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TIME-TEMPERATURE-TRANSFORMATION (TTT) DIAGRAMS FOR FUTURE WASTE COMPOSITIONS

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EXECUTIVE SUMMARY

As a part of the Waste Acceptance Product Specifications (WAPS) for Vitrified High-Level Waste Forms defined by the Department of Energy – Office of Environmental Management, the waste form stability must be determined for each of the projected high-level waste (HLW) types at the Savannah River Site (SRS). Specifically, WAPS 1.4.1 requires the glass transition temperature (T_g) to be defined and time-temperature-transformation (TTT) diagrams to be developed. The T_g of a glass is an indicator of the approximate temperature where the supercooled liquid converts to a solid on cooling or conversely, where the solid begins to behave as a viscoelastic solid on heating. A TTT diagram identifies the crystalline phases that can form as a function of time and temperature for a given waste type or more specifically, the borosilicate glass waste form. In order to assess durability, the Product Consistency Test (PCT) was used and the durability results compared to the Environmental Assessment (EA) glass.

The measurement of glass transition temperature and the development of TTT diagrams have already been performed for the seven Defense Waste Processing Facility (DWPF) projected compositions as defined in the Waste Form Compliance Plan (WCP) and in SRNL-STI-2009-00025. Additional phase transformation information exists for other projected compositions, but overall these compositions did not cover composition regions estimated for future waste processing.

To develop TTT diagrams for future waste types, the Savannah River National Laboratory (SRNL) fabricated two caches of glass from reagent grade oxides to simulate glass compositions which would be likely processed with and without Al dissolution. These were used for glass transition temperature measurement and TTT diagram development. The glass transition temperatures of both glasses were measured using differential scanning calorimetry (DSC) and were recorded to be 448 °C and 452 °C.

Using the previous TTT diagrams as guidance, subsamples of each glass were isothermally heat treated for 1 to 768 hours at temperatures between 500 °C to 1000 °C. Each of the heat treated samples, along with quenched and centerline canister cooled (CCC) treated samples, were analyzed using X-ray diffraction (XRD) and the PCT. Maximum crystallization was detected in samples treated at 700 °C and 600 °C for more than 96 hours in both glasses. Phases crystallized were similar in composition if not the same as those found in the previous TTT studies. Six different crystalline phases were detected, including nepheline, aegirine, lithium silicate, trevorite (spinel based), krinovite, and calcium magnesium iron silicon oxide. Overall, phases were spinel (iron) based, lithium metasilicate, sodium aluminosilicate or alkali transition metal silicate in composition. No new crystalline families were detected. Durability, as measured by the PCT, decreased when lithium silicate or nepheline crystals were present. The conclusions of this study were consistent with previous studies.

In order to continue to meet the requirements of the WCP, a simplified strategy is suggested for the generation of future TTT diagrams. Only extremely significant changes in composition resulting from processing strategy changes would require generating more TTT diagrams.

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LIST OF ABBREVIATIONS

ARM	Approved Reference Material
BCH	Batch 1 Reference Glass
CCC	Centerline canister cooling
DOE	Department of Energy
DSC	Differential Scanning Calorimetry
DWPF	Defense Waste Processing Facility
EA	Environmental Assessment
HLW	High-Level Waste
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectroscopy
LM	Lithium Metaborate
MAR	Measurement Acceptability Region
PCT	Product Consistency Test
PF	Peroxide Fusion
PSAL	Process Science Analytical Laboratory
SB	Sludge Batch
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
T_g	Glass Transition Temperature
T_L	Liquidus Temperature
TTQAP	Task Technical & Quality Assurance Plan
TTR	Technical Task Request
TTT	Time-Temperature-Transformation
WAPS	Waste Acceptance Product Specifications
WCP	Waste Form Compliance Plan
WL	Waste Loading
WQR	Waste Form Qualification Report
XRD	X-ray Diffraction

1.0 Introduction

Glasses, which are amorphous by definition, can transform into more ordered crystalline phases at temperatures below the liquidus (T_L) and above the glass transition temperature (T_g). By annealing a glass within this glass transformation region, the potential for crystal nucleation and growth is high. In nuclear waste glasses, this transformation region is relatively large, encompassing approximately 400 °C to 1050 °C. The crystallization kinetics of nuclear waste glasses can be determined by creating time-temperature-transformation (TTT) diagrams. This provides information regarding the processing conditions necessary to avoid significant devitrification, which can alter the long-term durability of the waste glass. Generating these curves is also important for nuclear waste glasses as they provide the effects of different accident scenarios (low temperature melter idling, transportation fires).

The Defense Waste Processing Facility (DWPF) is currently immobilizing high-level liquid waste (HLW) by combining sludge and streams from salt processing with frit (a prefabricated glass), melting the slurry mix of waste streams and frit and pouring the molten glass into stainless steel canisters to create the final waste form at the Savannah River Site (SRS). Eventually, these canistered waste forms will be sent to the Civilian Radioactive Waste Management System (repository) for final disposal. In order to assure acceptance by the repository, the Department of Energy (DOE) has defined requirements which DWPF canistered waste forms must meet. These requirements are the Waste Acceptance Product Specifications (WAPS).[1] WAPS 1.4.1 requires the measurement of T_g and the development of TTT diagrams for the projected waste types to be processed through the facility. The TTT diagrams identify the duration of exposure at any temperature that causes significant changes in either the phase structure or the phase compositions. Additionally, the effects of changes of phase composition on the results of the Product Consistency Test (PCT) are determined. Prior to radioactive operations, glass transition temperatures and TTT diagrams were completed for seven projected compositions (known as the Waste Form Compliance Plan (WCP) glasses) originally anticipated to bound the range of waste types anticipated for the DWPF.[2] TTT diagrams were developed for the WCP glass compositions in addition to previously developed diagrams for specific frit and waste compositions. Since that time, higher waste loadings, less sludge washing, and different tank blending scenarios and salt processing strategies have been implemented. In addition, frit development strategies have significantly changed, resulting in higher alkali glass systems being processed to improve melt rate, waste loading, and waste throughput. As a result of these changes, a TTT diagram and the glass transition temperature were measured for one specific waste type previously processed at DWPF. A TTT diagram for Sludge Batch 3 (SB3), Frit 418 at a 38 wt % waste loading (WL) was created and the waste form was characterized for the required properties in the report by Billings and Edwards.[3] Results of that particular study suggested even with significant changes in the glass composition, the type of crystalline phases precipitated were part of the same compositional families as the seven WCP glasses. Properties of those heat treated glasses, such as the T_g and PCT release, were also similar with respect to the WCP glasses.

Future waste types and glass compositions are anticipated to be different than the previously evaluated SB3 – Frit 418 composition and WCP compositions. To identify the potential phase compositions for these future processing regions, a strategy has been developed that would require completing more TTT diagrams for two averaged, future, predicted waste types. This task was requested by DWPF under the Technical Task Request HLW-DWPF-TTR-2009-0006 and outlined by SRNL in the Task Technical & Quality Assurance Plan (TTQAP) SRNL-RP-2009-00284.[4,5] Since the results of the Frit 418-SB3 study showed little change in the types of crystalline phases formed after heat treatment as compared to the TTT diagrams for the WCP

glasses, it is unlikely that extreme differences will occur in the TTT diagram for future waste forms as long as the properties remain within the DWPF operating bounds. By creating TTT diagrams for the resulting glass compositions of future averaged waste types, insight will be provided to the crystallization regions possible for those averages. It will also supply experimental data to establish any possible difference in the phases formed or different temperatures at which crystallization will occur. If the results are not significantly different from the WCP glasses, the SB3-Frit 418 composition, or other analyzed glass compositions, it would negate the need to create TTT diagrams for each sludge batch or glass composition produced at the DWPF.

As discussed in the report, "Initial MAR Assessments to Access the Impact of Al-Dissolution on DWPF Operating Windows",[6] the majority of future waste compositions (as defined by Revision 13 of the High Level Waste System's Plan) could be grouped into two flowsheet scenarios, with and without Al-dissolution. Compositions Cluster 2 (without Al-dissolution) and Cluster 4 (with Al-dissolution) represent these average waste projections. Measurement Acceptability Region (MAR) assessments were completed on the two clusters that identified candidate frits that could be used to process these future waste types over waste loadings of interest. Based on that study, two specific glass forming systems were identified to support the development of TTT diagrams for future sludge batches. The specific glass forming systems selected were:

Cluster 2 combined with Frit 510 at a 34 wt % WL
Cluster 4 combined with Frit 418 at a 38 wt % WL

The compositions of these waste forms as evaluated in the report by Newell et al. are found in Table 1-1.

Table 1-1. Representative, Renormalized (without ThO_2 and U_3O_8) Cluster 2 and Cluster 4 Glass Compositions[6]

Oxide (wt %)	Cluster 2-Frit 510	Cluster 4-Frit 418
Al_2O_3	8.577	6.034
B_2O_3	9.240	4.960
BaO	0.078	0.104
CaO	0.976	1.345
Ce_2O_3	0.206	0.241
Cr_2O_3	0.099	0.141
CuO	0.030	0.043
Fe_2O_3	11.441	14.521
K_2O	0.068	0.094
La_2O_3	0.074	0.090
Li_2O	5.280	4.960
MgO	0.153	0.192
MnO	1.484	2.135
Na_2O	12.801	13.717
NiO	0.430	0.527
PbO	0.089	0.105
SiO_2	47.444	49.222
SO_4^{2-}	0.074	0.104
TiO_2	1.223	1.144
ZnO	0.046	0.067
ZrO_2	0.188	0.254
Sum	100.000	100.000

2.0 Experimental Procedure

2.1 Glass Formulation

Two single stocks of simulated Cluster 2 – Frit 510 (C2-510) glass and Cluster 4 – Frit 418 (C4-418) glass were used to support the chemical and physical characterization associated with developing new TTT diagrams for the future compositional regions. The current study was based on non-radioactive glasses in order to be consistent with the earlier TTT studies.[2,3] More specifically, the sludge composition was renormalized without U_3O_8 and ThO_2. As mentioned earlier, glass compositions were taken from the report, "Initial MAR Assessments to Access the Impact of Al-Dissolution on DWPF Operating Windows".[6] RuO_2 was also added to the glass compositions at 0.10 wt % because it is present as a minor component in the sludge and represents an average of what is projected to be present in future waste compositions. It was included in this testing because noble metals such as RuO_2 are not fully soluble in the glass and will often serve as nucleation sites for crystallization.[7] The final targeted compositions are listed in Table 2-1.

Table 2-1. Targeted Glass Compositions for TTT Study

Name	Cluster 2-Frit 510	Cluster 4-Frit 418
Waste Loading	34 wt %	38 wt %
Oxide (wt %)		
Al_2O_3	8.55	6.02
B_2O_3	9.24	4.96
BaO	0.08	0.10
CaO	0.97	1.34
Ce_2O_3	0.21	0.24
Cr_2O_3	0.10	0.14
CuO	0.03	0.04
Fe_2O_3	11.41	14.48
K_2O	0.07	0.09
La_2O_3	0.07	0.09
Li_2O	5.28	4.96
MgO	0.15	0.19
MnO	1.48	2.13
Na_2O	12.78	13.69
NiO	0.43	0.53
PbO	0.09	0.11
RuO_2	0.10	0.10
SiO_2	47.44	49.22
SO_4^{2-}	0.07	0.10
TiO_2	1.22	1.14
ZnO	0.05	0.07
ZrO_2	0.19	0.25
Sum	100.00	100.00

2.2 Glass Fabrication

It should be noted that kilogram quantities of each of the glasses were required to support this task. This required multiple individual batches targeting the same composition to be melted and then combined into one large cache of glass. Glass was batched and melted following the standard SRNL procedures.[8,9] The glasses were prepared from the proper proportions of reagent-grade oxides, carbonates, boric acid, and salts in twelve 300 g batches (numbered 1-12). The batch sheets and other experimental notes can be found in the laboratory notebooks WSRC-NB-2006-00074 and SRNL-NB-2009-00121.[10,11] The raw materials were thoroughly mixed and placed into 95% platinum/5% gold, 600 mL crucibles. The crucibles were placed into an electrically heated, high-temperature furnace at the target melt temperature of 1150 °C. After an isothermal hold at 1150 °C for 1.0 hour, the crucibles were removed from the furnace and poured onto a clean, stainless steel plate and allowed to air cool (quench). The glasses were then crushed and pairs of the twelve 300 g batches were combined into six 600 g batches (named C2-510 A-F and C4-418 A-F) and re-melted at 1150 °C for 1.0 h of homogenization following the same procedure as above.

2.3 Chemical Analysis

To confirm that the as-fabricated glasses corresponded to the defined target composition, representative samples of each of the 600 g glass batches were submitted to the SRNL Process Science Analytical Laboratory (PSAL) for chemical analysis under the auspices of the analytical plan SRNL-L5200-2009-00019.[12] The cations were analyzed by means of two dissolution techniques, sodium peroxide fusion (PF) and lithium-metaborate fusion (LM). The samples prepared by LM were used to measure aluminum (Al), barium (Ba), calcium (Ca), cerium (Ce), chromium (Cr), copper (Cu), iron (Fe), potassium (K), lanthanum (La), magnesium (Mg), manganese (Mn), sodium, (Na), nickel (Ni), lead (Pb), ruthenium (Ru), sulfur (S), silicon (Si), titanium (Ti), zinc (Zn), and zirconium (Zr) concentrations. Samples prepared by PF were used to measure boron (B) and lithium (Li) concentrations. Each glass was prepared in duplicate for each cation dissolution technique. All of the prepared samples were analyzed by Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) with the instrumentation being re-calibrated between the duplicate analyses. Glass standards were also intermittently measured to assess the performance of the ICP-AES instrument over the course of the analyses. Specifically, several samples of WCP Batch 1 (BCH)[13] were included in the sample analysis.

