98.48**	**100.00**	**96.39**	**100.00**	**94.20**	**100.00**	**95.93**	**100.00**	**96.68**	**100.00**	**100.35**

"<" indicates the element was below detection, 0.05 wt %, and the oxide is computed and reported as less than (<).
n.m. indicates the element was not measured.

Table 3-1. Target and Measured Composition (wt %) of Test Glasses. (continued)

ID/ Oxide	SIR22-08[1]		SIR22-09		SIR22-10		SIR22-11		SIR22-12	
	TARGET	MEAS	TARGET	MEAS	TARGET	MEAS	TARGET	MEAS	TARGET	MEAS
Al_2O_3	33.01	31.27	31.71	30.80	30.84	29.85	29.11	28.53	28.24	27.78
B_2O_3	22.54	22.18	21.65	21.44	21.06	20.66	19.87	19.53	21.21	21.04
BaO	0.07	0.08	0.07	0.08	0.07	0.07	0.07	0.06	0.06	0.06
Bi_2O_3	1.58	1.50	1.52	1.44	1.47	1.41	1.39	1.29	1.35	1.24
CaO	1.48	1.25	1.43	1.29	1.39	1.19	1.31	1.14	1.27	1.09
CdO	0.03	<0.06	0.03	<0.06	0.03	<0.06	0.03	<0.06	0.03	<0.06
Cr_2O_3	0.72	0.47	0.69	0.41	0.67	0.39	0.63	0.40	0.61	0.37
Cs_2O	0.31	n.m.	0.30	n.m.	0.29	n.m.	0.27	n.m.	0.27	n.m.
F	0.92	n.m.	0.88	n.m.	0.86	n.m.	0.81	n.m.	0.78	n.m.
Fe_2O_3	8.12	7.58	7.80	7.15	7.59	6.91	7.16	6.76	6.95	6.56
K_2O	0.19	0.18	0.19	0.16	0.18	0.17	0.17	0.16	0.17	0.16
Li_2O	5.73	5.83	6.81	6.85	7.54	7.52	8.98	9.09	7.96	8.09
MgO	0.16	0.13	0.16	0.13	0.15	0.12	0.14	0.12	0.14	0.11
Na_2O	4.93	8.25	4.74	8.05	4.61	7.81	4.35	7.31	4.22	7.08
NiO	0.55	0.45	0.53	0.40	0.51	0.38	0.48	0.38	0.47	0.37
P_2O_5	1.45	1.02	1.39	1.11	1.35	0.98	1.28	0.86	1.24	0.90
PbO	0.56	0.50	0.54	0.51	0.52	0.48	0.49	0.45	0.48	0.45
RuO_2	0.06	<0.07	0.06	<0.07	0.06	<0.07	0.05	<0.07	0.05	<0.07
SiO_2	16.63	16.40	18.61	18.69	19.93	20.09	22.57	22.68	23.71	23.85
SO_3	0.27	0.16	0.26	0.11	0.26	0.14	0.24	0.13	0.23	0.12
TiO_2	0.01	<0.08	0.01	<0.08	0.01	<0.08	0.01	<0.08	0.01	<0.08
ZnO	0.11	0.10	0.11	0.11	0.10	0.10	0.10	0.09	0.10	0.09
ZrO_2	0.54	0.19	0.52	0.30	0.51	0.20	0.48	0.18	0.46	0.22
	100.00	**97.57**	**100.00**	**99.02**	**100.00**	**98.49**	**100.00**	**99.18**	**100.00**	**99.60**

[1] B and Li concentrations were taken from a single replicate.
"<" indicates the element was below detection, 0.05 wt %, and the oxide is computed and reported as less than (<).
n.m. indicates the element was not measured.