Results of the chemical analyses were reviewed before initiation of any measurements or heat treatments.[14] The objective of the review was to facilitate a decision on the use of all or only a subset of the available batches of glass (A-F) for each glass composition. The individual batches determined to be compositionally consistent could then be combined in order to create a cache of compositionally consistent glass that could be used to support the glass transition measurement and TTT study. The result of the statistical review of the measured compositions found no major issues with the measured compositions of the six batches associated with each of the two targeted compositions. There were some minor issues, however, with the CaO measurements for one of the C2-510 system batches, namely C2-510-F; and as a result, this batch, C2-510-F, was excluded from the cache of glass for the C2-510 TTT diagram generation. Eliminating batch F from the cache ensured that a compositionally consistent glass would be used to support programmatic objectives. In addition, based upon the results of this review, it was recommended that all six of the C4-418 batches were to be used to prepare the cache of glass for the C4-418 system.[14] Batches C4-418 A-F were then combined and mixed thoroughly in one container where samples could subsequently be drawn for heat treatments and the same was done for C2-510 A-E.

2.4 Glass Transition Temperature Determination

A Netzsch 409 PC Luxx differential scanning calorimeter (DSC) was used to measure the glass transition temperature (T_g) of each of the glasses. The ASTM procedure E 1356 was also used as a guide for determining the T_g.[15] Small chips of glass from each cache of TTT glass were used for analysis. A heating rate of 20 K/min was used to heat three separate samples from room temperature to 1000 °C in a platinum pan. The value of T_g reported in this document was determined by the slope intercept method at the onset of the endothermic inflection and is the average of three separate tests.

2.5 Heat Treatments

In order to develop TTT diagrams for each glass composition, glasses were heat treated as follows. Approximately 30 g of glass from the chemically verified cache were placed in open platinum alloy crucibles and re-melted at 1150 °C for 1 hour. Durations were kept at one hour holds at melting temperature in order to minimize any volatilization of the chemically verified glass, yet still maintain a homogenized melt. After an hour, the crucibles were removed from the

furnace and placed into separate furnaces preheated to the desired isothermal hold temperature. Once the desired duration of heat treatment was reached, crucibles were removed from the furnace and immersed in a shallow water bath to quickly cool or "quench" the glass. This process only exposed the exterior of the crucible to the water (i.e., water did not contact the glass). Each glass sample was heat treated at a unique time and temperature in order to cover the anticipated crystallization region. Sample names, temperatures and durations of heat treatments are listed in Table 2-2 and Table 2-3. An independent thermocouple and temperature recorder were used during heat treatments to ensure that the temperature remained relatively constant during the treatments. A sample of each glass was also heat treated according to the centerline canister cooling (CCC) temperature profile in order to simulate DWPF pouring conditions.[16] The CCC glass, along with samples of the original "quenched" glasses (non-heat treated glass from the glass cache), were submitted along with all other heat treated samples for further analysis.

Table 2-2. Sample Identification, Treatment Times and Temperatures for C2-510 Glasses

Sample Name	Glass Type	Temp. (°C)	Time (hours)	Sample Name	Glass Type	Temp. (°C)	Time (hours)
C2-1000-1	C2-510	1000	1	C2-800-192	C2-510	800	192
C2-1000-3	C2-510	1000	3	C2-800-384	C2-510	800	384
C2-1000-6	C2-510	1000	6	C2-800-768	C2-510	800	768
C2-1000-12	C2-510	1000	12	C2-700-6	C2-510	700	6
C2-1000-24	C2-510	1000	24	C2-700-12	C2-510	700	12
C2-1000-48	C2-510	1000	48	C2-700-24	C2-510	700	24
C2-1000-96	C2-510	1000	96	C2-700-48	C2-510	700	48
C2-1000-192	C2-510	1000	192	C2-700-96	C2-510	700	96
C2-1000-384	C2-510	1000	384	C2-700-192	C2-510	700	192
C2-1000-768	C2-510	1000	768	C2-700-384	C2-510	700	384
C2-900-1	C2-510	900	1	C2-700-768	C2-510	700	768
C2-900-3	C2-510	900	3	C2-600-12	C2-510	600	12
C2-900-6	C2-510	900	6	C2-600-24	C2-510	600	24
C2-900-12	C2-510	900	12	C2-600-48	C2-510	600	48
C2-900-24	C2-510	900	24	C2-600-96	C2-510	600	96
C2-900-48	C2-510	900	48	C2-600-192	C2-510	600	192
C2-900-96	C2-510	900	96	C2-600-384	C2-510	600	384
C2-900-192	C2-510	900	192	C2-600-768	C2-510	600	768
C2-900-384	C2-510	900	384	C2-500-24	C2-510	500	24
C2-900-768	C2-510	900	768	C2-500-48	C2-510	500	48
C2-800-3	C2-510	800	3	C2-500-96	C2-510	500	96
C2-800-6	C2-510	800	6	C2-500-192	C2-510	500	192
C2-800-12	C2-510	800	12	C2-500-384	C2-510	500	384
C2-800-24	C2-510	800	24	C2-500-768	C2-510	500	768
C2-800-48	C2-510	800	48	C2-quenched	C2-510	quenched	
C2-800-96	C2-510	800	96	C2-CCC	C2-510	CCC	

Table 2-3. Sample Identification, Treatment Times and Temperatures for C4-418 Glasses

Sample Name	Glass Type	Temp. (°C)	Time (hours)	Sample Name	Glass Type	Temp. (°C)	Time (hours)
C4-1000-1	C4-418	1000	1	C4-800-192	C4-418	800	192
C4-1000-3	C4-418	1000	3	C4-800-384	C4-418	800	384
C4-1000-6	C4-418	1000	6	C4-800-768	C4-418	800	768
C4-1000-12	C4-418	1000	12	C4-700-6	C4-418	700	6
C4-1000-24	C4-418	1000	24	C4-700-12	C4-418	700	12
C4-1000-48	C4-418	1000	48	C4-700-24	C4-418	700	24
C4-1000-96	C4-418	1000	96	C4-700-48	C4-418	700	48
C4-1000-192	C4-418	1000	192	C4-700-96	C4-418	700	96
C4-1000-384	C4-418	1000	384	C4-700-192	C4-418	700	192
C4-1000-840[a]	C4-418	1000	840	C4-700-384	C4-418	700	384
C4-900-1	C4-418	900	1	C4-700-768	C4-418	700	768
C4-900-3	C4-418	900	3	C4-600-12	C4-418	600	12
C4-900-6	C4-418	900	6	C4-600-24	C4-418	600	24
C4-900-12	C4-418	900	12	C4-600-48	C4-418	600	48
C4-900-24	C4-418	900	24	C4-600-96	C4-418	600	96
C4-900-48	C4-418	900	48	C4-600-192	C4-418	600	192
C4-900-96	C4-418	900	96	C4-600-384	C4-418	600	384
C4-900-192	C4-418	900	192	C4-600-768	C4-418	600	768
C4-900-384	C4-418	900	384	C4-500-24	C4-418	500	24
C4-900-840[a]	C4-418	900	840	C4-500-48	C4-418	500	48
C4-800-3	C4-418	800	3	C4-500-96	C4-418	500	96
C4-800-6	C4-418	800	6	C4-500-192	C4-418	500	192
C4-800-12	C4-418	800	12	C4-500-384	C4-418	500	384
C4-800-24	C4-418	800	24	C4-500-840[a]	C4-418	500	840
C4-800-48	C4-418	800	48	C4-quenched	C4-418	quenched	
C4-800-96	C4-418	800	96	C4-CCC	C4-418	CCC	

[a] These samples were left in furnace longer than targeted treatment time. The samples were exposed to temperature 840 hours instead of the planned 768 hours.

2.6 Phase Analysis

Glass samples were evaluated for crystallization using X-ray Diffraction (XRD). Depending on the type and extent of crystallization, the existence of crystalline phases in the glass can impact properties such as durability. The crystallization information may also provide insight into the potential liquidus temperature (T_L) of the glass since crystals should not be identified above the T_L. Samples were run under conditions providing a detection limit of approximately 0.5 vol %. That is, if crystals (or undissolved solids) were present at 0.5 vol % or greater, the diffractometer would not only be capable of detecting the crystals but would also allow a qualitative determination of the type of crystal(s) present. Jade 9.0© software was used for phase analysis.

For those samples which exhibited a crystalline phase other than Trevorite (or other spinel based phase) or RuO_2, quantitative XRD measurements were also conducted. A whole pattern Rietveld least squared refinement was conducted on samples using 10 wt % high purity alumina as an internal intensity standard. The Archimedes method was used to measure the density of the

original glass[17] and standard densities of the crystalline phases were referenced. Once both densities were determined, total volume percent crystallinity was calculated.

2.7 Product Consistency Test

The ASTM procedure C1285, PCT Method-A,[18] was performed in triplicate on each isothermally heat treated, quenched and CCC glass to assess chemical durability. Also included in the experimental test matrix was the Environmental Assessment (EA) benchmark glass,[19] the Approved Reference Material (ARM) glass and blanks from the sample cleaning batch. Samples were ground, washed and prepared following the standard procedure.[18] Approximately fifteen milliliters of Type I ASTM water were added to 1.5 g of glass in stainless steel vessels. The vessels were closed, sealed and placed into an oven at 90 ± 2 °C where the samples were maintained at temperature for 7 days ± 3.4 hours. Once cooled, the resulting solutions were sampled (filtered and acidified), then labeled and analyzed by PSAL under the auspices of an analytical plan.[20] The resulting solutions (leachates) were analyzed via ICP-AES for Si, B, Na, and Li release. Samples of a multi-element, standard solution were also included in the analytical plans as a check on the accuracy of the analytical instrumentation used for these measurements. Normalized release rates were calculated based measured compositions using the average of the common logarithms of the leachate concentrations.

3.0 Results and Discussion

3.1 Chemical Compositions

The targeted and measured composition of the final glass caches, which were used for heat treatments are found in Table 3-1. No significant discrepancies were found between the targeted and analyzed compositions. This indicates the batching was successful and any sample taken from the glass cache will be representative of the measured composition. For a more detailed description of the statistical analysis of the glass batches, see the referenced report by Edwards.[14]

Table 3-1. Target and Overall Measured Concentrations by Weight Percent Oxide for the Cache of C2-510 and C4-418 Glass[14]

Oxide	C2-510 (Cluster 2 with Frit 510)		C4-418 (Cluster 4 with Frit 418)	
	Target	Measured*	Target	Measured+
Al_2O_3	8.55	8.51	6.02	6.00
B_2O_3	9.24	9.17	4.96	4.84
BaO	0.08	0.07	0.10	0.10
CaO	0.97	1.01	1.34	1.32
Ce_2O_3	0.21	0.20	0.24	0.23
Cr_2O_3	0.10	0.10	0.14	0.13
CuO	0.03	0.04	0.04	0.05
Fe_2O_3	11.41	11.30	14.48	14.08
K_2O	0.07	0.07	0.09	0.10
La_2O_3	0.07	0.07	0.09	0.08
Li_2O	5.28	5.22	4.96	4.89
MgO	0.15	0.15	0.19	0.20
MnO	1.48	1.46	2.13	2.13
Na_2O	12.78	12.71	13.69	13.33
NiO	0.43	0.40	0.53	0.49
PbO	0.09	0.08	0.11	0.10
RuO_2	0.10	0.04	0.10	0.04
SiO_2	47.44	46.48	49.22	48.16
SO_4^{2-}	0.07	0.10	0.10	0.13
TiO_2	1.22	1.17	1.14	1.09
ZnO	0.05	0.05	0.07	0.06
ZrO_2	0.19	0.18	0.25	0.25
Sum	100.00	98.58	100.00	97.79

* The measured composition is an average of the measured compositions of batches A-E
\+ The measured composition is an average of the measured compositions of batches A-F

3.2 Glass Transition Temperatures

The glass transition onset temperature was measured using DSC. The onset of T_g for C2-510 glass was determined to occur at 452 ±0.2 °C. The onset of T_g for the C4-418 glass was determined to occur at 448 ±1 °C. The T_g is an indicator of the approximate temperature where the supercooled liquid converts to a solid on cooling or conversely, where the solid begins to behave as a viscoelastic solid on heating. This is extremely important because crystallization cannot occur below the onset of T_g. The T_g of the current glasses are also similar to the measured glass transition ranges for the seven WCP glasses and the SB3-Frit 418 glass. The glass transition range for the WCP glasses were between 418 °C and 460 °C and the SB3-Frit 418 glass had a T_g of 443 °C .[3,21] Measured glass transition temperatures of 448 °C and 452 °C also satisfies the requirement for glass stability as stated in the WCP and is above the lower limit of 400 °C.[22]

3.3 Phase Analysis (XRD Qualitative and Quantitative)

XRD was completed on every heat treated sample as well as quenched and CCC heat treated samples. Table 3-2 lists the results of the XRD analysis on the C2-510 glass samples and Table 3-3 lists the results of the XRD results of the C4-418 glass samples. Extensively more crystallization was observed in these glass compositions as compared to the crystallization observed in the SB3-Frit 418 TTT study.[3] Ruthenium oxide (RuO_2) was observed in almost every sample. This is due to the higher additions of RuO_2, which is not soluble into a borosilicate glass composition.[7] Because of the elevated amount of RuO_2 more nucleation sites are bound to be present which will cause more crystallization sites. Often RuO_2 will initiate crystallization of a spinel type crystal such as trevorite. This was observed extensively in both glass compositions. Trevorite was formed in the CCC glasses and at times as short as one hour at higher temperatures (> 900°C). This is also consistent with what was observed in the WCP glasses.[2]

Other extensive crystallization occurred with more extended durations of heat treatment time (24 hours and longer) at temperatures between 500 °C and 700 °C. Phases that were detected in both glasses included phases which could potentially affect the durability of the residual glass such as nepheline ($NaAlSiO_4$) and lithium metasilicate (Li_2SiO_3). The time and temperature at which these durability affecting phases are forming in the current glass systems are consistent with the diagrams of the HM and Blend compositions covered by the WCP TTT study.[2] Sodium transition metal silicate-based phases such as aegirine ($NaFe^{3+}(SiO_3)_2$) (which is synonymous to acmite), and spinel structured phases such trevorite ($NiFe_2O_4$), magnetite ($Fe^{2+}Fe_2^{3+}O_4$), and hematite (Fe_2O_3) formed in both glasses, but are not expected to exhibit a significant decrease in durability for the remaining glass.

Glass C2-510 had a single new phase, which was not detected in previous TTT studies. This phase detected was calcium magnesium iron silicon oxide ($Ca_4(Mg_{4.9}Fe_{8.7}Si_{10.4})O_{40}$). Krinovite ($NaMg_2CrSi_3O_{10}$) was again observed in one specific time and temperature sample as it was in the SB3-Frit 418 TTT glass. It was observed at the temperature of 600 °C. These alkaline earth iron/chromium silicate phases were hard to identify due to the complex XRD pattern and overlapping peaks when phases such as nepheline, hematite and lithium silicate were present.

Table 3-2. Crystalline Phases of the Heat Treated Sample Detected With X-ray Diffraction for C2-510 Glass

Sample	Phases	Sample	Phases
C2-1000-1	RuO_2	C2-800-96	Trevorite, RuO_2
C2-1000-3	RuO_2	C2-800-192	Trevorite, RuO_2
C2-1000-6	RuO_2	C2-800-384	Trevorite, RuO_2
C2-1000-12	RuO_2	C2-800-768	Trevorite, RuO_2
C2-1000-24	RuO_2	C2-700-6	Trevorite
C2-1000-48	RuO_2	C2-700-12	Trevorite
C2-1000-96	RuO_2	C2-700-24	Trevorite
C2-1000-192	RuO_2	C2-700-48	Trevorite
C2-1000-384	RuO_2	C2-700-96	Aegirine, Trevorite
C2-1000-768	RuO_2	C2-700-192	Aegirine
C2-900-1	Trevorite, RuO_2	C2-700-384	Aegirine, Lithium Silicate
C2-900-3	Trevorite, RuO_2	C2-700-768	Aegirine, Lithium Silicate
C2-900-6	Trevorite, RuO_2	C2-600-12	Amorphous
C2-900-12	Trevorite, RuO_2	C2-600-24	Trevorite
C2-900-24	Trevorite, RuO_2	C2-600-48	RuO_2, Krinovite
C2-900-48	Trevorite, RuO_2	C2-600-96	Nepheline, Calcium Magnesium Iron Silicon Oxide, Hematite
C2-900-96	Trevorite, RuO_2	C2-600-192	Nepheline, Calcium Magnesium Iron Silicon Oxide, Hematite, Lithium Silicate
C2-900-192	Trevorite, RuO_2	C2-600-384	Nepheline, Calcium Magnesium Iron Silicon Oxide, Aegirine, Lithium Silicate
C2-900-384	Trevorite, RuO_2	C2-600-768	Nepheline, Calcium Magnesium Iron Silicon Oxide, Aegirine, Lithium Silicate
C2-900-768	Trevorite, RuO_2	C2-500-24	Amorphous
C2-800-3	Trevorite	C2-500-48	RuO_2
C2-800-6	Trevorite	C2-500-96	RuO_2
C2-800-12	Trevorite	C2-500-192	RuO_2
C2-800-24	Trevorite	C2-500-384	RuO_2
C2-800-48	Trevorite	C2-500-768	Nepheline
C2-quenched	RuO_2	C2-CCC	Trevorite

Table 3-3 Crystalline Phases of the Heat Treated Sample Detected With X-ray Diffraction for C4-418 Glass

Sample	Phases	Sample	Phases
C4-1000-1	Trevorite	C4-800-192	Trevorite/Magnetite
C4-1000-3	Trevorite	C4-800-384	Trevorite/Magnetite
C4-1000-6	Trevorite	C4-800-768	Trevorite/Magnetite
C4-1000-12	Amorphous	C4-700-6	Trevorite/Magnetite
C4-1000-24	Amorphous	C4-700-12	Trevorite/Magnetite
C4-1000-48	Amorphous	C4-700-24	Trevorite/Magnetite
C4-1000-96	RuO_2	C4-700-48	Trevorite/Magnetite
C4-1000-192	Amorphous	C4-700-96	Trevorite/Magnetite, Aegirine
C4-1000-384	Amorphous	C4-700-192	Aegirine, Lithium Silicate
C4-1000-840	Amorphous	C4-700-384	Aegirine, Lithium Silicate
C4-900-1	Trevorite	C4-700-768	Aegirine, Lithium Silicate
C4-900-3	Trevorite, RuO_2	C4-600-12	RuO_2
C4-900-6	Trevorite	C4-600-24	Aegirine
C4-900-12	Trevorite/Magnetite	C4-600-48	Aegirine, Nepheline, RuO_2
C4-900-24	Trevorite/Magnetite, RuO_2	C4-600-96	Aegirine, Nepheline, Lithium Silicate
C4-900-48	Trevorite/Magnetite, RuO_2	C4-600-192	Aegirine, Nepheline, Lithium Silicate
C4-900-96	Trevorite/Magnetite	C4-600-384	Aegirine, Nepheline, Lithium Silicate
C4-900-192	Trevorite/Magnetite	C4-600-768	Aegirine, Nepheline, Lithium Silicate
C4-900-384	Trevorite/Magnetite	C4-500-24	RuO_2
C4-900-840	Trevorite/Magnetite	C4-500-48	RuO_2
C4-800-3	Trevorite	C4-500-96	RuO_2
C4-800-6	Trevorite	C4-500-192	RuO_2
C4-800-12	Trevorite/Magnetite	C4-500-384	RuO_2
C4-800-24	Trevorite/Magnetite	C4-500-840	RuO_2
C4-800-48	Trevorite/Magnetite	C4-quenched	RuO_2
C4-800-96	Trevorite/Magnetite	C4-CCC	Trevorite

After evaluating the XRD data, TTT diagrams could be developed and are found in Figure 3-1 (for C2-510) and Figure 3-2 (for C4-418). Qualitative phase analysis results were used to determine the preferred regions for crystallization. All heat treated glass samples were plotted on a temperature (in degrees Celsius) versus log time (in hours) graph. Those samples which contained crystals are represented by a shape and color (see key). The phase identification of the CCC glass sample is shown in the upper left and the quenched glass sample is shown in the lower left of the figures for each glass. All samples that remained amorphous, as determined by XRD after the specified treatment temperature and duration are represented by an open circle. The location and arrangement of the crystalline phase data points are used to define the estimated location of the phase transformation region, which indicate the time and temperature where the phase transitions occur. This phase region is outlined by blue dashed lines. The profile of the CCC curve (blue solid lines) is also plotted on the TTT diagrams for reference.

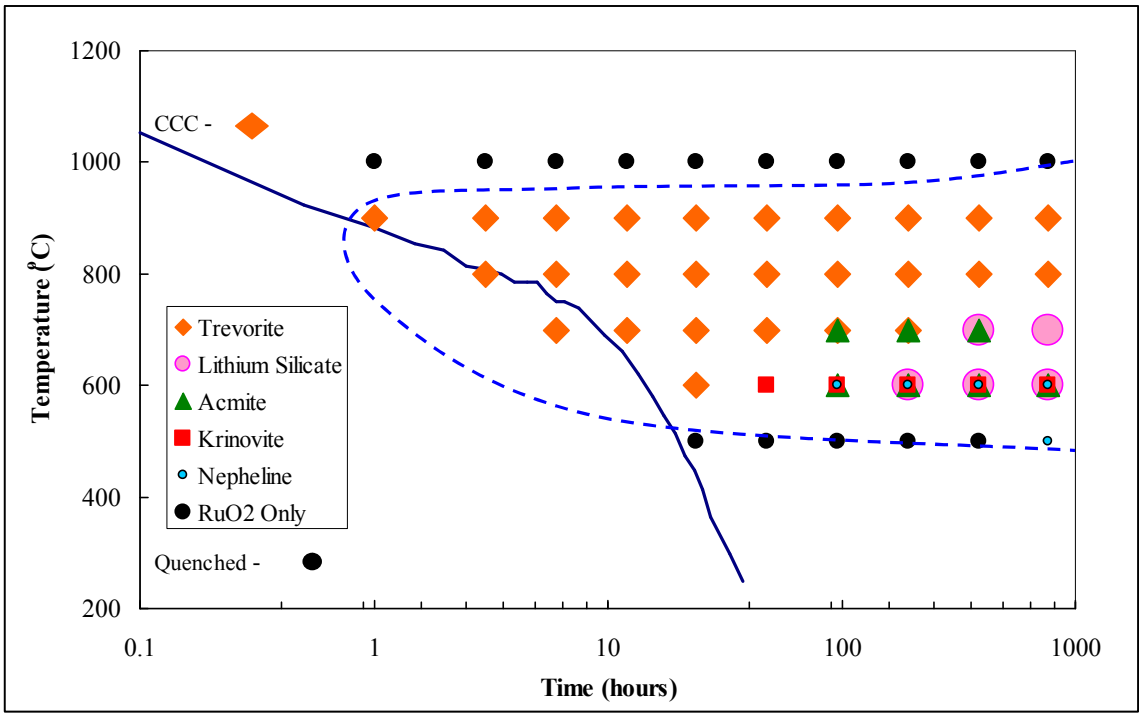

Figure 3-1. TTT diagram for Glass C2-510

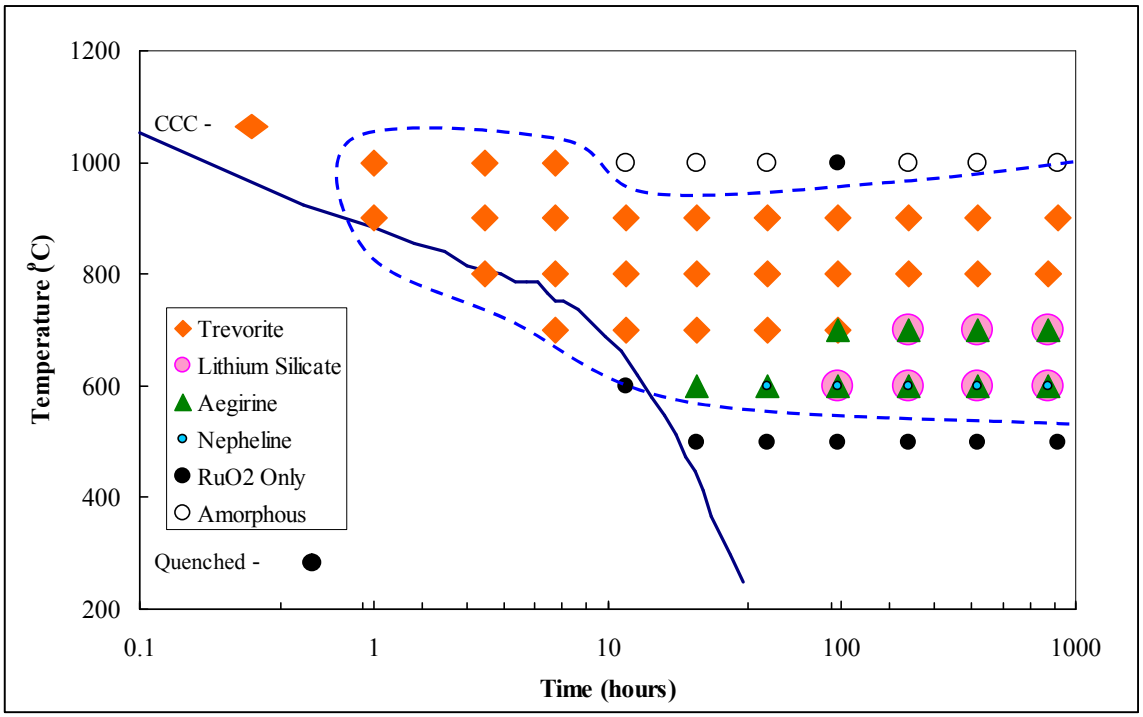

Figure 3-2. TTT diagram for Glass C4-418

Samples, which contained crystallization in the greatest region of interest (500-700 °C region), were submitted for quantitative XRD measurements of each of the phases. The results of the quantitative XRD analysis can be found in Table 3-4. In this table, weight percent crystallinity for each phase detected by XRD, as well as weight percent residual phase (the sum of amorphous and minor component fractions), is listed. The quantitative results show that the maximum amount of crystallization for the C2-510 glass (for those times and temperatures tested) occurred at 600 °C for 384 hours of treatment. After that duration of treatment, approximately 51.1 wt % of the sample was crystalline. The quantitative results show that the maximum amount of crystallization for the C4-418 glass (for those times and temperatures tested) occurred at 700 °C also at 384 hours of treatment. After that duration of treatment, approximately 32.3 wt % of the sample was crystalline. These results fall in the same temperature and heat treatment time region as the previous SB3-Frit 418 TTT study and the WCP glass study.[2,3] The greatest amount of crystallization for all DWPF TTT study glasses has occurred at temperatures between 600 °C and 700°C for durations of time ≥ 384 hours.