3.2 Crystallization and Phase Identification

Images of the heat treated glasses are shown in Figure 3-1 and Figure 3-2. Several of the test glasses exhibited crystallization as evidenced by visibly distinguishable surface features. X-ray diffraction (XRD) confirmed the presence of nepheline, spinel, and other crystalline phases were present in all of the heat treated glasses. Phase quantification has not yet been completed, but the qualitative phase identification results are summarized in Table 3-2. Scanning Electron Microscopy (SEM) further confirmed the presence of crystalline phases identified by XRD. Figure 3-3 shows micrographs of polished sections from four glasses representative of the test glasses. The characteristic spinel/ trevorite phases are easily visible, as are two other distinct crystalline phases, which EDS confirmed to be enriched in phosphorous or phosphorous and calcium. Analysis is ongoing to determine the stoichiometry of the P- and P/Ca- containing phases. Additionally, Figure 3-3 shows the bulk volume as a mid-tone gray color, or in the case of glasses which precipitated nepheline, a mixture of two mid-tone gray phases, one of which is enriched in Al and Si. The crystallization present in the heat treated glasses is expected and is in agreement with previous work.[8, 11]

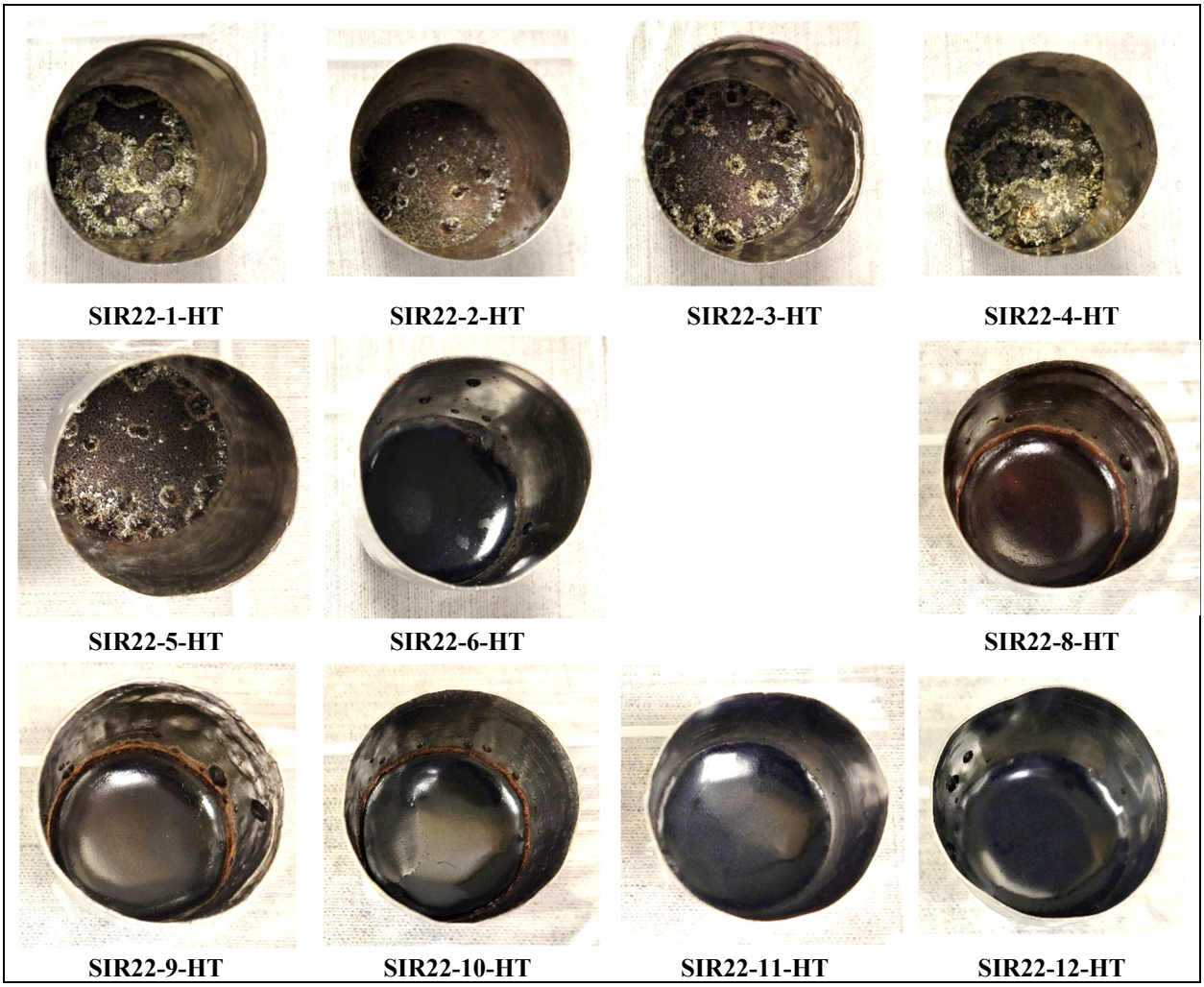
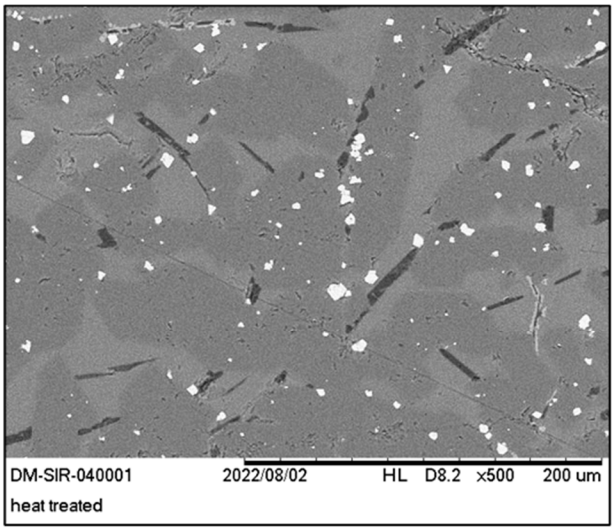