Table 3-4. Quantitative XRD Results for Selected Glasses

Sample	Phases	Wt % Phase	Sample	Phases	Wt % Phase
C2-600-96	Nepheline	6.4	C4-600-24	Aegirine	1.2
	Calcium Magnesium Iron Silicon Oxide	10.9		Others + Amorphous	98.8
	Hematite	1.4	C4-600-48	Aegirine	1.6
	Others + Amorphous	81.3		Nepheline	1.5
C2-600-192	Nepheline	12.8		Others + Amorphous	96.9
	Calcium Magnesium Iron Silicon Oxide	13.4	C4-600-96	Aegirine	9.2
	Hematite	3.6		Lithium Silicate	5.7
	Lithium Silicate	3.6		Nepheline	5.0
	Others + Amorphous	66.6		Others + Amorphous	80.1
C2-600-384	Nepheline	23.5	C4-600-192	Aegirine	11.8
	Calcium Magnesium Iron Silicon Oxide	18.2		Lithium Silicate	7.5
	Lithium Silicate	6.4		Nepheline	7.2
	Aegirine	3.0		Others + Amorphous	73.6
	Others + Amorphous	48.9	C4-600-384	Aegirine	9.9
C2-600-768	Nepheline	18.9		Lithium Silicate	6.7
	Calcium Magnesium Iron Silicon Oxide	11.8		Nepheline	6.7
	Lithium Silicate	7.3		Others + Amorphous	76.7
	Aegirine	2.6	C4-600-840	Aegirine	14.3
	Others + Amorphous	59.4		Lithium Silicate	9.5
C2-500-768	Nepheline	2.2		Nepheline	7.1
	RuO_2	0.1		Others + Amorphous	69.1
	Others + Amorphous	97.7	C4-700-96	Aegirine	1.5
C2-700-96	Aegirine	2.7		Trevorite	0.7
	Others + Amorphous	97.3		Others + Amorphous	97.8
C2-700-192	Aegirine	6.4	C4-700-192	Aegirine	12.7
	Lithium Silicate	0.7		Lithium Silicate	6.0
	Others + Amorphous	92.9		Others + Amorphous	81.3
C2-700-384	Aegirine	14.3	C4-700-384	Aegirine	21.0
	Lithium Silicate	3.7		Lithium Silicate	11.3
	Others + Amorphous	82.0		Others + Amorphous	67.7
C2-700-768	Aegirine	14.7	C4-700-768	Aegirine	20.3
	Lithium Silicate	4.4		Lithium Silicate	8.8
	Others + Amorphous	80.9		Others + Amorphous	70.9

3.4 Chemical Durability (PCT Test)

The normalized releases for all heat treated samples as indicated by the PCT are listed in Table 3-5 and in Table 3-6. The measured PCT response of the reference glasses ARM and EA are also listed in Table 3-7. Tables of measured elemental release of each individual leachate generated by these PCT experiments are listed in Appendix A. The normalized releases are calculated from the measured elemental releases, corrected for dilution and normalized to the concentration of the element in the glass. Based upon the normalized releases for ARM, all of the PCT tests were consistent with previous studies and acceptable according to the ASTM procedure. For the C2-510 glass, only one heat treated sample exhibited normalized releases greater than those of EA glass which is 16.695 g/L for B, 9.565 g/L for Li, 13.346 g/L for Na and 3.922 g/L for Si.[19] The glass sample heat treated at 600 °C for 768 hours had normalized releases of 17.335, 9.929, 7.181 and 1.774 g/L of B, Li, Na and Si respectively. Based on the XRD results, this sample had approximately 40.6 wt % overall crystallization of nepheline, aegirine, lithium silicate, and calcium magnesium iron silicon oxide. Presence of the first 3 crystalline phases have all historically been shown to have a negative impact on glass durability as measured by the PCT.[2] The fourth phase has an unknown direct effect on durability since it is only coincides in these experiments with other durability effecting phases. Keep in mind that this treatment temperature and time are not typical and would even be hard to obtain during an atypical accident scenario. Therefore, PCT results similar to these samples would not be reproducible during normal processing at the DWPF for this glass.

For the C4-418 glass, four heat treated samples exhibited normalized releases greater than those of EA glass. The glass samples heat treated at 600 °C for 96, 192, 384, and 768 hours had B normalized releases of 21.519, 44.857, 55.533, and 58.928 g/L respectively. Based on the XRD results, these samples had approximately ≥20 wt % overall crystallization of nepheline, aegirine, and lithium silicate. Presence of these crystalline phases have all historically been shown to have a negative impact on glass durability as measured by the PCT.[2] Keep in mind that this treatment temperature and time are not typical and would even be hard to obtain during an atypical accident scenario. PCT results similar to these samples would not be reproducible during normal processing at the DWPF for this glass either.

To better illustrate the PCT results for both glasses, normalized releases were graphed three-dimensionally as a function of heat treatment time and temperature. Figure 3-3 through Figure 3-10 represent the PCT response of the entire heat treated matrix of glass samples for the C2-510 glass. As shown, normalized releases only become elevated at times of 96 hours and longer at temperatures between 600 °C and 700 °C and at 768 hours at 500 °C. This also corresponds to the region where non-durable crystalline phases were detected. Figure 3-3 through Figure 3-10 represent the PCT response of the entire heat treated matrix of glass samples for the C4-418 glass. As shown, normalized releases are again only elevated at times of 96 hours and longer at temperatures between 600 °C and 700 °C. No significant difference in PCT response was seen at 500 °C for this glass as a function of time. Also, the increase of normalized release for this glass directly corresponds to the region where non-durable crystalline phases such as nepheline and lithium silicate were crystallized.

Table 3-5. PCT Response of the C2-510 Glass Samples

Glass ID	NL (g/L)				Glass ID	NL (g/L)			
	Li	B	Na	Si		Li	B	Na	Si
C2-1000-1	0.668	0.625	0.619	0.404	C2-800-768	0.650	0.576	0.622	0.440
C2-1000-3	0.658	0.629	0.630	0.396	C2-700-6	0.635	0.558	0.634	0.427
C2-1000-6	0.666	0.617	0.641	0.405	C2-700-12	0.655	0.578	0.634	0.436
C2-1000-12	0.637	0.587	0.605	0.392	C2-700-24	0.684	0.594	0.657	0.457
C2-1000-24	0.647	0.597	0.610	0.400	C2-700-48	0.664	0.573	0.629	0.443
C2-1000-48	0.657	0.592	0.619	0.402	C2-700-96	0.805	0.776	0.748	0.451
C2-1000-96	0.684	0.628	0.640	0.415	C2-700-192	3.087	2.334	1.645	0.818
C2-1000-192	0.678	0.605	0.634	0.415	C2-700-384	4.095	2.612	1.828	0.997
C2-1000-384	0.671	0.586	0.640	0.420	C2-700-768	4.196	2.732	1.866	0.999
C2-1000-768	0.641	0.552	0.581	0.394	C2-600-12	0.657	0.603	0.631	0.424
C2-900-1	0.650	0.579	0.609	0.403	C2-600-24	0.679	0.617	0.652	0.437
C2-900-3	0.631	0.566	0.592	0.392	C2-600-48	1.074	0.758	0.796	0.536
C2-900-6	0.658	0.590	0.617	0.411	C2-600-96	2.136	1.218	1.008	0.745
C2-900-12	0.675	0.603	0.623	0.419	C2-600-192	5.690	4.045	2.018	1.307
C2-900-24	0.686	0.600	0.638	0.430	C2-600-384	7.247	8.556	3.857	1.606
C2-900-48	0.671	0.589	0.627	0.418	C2-600-768	9.929	17.335	7.181	1.774
C2-900-96	0.689	0.606	0.652	0.424	C2-500-24	0.689	0.773	0.659	0.415
C2-900-192	0.669	0.597	0.621	0.418	C2-500-48	0.680	0.709	0.662	0.419
C2-900-384	0.696	0.603	0.651	0.432	C2-500-96	0.682	0.699	0.676	0.415
C2-900-768	0.670	0.592	0.624	0.426	C2-500-192	0.837	0.867	0.762	0.458
C2-800-3	0.623	0.554	0.593	0.413	C2-500-384	0.988	1.098	0.857	0.496
C2-800-6	0.623	0.548	0.603	0.415	C2-500-768	2.435	3.037	1.691	0.783
C2-800-12	0.647	0.573	0.622	0.432	C2-CCC	0.674	0.575	0.617	0.422
C2-800-24	0.642	0.568	0.617	0.429	C2-CCC	0.652	0.578	0.604	0.434
C2-800-48	0.631	0.570	0.610	0.422	C2-Q	0.692	0.620	0.645	0.422
C2-800-96	0.663	0.589	0.632	0.439	C2-Q	0.664	0.607	0.621	0.430
C2-800-192	0.637	0.572	0.618	0.429	C2-Q	0.685	0.717	0.645	0.424
C2-800-384	0.631	0.556	0.617	0.426					

Table 3-6. PCT Response of the C4-418 Glass Samples

Glass ID	NL (g/L)				Glass ID	NL (g/L)			
	Li	B	Na	Si		Li	B	Na	Si
C4-1000-1	0.971	0.908	1.060	0.597	C4-800-768	0.905	0.830	1.016	0.564
C4-1000-3	0.946	0.892	1.026	0.582	C4-700-6	0.913	0.910	1.021	0.556
C4-1000-6	0.916	0.865	0.989	0.561	C4-700-12	0.947	0.989	1.061	0.570
C4-1000-12	0.961	0.921	1.074	0.598	C4-700-24	0.949	0.951	1.069	0.579
C4-1000-24	0.934	0.875	1.029	0.570	C4-700-48	0.978	0.846	1.085	0.582
C4-1000-48	0.927	0.898	1.026	0.574	C4-700-96	1.256	1.003	1.269	0.682
C4-1000-96	0.932	0.875	1.012	0.579	C4-700-192	3.910	1.437	1.939	1.195
C4-1000-192	0.958	0.918	1.060	0.592	C4-700-384	3.936	1.476	1.953	1.213
C4-1000-384	0.930	0.907	1.051	0.582	C4-700-768	3.929	2.012	2.428	1.264
C4-1000-840	0.900	0.772	0.954	0.526	C4-600-12	0.874	1.062	0.949	0.522
C4-900-1	0.939	0.859	0.979	0.575	C4-600-24	0.936	1.018	1.026	0.567
C4-900-3	0.956	0.897	1.055	0.591	C4-600-48	1.390	1.909	1.323	0.643
C4-900-6	0.900	0.817	0.997	0.550	C4-600-96	7.566	21.519	9.237	2.395
C4-900-12	0.923	0.839	1.006	0.567	C4-600-192	9.434	44.857	16.957	3.586
C4-900-24	0.894	0.820	1.015	0.557	C4-600-384[a]	10.248	55.533	20.392	4.113
C4-900-48	0.886	0.823	1.016	0.564	C4-600-768	10.696	58.928	21.291	4.325
C4-900-96	0.894	0.855	0.995	0.552	C4-500-24	1.045	1.055	1.151	0.624
C4-900-192	0.896	0.833	1.024	0.574	C4-500-48	0.963	0.948	1.066	0.578
C4-900-384	0.859	0.790	0.967	0.540	C4-500-96	0.968	0.942	1.056	0.575
C4-900-840	0.857	0.800	0.960	0.535	C4-500-192	1.002	0.991	1.107	0.601
C4-800-3	0.973	0.894	1.076	0.589	C4-500-384	1.137	1.141	1.192	0.648
C4-800-6	0.953	0.876	1.064	0.581	C4-500-840	1.151	1.128	1.134	0.634
C4-800-12	1.009	0.927	1.133	0.611	C4-CCC	0.896	0.803	0.914	0.546
C4-800-24	0.980	0.902	1.100	0.593	C4-CCC	0.895	0.806	0.906	0.534
C4-800-48	0.963	0.886	1.089	0.589	C4-Q	0.958	1.087	1.052	0.574
C4-800-96	0.917	0.848	1.023	0.563	C4-Q	0.910	0.907	0.967	0.535
C4-800-192	0.956	0.892	1.096	0.601	C4-Q	0.925	0.897	0.985	0.552
C4-800-384	0.934	0.863	1.077	0.580					

[a] The sample C4-418 PCT normalized releases were based upon the average of 2 replicates instead of 3.

Table 3-7. PCT Response of the EA and ARM Glass References

Glass ID	NL (g/L)			
	Li	B	Na	Si
ARM 1	0.588	0.504	0.499	0.262
ARM 2	0.648	0.604	0.573	0.291
ARM 3	0.600	0.494	0.508	0.273
ARM 4	0.633	0.522	0.529	0.278
ARM 5	0.554	0.473	0.476	0.262
EA 1	10.002	18.232	13.944	3.796
EA 2	8.089	14.309	11.182	3.385
EA 3	10.106	20.349	13.724	3.921
EA 4	8.545	15.310	11.927	3.471
EA 5	6.101	9.477	7.576	2.529

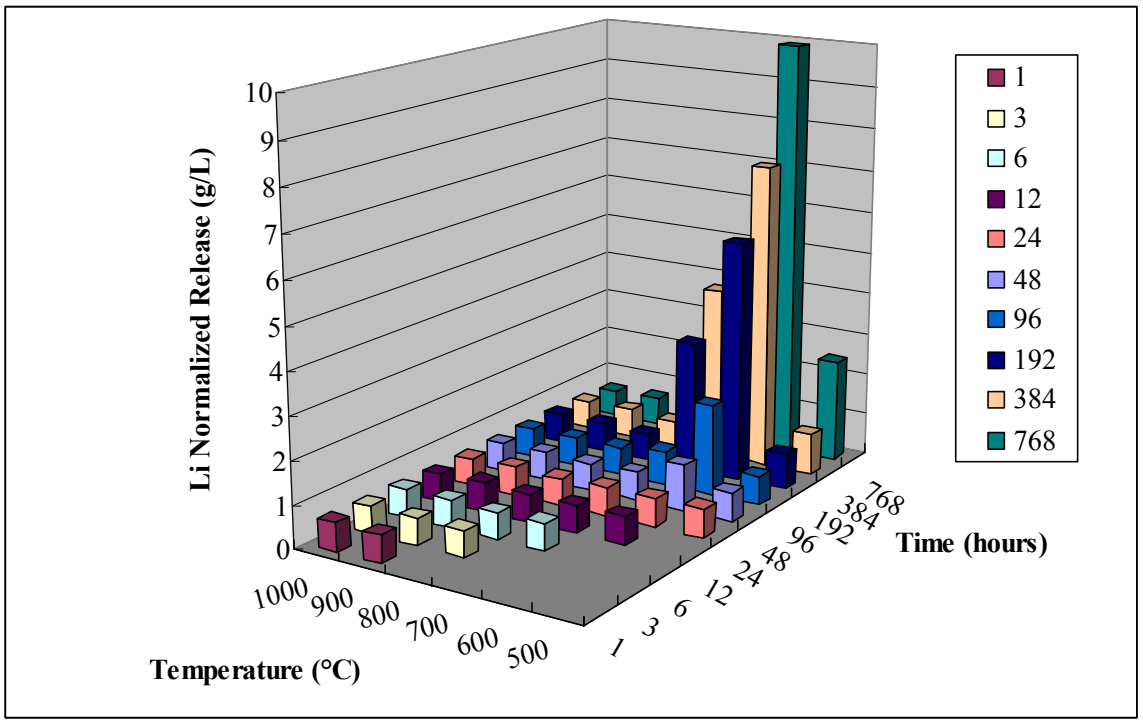

Figure 3-3. Normalized Li Release as a Function of Temperature and Duration of Heat Treatment for the C2-510 Glass Samples

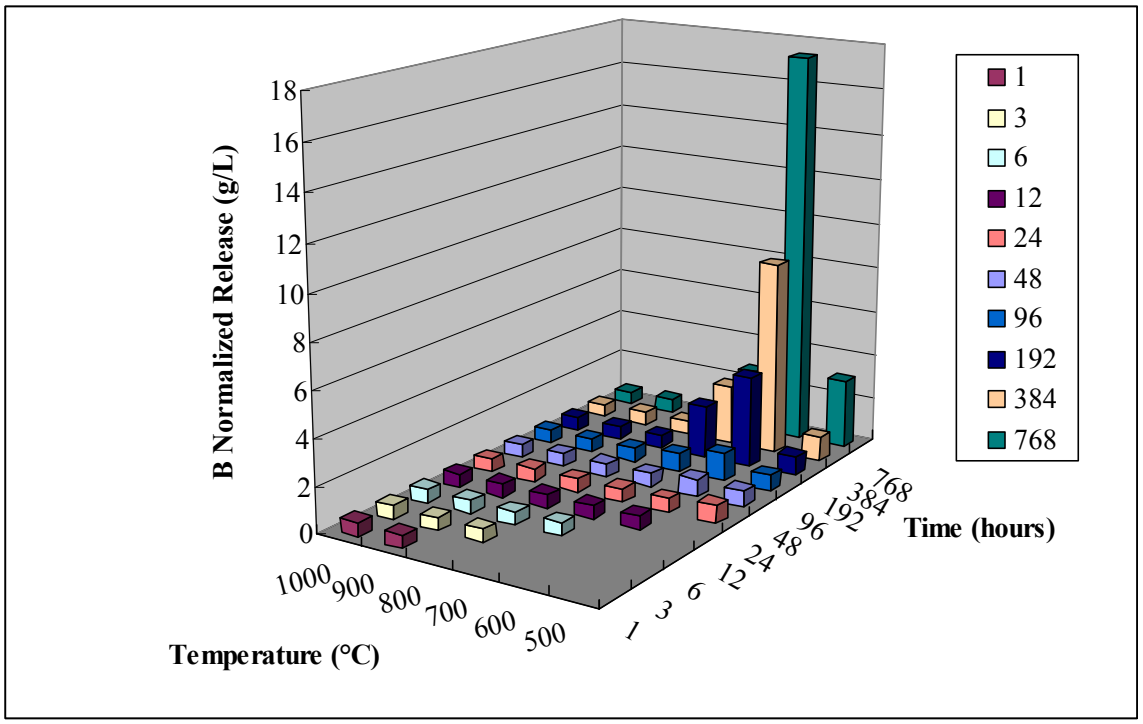

Figure 3-4. Normalized B Release as a Function of Temperature and Duration of Heat Treatment for the C2-510 Glass Samples

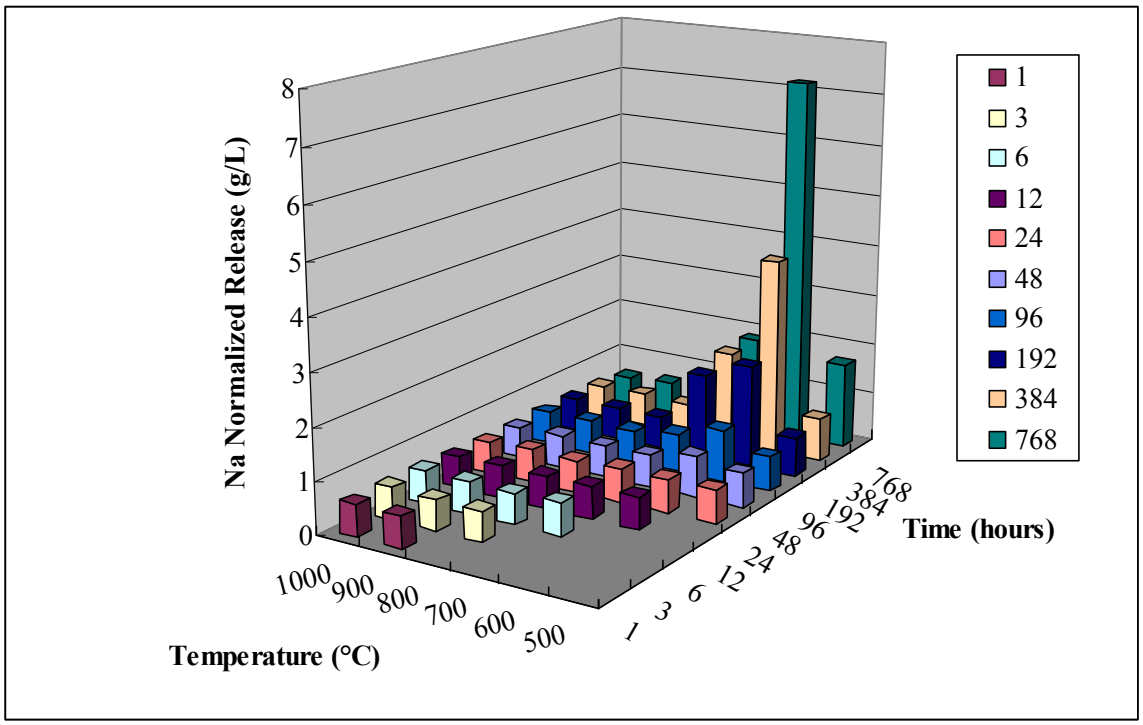

Figure 3-5. Normalized Na Release as a Function of Temperature and Duration of Heat Treatment for the C2-510 Glass Samples

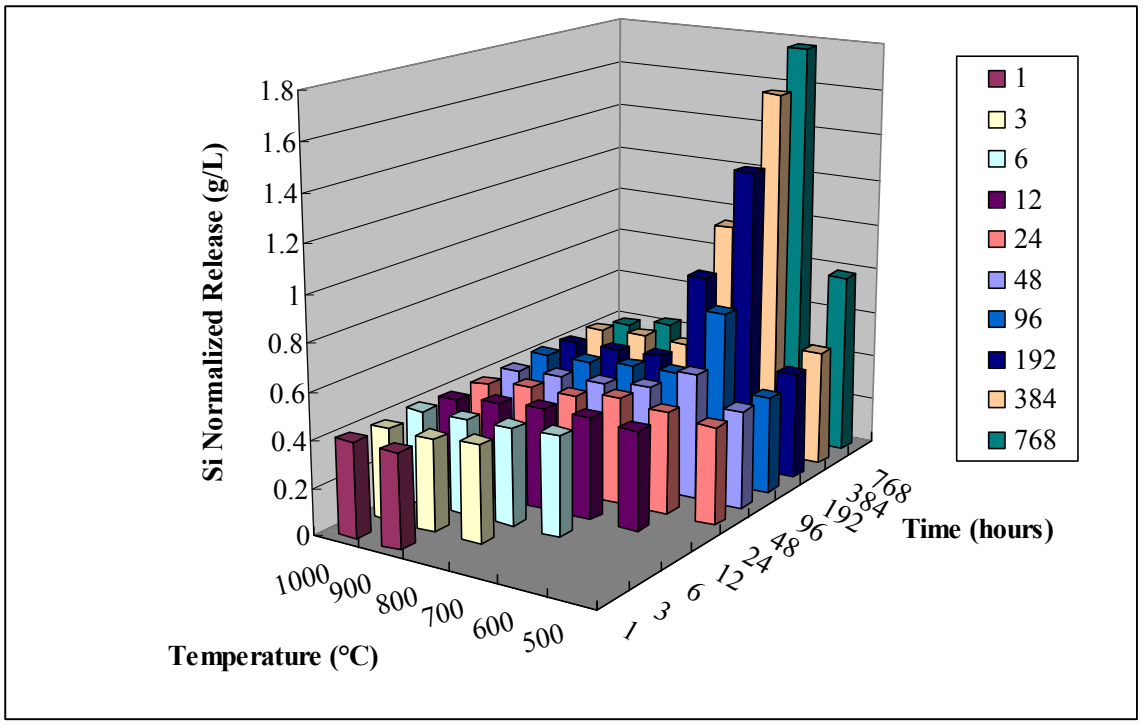

Figure 3-6. Normalized Si Release as a Function of Temperature and Duration of Heat Treatment for the C2-510 Glass Samples

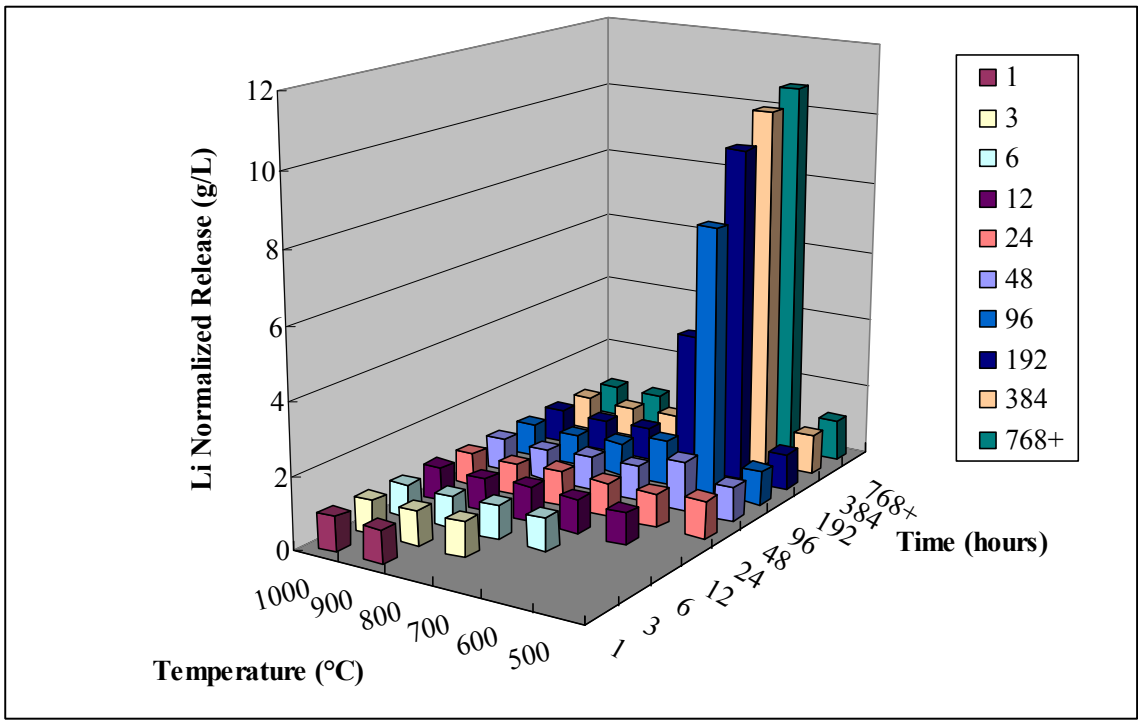

Figure 3-7. Normalized Li Release as a Function of Temperature and Duration of Heat Treatment for the C4-418 Glass Samples