Figure 3-1. Images of glass ingots after heat treatment showing top surface.

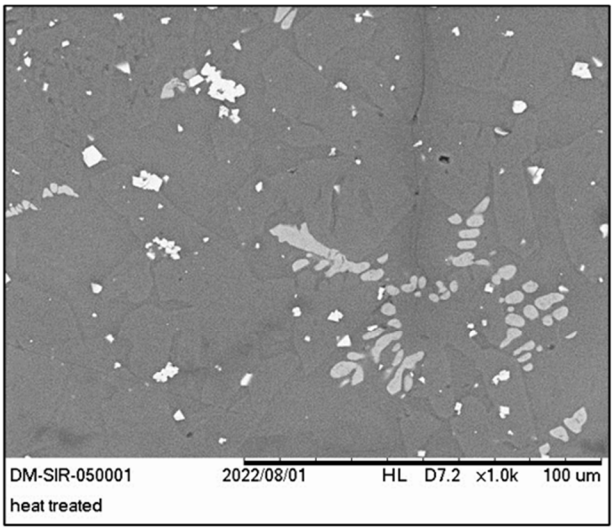
Figure 3-2. Images of glass ingots after heat treatment and removal from crucible.

Table 3-2. Crystalline Phases Identified in the Heat Treated Glasses.

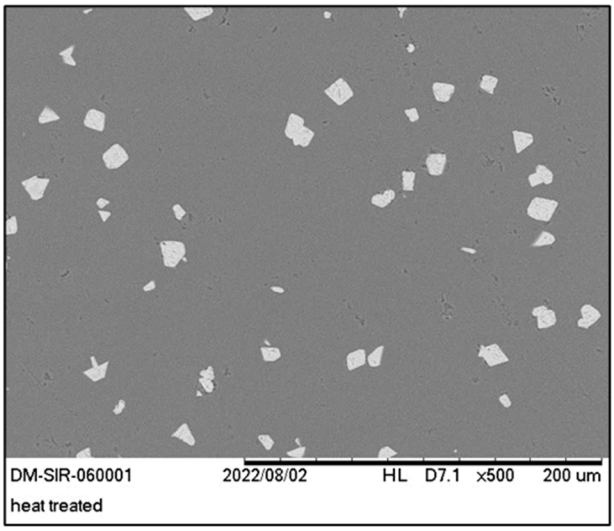
	Nepheline ($NaAlSiO_4$)	**Trevorite** $(Ni,Fe)_2O_4$	**Other Spinel**	**Other**
SIR22-1-HT	X	X		X
SIR22-2-HT	X	X		X
SIR22-3-HT	X	X		X
SIR22-4-HT	X	X		X
SIR22-5-HT	X	X		X
SIR22-6-HT		X		
SIR22-8-HT		X		X
SIR22-9-HT		X	X	
SIR22-10-HT			X	
SIR22-11-HT			X	
SIR22-12-HT			X	