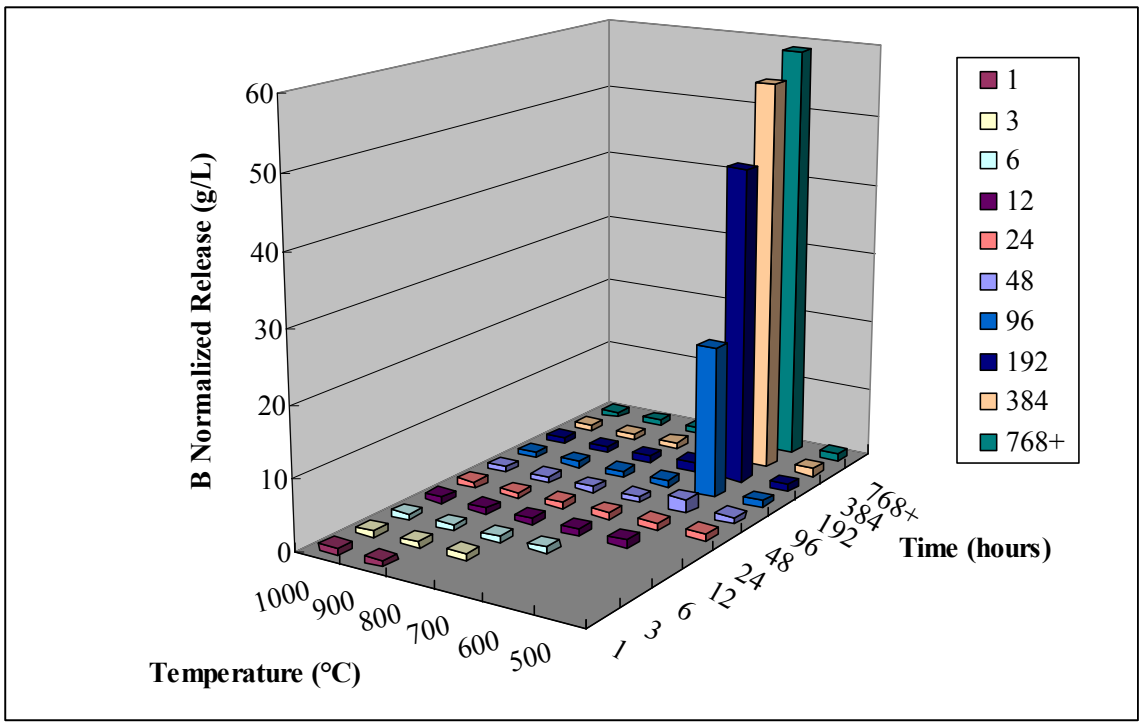

Figure 3-8. Normalized B Release as a Function of Temperature and Duration of Heat Treatment for the C4-418 Glass Samples

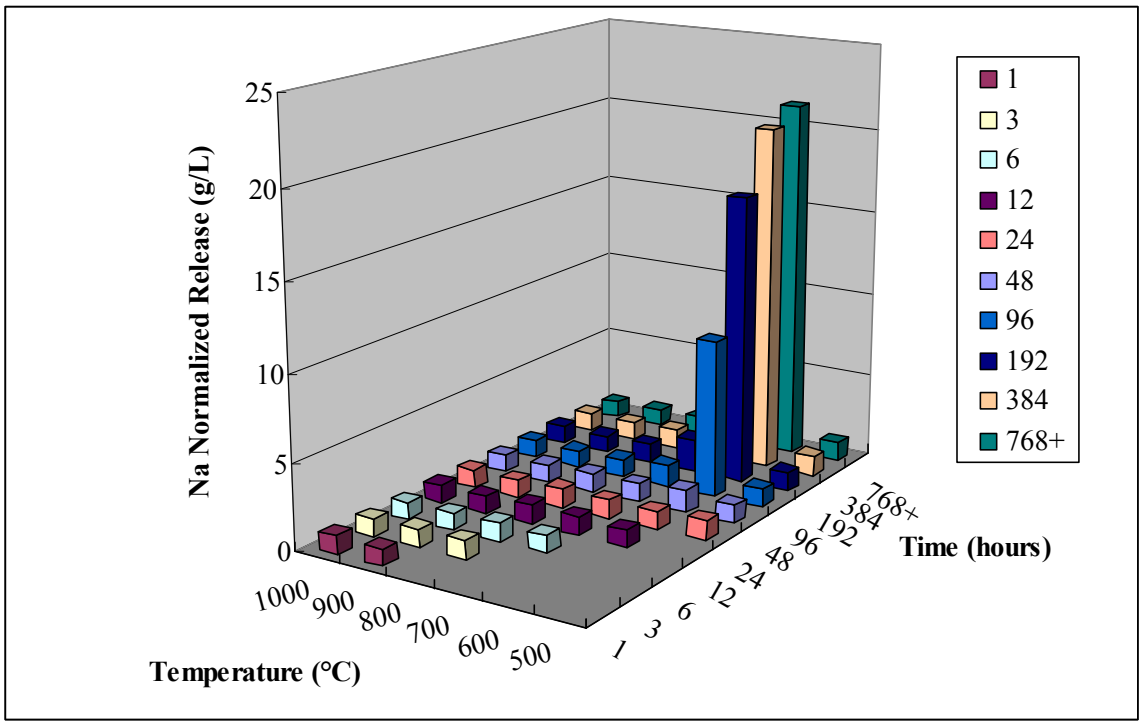

Figure 3-9. Normalized Na Release as a Function of Temperature and Duration of Heat Treatment for the C4-418 Glass Samples

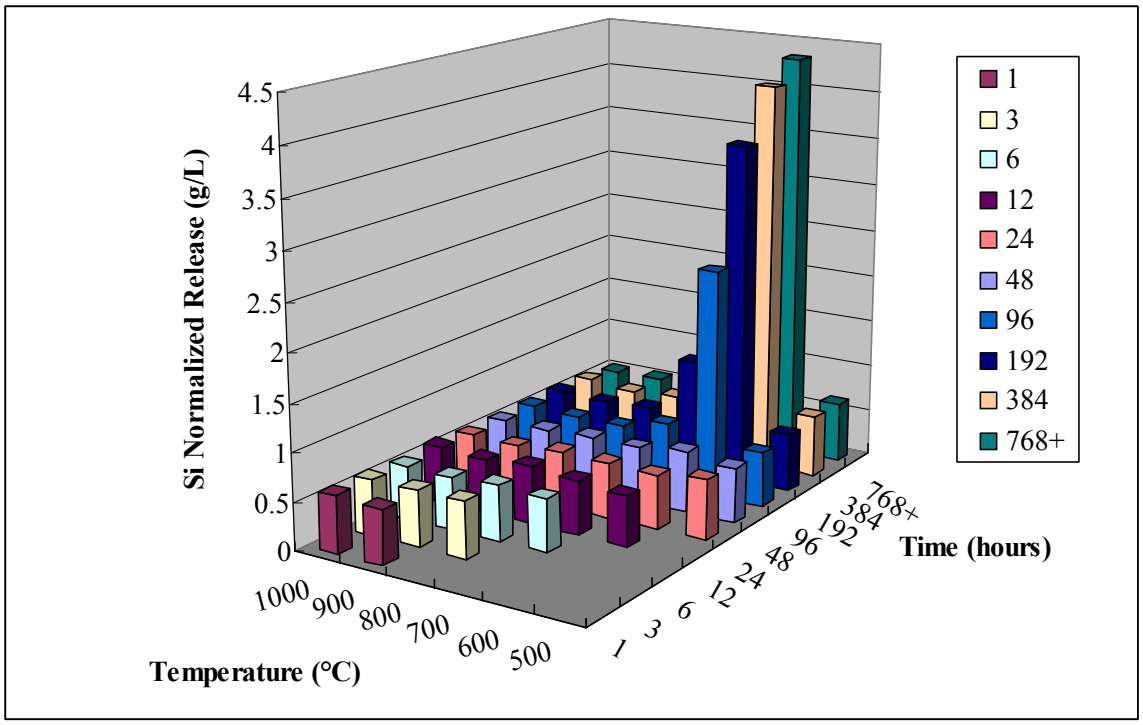

Figure 3-10. Normalized Si Release as a Function of Temperature and Duration of Heat Treatment for the C4-418 Glass Samples

In order to emphasize the change in PCT response as a function of crystalline phase, Table 3-8 and Table 3-9 list the weight percent crystallinity and phase type parallel to the normalized release of B for the C2-510 glass samples and C4-418 glass samples. To illustrate the significance of the identity of the crystalline phase present, compare the normalized B releases for C2-700-96 and C2-500-768. For the C2-510 glass, when aegirine is the only phase present (C2-700-96), the normalized B release is low (0.776 g/L). Conversely, when approximately the same wt % of nepheline is present in sample C2-500-768 the normalized B release is significantly higher (3.037 g/L). Those samples, whose normalized B release is elevated, contain higher weight fractions of total crystals and nepheline and/or lithium silicate.

Glass samples of the C4-418 glass exhibit similar behavior relative to the crystallization of nepheline and lithium silicate's effect on normalized B release. For the C4-418 glass, those samples, whose normalized B release is elevated, contain higher weight fractions of total crystals and nepheline and/or lithium silicate present. However, the normalized B release values relative to the quantity of crystalline phase present were significantly higher for this glass as compared to C2-510. For example, the C2-510 glass sample C2-600-768 contains 18.9 wt % nepheline and 7.3 wt % lithium silicate and has a normalized B release of 17.335 g/L. The C4-418 glass sample C4-600-384 contains lower concentrations of each phase, 6.7 wt % nepheline and 6.7 wt % lithium silicate, but has a much higher normalized B release (55.533 g/L). This emphasizes the importance of the glass composition. Identity and amount of crystalline phases are important to the durability but often have significantly different tolerances to the weight or volume fraction of each phase which forms. The C4-418 glass composition is significantly more sensitive, with respect to impact on durability, to the presence of small concentrations of durability affecting phases such as nepheline and lithium silicate.

Table 3-8. Quantitative XRD Results and Normalized B Release for Select Samples of the C2-510 Glass

Sample	Phases	Wt % Phase	Normalized B Release (g/L)
C2-600-96	Nepheline	6.4	1.218
	Calcium Magnesium Iron Silicon Oxide	10.9	
	Hematite	1.4	
	Others + Amorphous	81.3	
C2-600-192	Nepheline	12.8	4.045
	Calcium Magnesium Iron Silicon Oxide	13.4	
	Hematite	3.6	
	Lithium Silicate	3.6	
	Others + Amorphous	66.6	
C2-600-384	Nepheline	23.5	8.556
	Calcium Magnesium Iron Silicon Oxide	18.2	
	Lithium Silicate	6.4	
	Aegirine	3.0	
	Others + Amorphous	48.9	
C2-600-768	Nepheline	18.9	17.335
	Calcium Magnesium Iron Silicon Oxide	11.8	
	Lithium Silicate	7.3	
	Aegirine	2.6	
	Others + Amorphous	59.4	
C2-500-768	Nepheline	2.2	3.037
	RuO_2	0.1	
	Others + Amorphous	97.7	
C2-700-96	Aegirine	2.7	0.776
	Others + Amorphous	97.3	
C2-700-192	Aegirine	6.4	2.334
	Lithium Silicate	0.7	
	Others + Amorphous	92.9	
C2-700-384	Aegirine	14.3	2.612
	Lithium Silicate	3.7	
	Others + Amorphous	82.0	
C2-700-768	Aegirine	14.7	2.732
	Lithium Silicate	4.4	
	Others + Amorphous	80.9	

Table 3-9. Quantitative XRD Results and Normalized B Release for Select Samples of the C4-418 Glass

Sample	Phases	Wt % Phase	Normalized B Release (g/L)
C4-600-24	Aegirine	1.2	1.018
	Others + Amorphous	98.8	
C4-600-48	Aegirine	1.6	1.909
	Nepheline	1.5	
	Others + Amorphous	96.9	
C4-600-96	Aegirine	9.2	21.519
	Lithium Silicate	5.7	
	Nepheline	5.0	
	Others + Amorphous	80.1	
C4-600-192	Aegirine	11.8	44.857
	Lithium Silicate	7.5	
	Nepheline	7.2	
	Others + Amorphous	73.6	
C4-600-384	Aegirine	9.9	55.533
	Lithium Silicate	6.7	
	Nepheline	6.7	
	Others + Amorphous	76.7	
C4-600-768	Aegirine	14.3	58.928
	Lithium Silicate	9.5	
	Nepheline	7.1	
	Others + Amorphous	69.1	
C4-700-96	Aegirine	1.5	1.003
	Trevorite	0.7	
	Others + Amorphous	97.8	
C4-700-192	Aegirine	12.7	1.437
	Lithium Silicate	6.0	
	Others + Amorphous	81.3	
C4-700-384	Aegirine	21.0	1.476
	Lithium Silicate	11.3	
	Others + Amorphous	67.7	
C4-700-768	Aegirine	20.3	2.012
	Lithium Silicate	8.8	
	Others + Amorphous	70.9	

4.0 Conclusions

Two TTT diagrams were completed for simulated waste glasses based on projected future wastes, Cluster 2 - Frit 510 and Cluster 4 - Frit 418. The diagrams were generated using both glass compositions heat treated at various temperatures and durations of time and phase identification using XRD. Types of phases which formed in these two glass systems were similar (if not the same) as has been detected in previous studies.[2,3] Trevorite, hematite, and magnetite, all spinel based phases, were often found. These phases also occurred when both glasses were treated according to the CCC profile. Aegirine (acmite) also formed frequently in both glasses. In addition, RuO_2 was often identified in XRD patterns that contained little to no crystallization

because RuO_2 is insoluble in borosilicate glass systems. Both C2-510 and C4-418 contained 0.10 wt % RuO_2. Major durability affecting crystallization only occurred in the temperature region of 500 - 700 °C at times greater than 48 hours. These phases included lithium silicate and nepheline. Also at 600 °C in the C2-510 glass, krinovite and calcium magnesium iron silicon oxide was formed, but did not seem to have an independent impact on durability of those samples. Phases and regions of maximum crystallization were within the same crystalline families, if not the same crystals as those previously observed.[2,3]

All glasses of the C2-510 composition, except the glass sample heat treated at 600 °C for 768 hours had a durability better than that of EA (as measured by the PCT). The aforementioned sample had a normalized B release of 17.335 g/L as compared to the accepted normalized B release of 16.7 g/L for EA.[19] The C4-418 heat treated glasses had much higher normalized B releases occurring at shorter times at temperatures of 600 °C 21.519 g/L after 96 hours of treatment and up to 58.928 g/L after 768 hours of treatment. The quenched and CCC heat treated samples for both glasses had normalized B releases less than 1.0 g/L. All other samples had normalized B releases less than EA. Of the matrix of times and temperatures tested, durability effecting crystallization did not occur until far beyond the temperatures and times represented by the CCC curve.

The onset of T_g for the C2-510 glass was determined to occur at 452 ±0.2 °C. The onset of T_g for the C4-418 glass was determined to occur at 448 ±1 °C. Therefore these glasses will never exhibit a change in morphology below those temperatures, no matter the duration. The T_g of these glasses fell within the region of measured temperatures of the WCP glasses and also satisfies the requirement of having a T_g above 400 °C.[22]

The data provided in this report supports that these future, average clustered waste compositions will behave similarly to previously studied glasses with respect to phase transformation when treated under abnormal temperature conditions. The conditions imposed on the glass during this study are highly unlikely to occur to any waste glass currently being stored at DWPF.

5.0 Path Forward

After years of waste processing and developing TTT diagrams on waste glasses representing various waste types and waste processing strategies, the outcomes are very similar. Compositions of these glasses have spanned a great deal of component variance (see Appendix A for table of compositions). Even after the changes in waste streams, sodium washing and frit development strategies, the phases formed are still the same. Particular crystalline phases will still form in the same temperature and time regions, with the main durability effecting phases (nepheline and lithium silicate) occurring at temperatures between 500 °C and 700 °C with the maximum quantity of crystallization likely to occur at 600°C. Other non-durability affecting phases remain in the same type of crystal families, such as the spinel structures which form in the higher temperature regions but below T_L.

Because of the outstanding similarity in results across great composition variance recommendations for generating future TTT diagrams would be limited to a few select conditions. It is recommended that TTT diagrams only be generated if DWPF would undergo a drastic change in processing strategy that would significantly alter the composition outside of the current region studied. Conditions where this may occur would include a large change in the frit compositions used. A large change in waste loading would also push the glass compositions far outside of the glass compositions currently studied. For example, the highest WL to date in

which a TTT diagram was generated was 38 wt %. Waste loadings over 45 wt % would risk pushing the Al, Na and Fe to significantly higher levels than was previously studied. Another example of an extreme composition change would be the incorporation of a secondary salt or waste stream which could contain much higher levels of minor elements such as Ti. If a significant change in composition is seen or projected, it is recommended that SRNL evaluate whether or not the significant composition change will be likely to change the crystallization kinetics. This could then be confirmed by generating data points in the temperature-time regions of most prevalent crystallization in order to verify similar or dissimilar behavior in phase formation. Full TTT diagrams will only be completed if significant differences in phases or durability response are detected in the confirmatory data points.

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Appendix A

Table A-1. Waste Form Compositions of Various Glasses Used to Generate TTT Diagrams[2,22-24]

Oxide (wt %)	SB3-Frit 418	Blend	HM	Purex	Batch #1	Batch #2	Batch #3	Batch #4	165 High Al	165 Av (TDS)	165 High Fe	131 High Al	131 Av (TDS)	131 High Fe
Al_2O_3	5.96	4.16	7.15	2.99	4.88	4.63	3.44	3.43	10.15	5.54	2.59	10.51	7.81	3.04
B_2O_3	5.16	8.05	7.03	10.33	7.78	7.88	7.69	8.14	8.53	8.23	6.44	11.09	9.44	10.98
BaO	0.06	0.18	0.11	0.20	0.15	0.16	0.18	0.25	0.16	0.33	0.10	0.04	0.07	0.04
CaO	1.13	1.03	1.01	1.09	1.22	1.08	0.99	0.84	1.42	1.67	1.14	1.49	1.56	1.63
Ce_2O_3	0.09	-	-	-	-	-	-	-	-	-	-	-	-	-
Cr_2O_3	0.09	0.13	0.09	0.15	0.11	0.13	0.14	0.14	0.19	0.19	0.14	0.17	0.20	0.19
Cs_2O	-	0.08	0.06	0.06	0.06	0.02	0.06	0.09	0.00	0.03	0.03	0.03	0.03	0.03
CuO	0.04	0.44	0.25	0.42	0.40	0.42	0.40	0.45	0.06	0.00	0.06	0.06	0.06	0.08
Fe_2O_3	12.75	10.91	7.78	13.25	12.84	11.12	11.71	11.71	7.53	12.14	15.52	11.36	11.44	13.52
K_2O	0.08	3.67	2.21	3.41	3.33	3.38	3.40	3.86	-	-	-	-	-	-
La_2O_3	0.04	-	-	-	-	-	-	-	0.05	0.11	0.07	0.14	0.16	0.21
Li_2O	5.16	4.44	4.62	3.22	4.43	4.50	4.51	4.29	3.99	3.96	4.51	3.09	3.24	3.53
MgO	1.39	1.41	1.49	1.41	1.42	1.42	1.42	1.43	0.87	0.89	0.95	1.40	1.71	1.59
MnO	2.59	1.67	1.75	1.69	1.72	1.41	1.53	2.54	1.45	2.08	2.71	2.39	1.96	2.59
MoO_3	-	0.15	0.22	0.08	0.11	0.17	0.12	0.20	-	-	-	-	-	-
Na_2O	13.88	9.13	8.56	12.62	9.00	9.21	9.01	9.16	8.48	8.26	9.88	8.90	10.89	12.29
Nd_2O_3	-	0.22	0.55	0.06	0.15	0.26	0.17	0.39	-	-	-	-	-	-
NiO	0.69	0.89	0.41	1.19	0.75	0.90	1.05	1.06	0.97	1.15	1.94	0.94	1.26	1.03
P_2O_5	-	-	-	-	-	-	-	-	0.14	0.16	0.09	0.12	0.14	0.13
PbO	0.06	-	-	-	-	-	-	-	0.26	0.35	0.51	0.42	0.43	0.46
RuO_2	0.02	0.03	0.04	0.01	0.02	0.04	0.03	0.05	0.07	0.10	0.05	0.06	0.05	0.06
SiO_2	50.20	51.90	55.80	46.50	50.20	52.10	52.60	50.10	52.52	52.13	50.26	43.25	46.00	45.08
SO_4	0.43	-	-	-	-	-	-	-	-	-	-	-	-	-
SrO	-	-	-	-	-	-	-	-	0.05	0.05	0.08	0.05	0.06	0.05
ThO_2*	-	-	-	-	-	-	-	-	1.07	0.30	0.03	1.07	0.30	0.03
TiO_2	0.01	0.89	0.56	0.68	0.68	0.69	0.68	1.03	0.07	0.07	0.16	0.72	0.75	0.74
U_3O_8		-	-	-	-	-	-	-	0.91	1.13	1.91	2.16	1.93	2.11
ZnO	0.06	-	-	-	-	-	-	-	0.04	0.05	0.08	0.09	0.05	0.09
ZrO_2	0.11	0.14	0.33	0.05	0.10	0.17	0.12	0.22	1.05	1.09	0.77	0.47	0.47	0.50
SUM	100.00	99.52	100.02	99.41	99.35	99.69	99.25	99.38	100.00	100.00	100.01	100.01	100.01	100.01

* ThO_2 was calculated from batch compositions.

Table A-2. Measured Elemental Release of the PCT Leachates of ARM, EA and Blank Samples

		Elemental Release from PSAL (mg/L)						Elemental Release from PSAL (mg/L)			
Solution Identifier	**Original Sample ID**	**Li**	**B**	**Na**	**Si**	**Solution Identifier**	**Original Sample ID**	**Li**	**B**	**Na**	**Si**
D27	ARM	8.46	10.7	20.5	34.8	D24	EA	12.3	39.7	104	53.7
D01	ARM	8.35	10.4	22.1	33.4	D73	EA	11.8	38.5	105	51.5
D45	ARM	8.19	10.7	21.8	34.4	D29	EA	11.5	37.0	104.4	50.5
F58	ARM	9.42	12.6	23.9	37.7	E52	EA	9.71	30.8	85.2	46.6
F48	ARM	9.21	13.5	25.1	37.8	E54	EA	9.47	29.1	82.7	45.9
F07	ARM	8.89	12.1	25.0	38.4	E18	EA	9.64	30.5	82.9	46.3
G57	ARM	8.53	10.6	21.7	35.0	F63	EA	12.4	41.2	101	54.3
G67	ARM	8.54	10.3	21.9	35.3	F74	EA	11.8	45.1	103	53.9
G15	ARM	8.43	10.33	21.9	36.8	F10	EA	11.8	42.3	104.1	52.6
H03	ARM	9.0	11.0	22.4	36.1	G40	EA	10.3	32.7	92.6	48.1
H67	ARM	8.86	11.1	22.9	36.5	G03	EA	9.49	28.3	79.3	44.7
H13	ARM	9.05	10.9	22.9	36.2	G28	EA	10.6	36.2	96.7	49.7
E65	ARM	7.75	9.88	20.4	33.7	H18	EA	7.44	20.4	57.7	35.4
E09	ARM	7.84	9.80	20.5	34.4	H05	EA	7.10	19.4	56.0	33.9
E30	ARM	7.96	10.2	20.5	34.6	H57	EA	7.20	20.0	56.4	34.5
D44	Blank	<0.100	0.416	<0.100	1.23	F13	Blank	<0.100	<0.100	<0.100	<0.100
D05	Blank	<1.00	0.847	<0.100	0.131	G24	Blank	<0.100	<0.100	<0.100	<0.100
E28	Blank	<0.100	<0.100	<0.100	<0.100	G07	Blank	<0.100	<0.100	<0.100	<0.100
E70	Blank	<0.100	0.316	<0.100	<0.100	H74	Blank	<0.100	<0.100	0.166	<0.100
F30	Blank	<0.100	0.181	<0.100	<0.100	H28	Blank	<0.100	<0.100	<0.100	<0.100

Table A-3. Measured Elemental Results of the ICP Standards

		Elemental Release from PSAL (mg/L)						Elemental Release from PSAL (mg/L)			
Solution Identifier	**Original Sample ID**	**Li**	**B**	**Na**	**Si**	**Solution Identifier**	**Original Sample ID**	**Li**	**B**	**Na**	**Si**
std-11-1	ICP Standard	9.91	20.7	80.4	46.5	std-32-3	ICP Standard	10.1	21.6	85.3	49.5
std-11-2	ICP Standard	10.2	20.1	79.9	47.6	std-33-1	ICP Standard	9.91	21.0	84.7	49.2
std-11-3	ICP Standard	10.0	20.0	80.9	47.0	std-33-2	ICP Standard	10.1	20.9	85.8	48.2
std-12-1	ICP Standard	10.0	20.7	80.7	47.1	std-33-3	ICP Standard	10.0	21.4	84.1	47.5
std-12-2	ICP Standard	10.2	19.7	83.2	46.7	std-41-1	ICP Standard	10.2	21.1	82.7	47.7
std-12-3	ICP Standard	10.0	19.6	80.0	47.0	std-41-2	ICP Standard	10.4	20.8	83.8	49.2
std-13-1	ICP Standard	9.80	21.0	80.9	47.6	std-41-3	ICP Standard	10.4	20.6	83.8	49.4
std-13-2	ICP Standard	10.0	19.6	86.4	46.5	std-42-1	ICP Standard	10.1	21.0	83.7	48.5
std-13-3	ICP Standard	9.93	19.8	83.6	47.4	std-42-2	ICP Standard	10.2	20.0	83.3	47.9
std-21-1	ICP Standard	9.93	21.3	84.2	49.6	std-42-3	ICP Standard	10.3	20.5	83.2	50.0
std-21-2	ICP Standard	9.81	20.5	82.2	48.4	std-43-1	ICP Standard	9.91	21.1	83.4	47.5
std-21-3	ICP Standard	9.77	20.4	82.0	48.4	std-43-2	ICP Standard	10.2	20.7	84.2	49.7
std-22-1	ICP Standard	9.84	20.9	82.4	49.6	std-43-3	ICP Standard	10.3	21.1	85.3	51.0
std-22-2	ICP Standard	9.85	20.0	82.9	49.0	std-51-1	ICP Standard	10.2	20.4	82.6	46.7
std-22-3	ICP Standard	9.75	19.6	82.9	48.1	std-51-2	ICP Standard	10.2	20.6	81.5	47.5
std-23-1	ICP Standard	9.80	20.8	81.8	49.1	std-51-3	ICP Standard	10.4	20.7	83.5	48.4
std-23-2	ICP Standard	9.79	20.1	82.0	48.4	std-52-1	ICP Standard	10.0	20.8	81.5	46.6
std-23-3	ICP Standard	9.83	20.3	82.9	48.5	std-52-2	ICP Standard	10.0	20.3	79.8	47.0
std-31-1	ICP Standard	10.0	20.6	83.3	47.7	std-52-3	ICP Standard	10.0	20.4	80.3	46.9
std-31-2	ICP Standard	10.3	26.5	82.4	48.1	std-53-1	ICP Standard	10.0	20.6	81.2	46.3
std-31-3	ICP Standard	10.2	21.5	81.7	46.5	std-53-2	ICP Standard	10.2	20.1	82.3	47.4
std-32-1	ICP Standard	10.0	20.8	84.3	48.8	std-53-3	ICP Standard	10.3	20.4	83.0	47.8
std-32-2	ICP Standard	10.0	24.6	83.4	47.6						

Table A-4. Measured Elemental Release of the PCT Leachates for C2 – Frit 510 Glass Samples