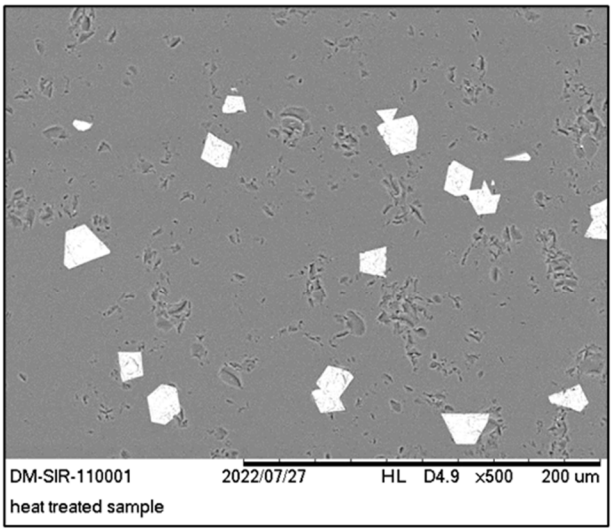
(A) SIR22-04-HT: The brightest phase is spinel/ trevorite and the darkest phase is enriched in P. The mid-tones represent a phase enriched in Al and Si that is intermixed with the residual glass.



(B) SIR22-05-HT: The brightest phase is spinel/ trevorite. The lighter nodular phase is enriched in Ca and P. The darker gray tones represent a phase enriched in Al and Si that is intermixed with the residual glass.



(D) SIR22-06-HT: The brightest phase is spinel/ trevorite within the residual glass phase.



(C) SIR22-11-HT: The brightest phase is spinel/ trevorite within the residual glass phase.

Figure 3-3. Representative SEM images of the heat treated glass microstructures showing phases identified by XRD.

3.3 Product Consistenct Test

Computed normalized mass loss for B, Al, Si, and Na as measured by the PCT are summarized in Table 3-3. The B and Na release from the 'Al limited' HLW formulations (SIR22- 6-12) was generally congruent and was correlated to the compositional trends. The B and Na release from the 'Al & Na limited' HLW formulations (SIR22- 1-5) was comparatively more variable. Na and Si release were nominally low for all samples. Although beyond the immediate scope of this document, interpretation of these results is ongoing to better understand correlations between chemical durability and composition to inform the SIR predictions. The reported normalized mass losses for B were used to further develop and evaluate the SIR model. One of the goals of this study was to add more glasses to the literature that exhibit pour durability, $NL_B < 7.19$

g/m^2, in order to decrease the potential for sample bias in the databases of glass durability.[4] Only 2 of the 11 glasses reported here exhibited an acceptable PCT response, which provides 9 additional glasses to the database that have pour durability. The addition of these 11 glasses to the database significantly decreases the pass result from 87.47 % (321/367) to 85.45 % (323/378).

Table 3-3. PCT-A Normalized Elemental Mass Loss (NL_i) from the Test Glasses.

Sample ID	HLW Stream	Normalized Mass Loss - NL_i) - (g/m^2)			
		B	Al	Si	Na
SIR22-1-HT	Al & Na limited	42.0	0.09	0.02	12.0
SIR22-2-HT	Al & Na limited	34.9	0.30	0.01	18.6
SIR22-3-HT	Al & Na limited	40.1	0.85	0.01	21.1
SIR22-4-HT	Al & Na limited	39.3	0.15	0.01	17.3
SIR22-5-HT	Al & Na limited	37.6	0.39	<0.0089	21.6
SIR22-6-HT	Al limited	1.6	0.09	0.03	1.1
SIR22-8-HT	Al limited	9.5	0.30	0.09	6.2
SIR22-9-HT	Al limited	6.0	0.05	0.03	5.1
SIR22-10-HT	Al limited	8.5	0.05	0.02	6.7
SIR22-11-HT	Al limited	13.0	0.23	0.03	8.6
SIR22-12-HT	Al limited	13.0	0.06	0.01	8.6

3.4 Statistical Analysis

Statistical software (JMP Pro 16.2.0)[10] was used to evaluate the SIR predictions based on the combined database of glass compositions described in Section 2.4 and the glasses fabricated in this study. To predict the durability of the glass, the SIR model applies non-bridging oxygen (NBO) estimates to quantify the integrity of the residual glass network structure, after theoretical nepheline precipitation. The SIR model then uses a series of defined parameters to make an explicit pass/fail prediction of the durability of the glass composition. A NL_B of <7.19 g/m^2 (equivalent to NC_B of <14.3 g/L), determined using Method A of ASTM C1285, is used to determine a durable (pass) glass for the SIR model. Any glass with a NL_B >7.19 g/m^2 as measured by the PCT is designated non-durable (fail).

The SIR parameter criteria were developed to maintain (a) a glass viscosity sufficiently to facilitate pouring, (b) Al_2O_3 as the limiting constituent in nepheline crystallization (i.e., ensure the residual glass will contain alkali and SiO_2), (c) boron as low as possible to maximize waste loading (since boron is not a primary component of the waste stream, its addition can only come from glass- forming chemicals), and (d) the residual glass has sufficient SiO_2 to maintain the structure and chemical durability post-crystallization. One of the challenges to increasing the accuracy of the SIR model is reducing the number of false negative predictions. While false negatives are acceptable from a glass production perspective, the greatest improvement to the accuracy of the model would be in reducing the number of non-durable predictions for durable glasses.[5]

The focus of these statistical analyses were not to develop or optimize the SIR model. Instead, the intention was to use statistical tools available to explore correlations and trends in the data to identify the most important parameters of the SIR model. One of the primary tools used was the JMP Pro 16.2.0 partition platform. That tool can be applied to create a diagnostic heuristic for continuous or categorical predictors. In the former, the partition tool identifies a threshold value (pass/fail) within the sample, or in latter case the sample is divided tiered groups. For this work, the partition tool was used to generate a hierarchy of splits (partitions), similar to a decision tree, based on the SIR model input parameters. Because the partition tool can handle large problems easily, this method was used as a screening tool to identify global predictors from the more than 70 terms that affect the SIR prediction, e. g. component oxides, NBO, (K,Na,Li)$AlSiO_4$,

[4] The sample data set used in this evaluation has ~86% positive values, which may represent an imbalanced data set.

$(Li,Na)_2SiO_3$, the glass residual, alkali-silicate ratio, etc. An example of the output from such an analysis is shown in Figure 3-4, in which four parameters, $(Li,Na)Si_2O_3$, B_2O_3, Al_2O_3, and NBO, are identified as critical partition levels. The blue colors represent a pass result and fail results are shown in red color. The count representation listed below is greater than 378 (total results in sample) because a weighting was applied to the data. This result can be interpreted to mean that the first split, $(Li,Na)Si_2O_3$, is the most accurate predictor of the pass/fail result. Sequential splits on B_2O_3, Al_2O_3, and NBO represent secondary, tertiary, etc. predictors of the pass/fail result in order of rank. Partition diagrams can include more or fewer splits. In this work, generally 4 or fewer splits were needed to achieve a satisfactory result without diminishing returns.

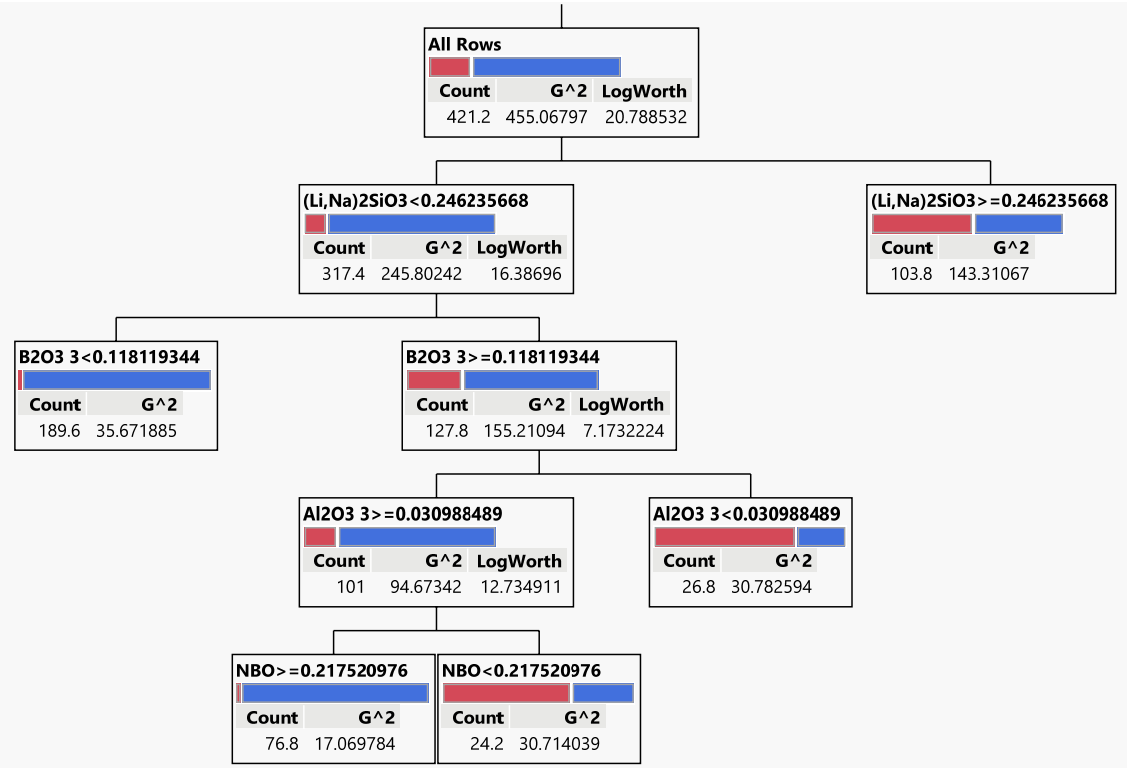


Figure 3-4. Statistical partition table for the 378 HLW glass compositions.

A statistical model was also developed to generate a contingency table, or table of predictions. It is understood, and re-iterated, that this analysis, although developed from the SIR methodology, is exploratory in nature, and the generated statistical model may not have the same physical meaning as the SIR defined in the literature.[5, 8, 11] Further analysis and work is ongoing to understand the statistical model results. Nevertheless, the potential for a durability model with improved accuracy over current models can be demonstrated by comparing the nepheline discriminator (ND) model to the SIR statistical model (SIR-SM) developed under the SIR methodology. Output from those models are shown in Table 3-4 and Table 3-5. Both of these models exhibit similar total predictions (123 fails for the ND compared to 114 fails for the SIR-SM, and 255 passes for the ND compared to 264 passes for the SIR-SM), however the distribution of the predictions is quite different. Whereas the ND model predicts 24 fails and passes 30 fails, the SIR-SM model predicts 51 fails and only passes 3 fails. Similarly, the ND model predicts 225 passes and fails 99 passes, whereas the SIR-SM model predicts 261 passes and fails 63 passes. The accuracy of the SIR-SM model presented is significantly higher than the ND model and, importantly, the number of false predictions of a passing durability are less than 1% for the SIR-SM compared to ~8% for the ND model. The overall accuracy of the SIR-SM model was 82.6 %. Work is ongoing to further interpret the statistical output, computationally refine the SIR model parameters, and quantify the sensitivity around the NL_B criteria.

Table 3-4. Prediction Results for the Nepheline Discriminator (ND) Model

		Predicted Result		
	Count ***Total (%)***	**Fail**	**Pass**	**Total**
Result	**Fail**	24 *6.3*	30 *7.9*	54 *14.3*
	Pass	99 *26.2*	225 *59.6*	324 *85.7*
	Total	123 *32.5*	255 *67.5*	378

Table 3-5. Prediction Results for the Structural Integrity of the Residual (SIR) Statistical Model

		Predicted Result		
	Count ***Total (%)***	**Fail**	**Pass**	**Total**
Result	**Fail**	51 *13.5*	3 *0.8*	54 *14.3*
	Pass	63 *16.7*	261 *69.1*	324 *85.7*
	Total	114 *30.2*	264 *69.8*	378

4.0 Conclusions and Recommendations

A set of 11 glasses specifically formulated for the Hanford HLW and to challenge the SIR model were fabricated, heat treated, and measured for chemical durability following the PCT Method A. As expected, all the glasses exhibited some crystallization upon heat treatment, including nepheline and spinel phases, which are integral to predicting durability response with the SIR. Nine of the glasses exhibited a PCT response $NL_B > 7.19$ g/m^2, which is valuable to include in the literature in order to decrease the potential for sample bias in the databases of glass durability. The PCT response and chemical composition information was added to obtain a database of 378 HLW glasses for which normalized mass loss of B has been reported. Data regression and statistical tools were used to asses correlations and develop models from the data. A statistical model developed from the SIR methodology achieved an accuracy of 82.6% while maintaining a positive prediction of non-durable glasses at less than 1%.

The ability to accurately predict glass durability, regardless of nepheline crystallization, will allow for maximizing aluminum and alkali loading in glass while maintaining acceptable durability. This work demonstrates the potential to achieve model predictions that can significantly open the composition region accessible to the WTP while maintaining high waste loadings in glass. Future work to expand the diversity of available glass compositions from which to perform statistical analyses on is recommended. However, additional validation data and targeted experiments to ensure physical property models are consistent with the SIR glass model results should be pursued in parallel. Processability and durability have yet to be correlated in a meaningful way, but will likely prove invaluable to refining some of the SIR model criteria, and should also be considered.

5.0 References

1. Certa, P.J., et al. River Protection Project System Plan; *US Department of Energy Report*, *ORP-11242, Revision 6*; US Department of Energy-Office of River Protection: Richland, WA, 2011.
2. Standard Test Methods for Determining Chemical Durability of Nuclear, Hazardous, and Mixed Waste Glasses and Multiphase Glass Ceramics: The Product Consistency Test (PCT); *ASTM C-1285-14*, 2014.
3. Jantzen, C.M. and D.F. Bickford. *Leaching of Devitrified Glass Containing Simulated SRP Nuclear Waste*. in *Materials Research Society*. Pittsburgh, PA.
4. Kim, D.S., D.K. Peeler, and P. Hrma, *Effect of Crystallization on the Chemical Durability of Simulated Nuclear Waste Glasses*, in *Ceramic Transactions*. 1995, The American Ceramic Society: Westerville, OH. p. 177-185.
5. Amoroso, J.W. Nepheline Crystallization Studies - Progress Towards Durability Prediction in High Level Waste Glasses; *US Department of Energy Report*, *SRNL-STI-2021-00489*; Savannah River National Laboratory: Aiken SC, 2021.
6. Kim, D.S., et al. Formulation and Characterization of Waste Glasses with Varying Processing Temperature; *U.S. Department of Energy Report*, *PNNL-20774*; Pacific Northwest National Laboratory: Richland, WA 2011.
7. Goel, A., et al., *Challenges with vitrification of Hanford High-Level Waste (HLW) to borosilicate glass – An overview.* Journal of Non-Crystalline Solids, 2019. **4**.
8. McClane, D.L., et al., *Derivation of the Structural Integrity of Residual (SIR) Glass Model for the Enhancement of Waste Loading.* Journal of the American Ceramic Society, 2021. **104**: p. 3235-3246.
9. McCloy, J.S. and J.D. Vienna Glass Composition Constraint Recommendations for Use in Life-Cycle Mission Modeling; *US Department of Energy Report*, Pacific Northwest National Laboratory: Richland, Washington, 2010.
10. *JMP Pro 16.2.0, SAS Institute Inc.*
11. McClane, D.L., et al., *Nepheline Crystallization and the Residual Glass Composition: Understanding Waste Glass Durability.* International Journal of Applied Glass Science, 2020(00): p. 1-11.