		Elemental Release from PSAL (mg/L)						Elemental Release from PSAL (mg/L)			
Solution Identifier	Original Sample ID	Li	B	Na	Si	Solution Identifier	Original Sample ID	Li	B	Na	Si
D26	C2-1000-1	9.71	10.5	34.8	51.4	F23	C2-500-192	12.5	14.8	42.6	61.0
D42	C2-1000-1	9.73	10.4	34.6	52.7	F03	C2-500-192	12.2	15.4	43.4	60.0
D64	C2-1000-1	9.74	11.1	35.6	54.0	F39	C2-500-192	11.8	14.3	43.5	57.9
D50	C2-1000-12	9.18	10.1	32.4	50.4	F56	C2-500-24	10.3	11.1	37.0	53.9
D31	C2-1000-12	9.36	10.2	34.1	51.3	F68	C2-500-24	10.0	13.7	37.6	54.9
D68	C2-1000-12	9.29	9.84	36.3	51.7	F01	C2-500-24	9.81	15.2	37.2	53.7
D60	C2-1000-192	9.85	10.2	35.7	53.5	F45	C2-500-384	15.0	18.8	48.5	65.7
D36	C2-1000-192	10.0	10.4	35.8	54.5	F11	C2-500-384	14.1	19.2	47.7	64.1
D17	C2-1000-192	9.75	10.4	36.0	54.2	F05	C2-500-384	14.1	18.3	49.2	64.2
D37	C2-1000-24	9.56	10.3	33.9	52.4	F69	C2-500-48	10.3	11.1	38.1	55.6
D18	C2-1000-24	9.45	10.1	34.3	52.2	F19	C2-500-48	9.88	12.9	38.0	55.4
D67	C2-1000-24	9.23	10.2	35.4	51.8	F70	C2-500-48	9.52	12.5	36.3	52.8
D66	C2-1000-3	9.74	10.7	35.5	51.8	F53	C2-500-768	36.0	52.7	93.8	101
D52	C2-1000-3	9.74	10.7	36.2	51.9	F02	C2-500-768	35.0	51.5	95.3	99.9
D38	C2-1000-3	9.25	10.8	35.3	51.2	F29	C2-500-768	35.4	51.5	98.0	106
D55	C2-1000-384	9.92	10.1	34.7	54.8	F32	C2-500-96	10.4	12.1	39.9	56.7
D28	C2-1000-384	9.68	9.88	33.3	54.2	F51	C2-500-96	9.80	11.8	38.4	53.6
D06	C2-1000-384	9.72	10.1	41.0	55.2	F61	C2-500-96	9.59	11.9	36.5	52.2
D30	C2-1000-48	9.85	10.4	35.2	54.6	E33	C2-600-12	9.86	10.8	36.8	57.2
D02	C2-1000-48	9.53	10.0	34.9	51.4	E55	C2-600-12	9.69	10.1	36.4	55.9
D16	C2-1000-48	9.30	10.0	34.9	51.4	E45	C2-600-12	9.14	10.1	33.9	52.7
D56	C2-1000-6	9.66	10.6	34.6	53.1	F54	C2-600-192	84.1	71.0	109	160
D39	C2-1000-6	9.74	10.5	34.9	51.7	F65	C2-600-192	84.7	71.2	119	184
D54	C2-1000-6	9.67	10.6	39.4	53.4	F60	C2-600-192	79.7	65.4	115	168
D08	C2-1000-768	9.65	9.20	33.4	52.3	E48	C2-600-24	9.82	10.3	36.7	56.2
D15	C2-1000-768	9.31	9.83	32.5	51.1	E59	C2-600-24	10.0	10.5	37.5	57.9
D47	C2-1000-768	9.04	9.27	32.8	50.6	E42	C2-600-24	9.84	10.8	36.5	56.8
D22	C2-1000-96	10.1	10.9	35.1	55.0	F17	C2-600-384	111	153	232	220
D13	C2-1000-96	9.82	10.3	36.4	52.1	F09	C2-600-384	103	142	212	205
D74	C2-1000-96	10.0	11.0	37.1	55.4	F40	C2-600-384	103	145	211	204

Table A-5. Measured Elemental Release of the PCT Leachates for C2 – Frit 510 Glass Samples

		Elemental Release from PSAL (mg/L)						Elemental Release from PSAL (mg/L)			
Solution Identifier	Original Sample ID	Li	B	Na	Si	Solution Identifier	Original Sample ID	Li	B	Na	Si
E06	C2-600-48	15.4	12.9	44.4	69.2	E71	C2-700-96	12.2	13.9	44.1	60.6
E03	C2-600-48	15.6	12.8	45.3	70.0	E64	C2-700-96	11.4	12.8	41.3	57.5
E57	C2-600-48	15.9	13.2	45.4	70.2	E21	C2-700-96	11.5	13.2	41.6	58.1
F16	C2-600-768	146	300	418	231	E56	C2-800-12	9.76	10.3	36.3	58.2
F42	C2-600-768	143	293	393	231	E38	C2-800-12	9.24	9.49	34.6	55.4
F64	C2-600-768	144	296	408	233	E36	C2-800-12	9.24	9.62	34.7	55.3
F73	C2-600-96	31.5	21.0	56.7	92.8	E58	C2-800-192	9.32	9.86	35.7	56.3
F33	C2-600-96	31.5	20.1	56.7	100	E41	C2-800-192	9.35	9.51	35.4	56.2
F34	C2-600-96	30.3	21.4	57.7	98.6	E31	C2-800-192	9.14	9.94	33.8	55.1
E49	C2-700-12	9.52	10.0	36.4	57.1	E27	C2-800-24	9.17	9.54	34.3	54.6
E19	C2-700-12	9.46	9.72	36.0	56.3	E34	C2-800-24	9.42	9.63	35.4	56.6
E26	C2-700-12	9.62	9.95	35.2	57.3	E51	C2-800-24	9.43	9.93	35.1	56.7
E53	C2-700-192	46.7	41.0	96.1	110	E61	C2-800-3	9.06	9.60	33.5	53.6
E16	C2-700-192	44.1	39.1	91.7	104.8	E17	C2-800-3	8.94	9.01	33.2	53.3
E05	C2-700-192	44.0	39.6	91.4	105	E74	C2-800-3	9.18	9.79	34.0	54.6
E04	C2-700-24	9.89	10.2	36.8	59.8	E67	C2-800-384	9.14	9.63	35.3	55.4
E24	C2-700-24	10.1	10.1	37.9	60.4	E10	C2-800-384	9.20	9.28	34.7	55.8
E47	C2-700-24	9.93	10.1	36.8	58.6	E50	C2-800-384	9.21	9.59	34.7	55.2
E66	C2-700-384	62.2	47.6	109	134	E73	C2-800-48	8.95	9.40	33.5	54.0
E35	C2-700-384	58.7	43.1	102	129	E44	C2-800-48	9.18	9.57	34.6	55.2
E01	C2-700-384	58.0	43.3	99.6	127	E20	C2-800-48	9.44	10.3	35.5	56.0
E62	C2-700-48	9.78	10.0	36.0	58.6	E40	C2-800-6	9.02	9.33	34.4	54.5
E32	C2-700-48	9.64	9.59	35.9	57.3	E11	C2-800-6	9.00	9.09	33.9	53.6
E12	C2-700-48	9.57	9.78	34.9	57.3	E29	C2-800-6	9.18	9.71	34.1	54.3
E63	C2-700-6	9.07	9.42	34.9	54.2	E13	C2-800-768	9.26	9.59	34.9	57.3
E14	C2-700-6	9.31	9.42	36.7	56.8	E08	C2-800-768	9.40	9.69	35.0	56.6
E60	C2-700-6	9.32	9.76	36.0	56.1	E43	C2-800-768	9.73	10.2	35.7	58.3
E15	C2-700-768	59.9	45.2	102	127	E69	C2-800-96	9.74	10.4	36.3	57.7
E25	C2-700-768	61.4	47.6	108	132	E46	C2-800-96	9.56	9.67	35.3	57.1
E39	C2-700-768	61.8	47.4	106	132	E68	C2-800-96	9.65	10.1	35.8	56.9

Table A-6. Measured Elemental Release of the PCT Leachates for C2 – Frit 510 and C4 – 418 Glass Samples

		Elemental Release from PSAL (mg/L)						Elemental Release from PSAL (mg/L)			
Solution Identifier	Original Sample ID	Li	B	Na	Si	Solution Identifier	Original Sample ID	Li	B	Na	Si
D59	C2-900-1	9.25	10.0	32.3	51.0	D04	C2-CCC	10.0	10.0	33.9	56.7
D71	C2-900-1	9.86	10.0	35.5	54.3	D57	C2-CCC	9.72	9.74	33.9	54.4
D41	C2-900-1	9.29	9.66	35.6	52.2	D63	C2-CCC	9.73	9.77	37.0	54.1
D25	C2-900-12	10.0	10.0	35.4	54.4	E72	C2-CCC	9.82	10.2	35.9	58.3
D12	C2-900-12	10.0	10.8	36.1	55.2	E07	C2-CCC	9.69	10.1	34.9	57.9
D69	C2-900-12	9.44	10.2	34.2	54.2	E22	C2-CCC	8.99	9.38	31.8	53.4
D43	C2-900-192	9.91	10.3	34.8	55.5	D72	C2-Q	10.2	10.7	35.9	55.7
D07	C2-900-192	9.69	10.0	33.4	54.3	D62	C2-Q	10.1	10.7	35.9	55.4
D09	C2-900-192	9.62	10.3	37.4	53.7	D33	C2-Q	10.0	10.4	37.7	53.9
D51	C2-900-24	9.82	9.92	35.3	54.3	E23	C2-Q	9.62	10.3	34.9	55.8
D35	C2-900-24	11.2	11.1	39.5	62.5	E02	C2-Q	9.54	9.78	34.9	54.8
D20	C2-900-24	9.04	9.80	33.6	51.8	E37	C2-Q	9.85	11.0	35.6	57.4
D65	C2-900-3	9.32	9.56	32.4	51.4	F47	C2-Q	10.2	10.8	35.9	55.2
D03	C2-900-3	9.20	9.85	33.7	51.0	F49	C2-Q	9.92	15.2	36.3	54.9
D58	C2-900-3	9.04	9.59	34.2	51.0	F21	C2-Q	9.76	11.2	37.3	55.5
D70	C2-900-384	10.3	10.5	36.1	57.2	G62	C4-CCC	12.4	7.86	54.1	74.5
D46	C2-900-384	10.0	10.2	35.8	55.6	G45	C4-CCC	12.0	6.85	53.9	70.9
D19	C2-900-384	10.1	10.3	38.6	56.3	G22	C4-CCC	12.3	7.07	54.7	76.1
D34	C2-900-48	9.87	10.1	35.1	54.5	H71	C4-CCC	12.2	7.30	53.3	71.3
D48	C2-900-48	9.70	10.0	33.4	54.8	H01	C4-CCC	12.3	7.23	53.7	73.5
D11	C2-900-48	9.73	10.1	38.1	54.2	H61	C4-CCC	12.2	7.29	54.2	71.7
D21	C2-900-6	9.61	10.0	34.5	53.2	F52	C4-Q	13.5	8.90	61.7	81.4
D40	C2-900-6	9.47	10.0	34.2	54.2	F22	C4-Q	12.9	9.23	63.2	76.0
D32	C2-900-6	9.63	10.3	36.2	53.5	F71	C4-Q	12.8	11.5	62.4	75.3
D49	C2-900-768	9.74	10.0	34.6	55.5	G17	C4-Q	12.6	8.46	56.8	74.6
D14	C2-900-768	9.82	9.89	34.6	55.8	G05	C4-Q	12.5	8.13	55.0	66.4
D23	C2-900-768	9.69	10.5	36.7	55.4	G74	C4-Q	12.1	7.96	60.5	76.2
D61	C2-900-96	10.2	10.3	36.4	55.3	H30	C4-Q	12.6	8.10	59.0	73.8
D53	C2-900-96	10.2	10.4	37.6	55.5	H17	C4-Q	12.6	8.14	57.9	76.0
D10	C2-900-96	9.75	10.4	36.7	55.0	H06	C4-Q	12.6	8.05	58.4	74.0

Table A-7. Measured Elemental Release of the PCT Leachates for the C4 – 418 Glass Samples

		Elemental Release from PSAL (mg/L)						Elemental Release from PSAL (mg/L)			
Solution Identifier	Original Sample ID	Li	B	Na	Si	Solution Identifier	Original Sample ID	Li	B	Na	Si
G53	C4-1000-1	13.63	8.7	64.0	81.9	H65	C4-500-192	13.4	8.7	64.1	78.7
G12	C4-1000-1	13.00	8.0	62.7	79.4	H08	C4-500-192	14.0	9.2	68.0	85.1
G30	C4-1000-1	13.07	8.0	62.0	80.5	H53	C4-500-192	13.5	8.9	65.0	79.9
G46	C4-1000-12	13.28	8.4	62.4	79.2	H40	C4-500-24	14.6	9.9	69.5	85.6
G47	C4-1000-12	13.05	8.3	61.7	79.7	H50	C4-500-24	13.9	9.3	66.0	83.4
G08	C4-1000-12	12.98	8.28	67.1	83.3	H46	C4-500-24	14.28	9.4	69.6	84.0
G36	C4-1000-192	13.24	8.3	63.2	80.1	H52	C4-500-384	15.9	10.5	71.8	88.2
G31	C4-1000-192	13.0	8.0	63.1	80.0	H15	C4-500-384	15.3	10.2	69.6	86.4
G65	C4-1000-192	12.92	8.6	62.4	79.7	H37	C4-500-384	15.3	10.2	70.9	88.0
G51	C4-1000-24	12.83	8.2	60.6	76.8	H68	C4-500-48	12.8	8.3	61.5	77.0
G02	C4-1000-24	12.76	7.9	62.0	76.7	H73	C4-500-48	13.03	8.3	62.6	77.0
G34	C4-1000-24	12.61	7.7	60.7	77.5	H11	C4-500-48	13.51	9.0	65.6	80.1
G33	C4-1000-3	13.04	8.1	61.4	77.9	H69	C4-500-768	15.9	10.3	67.7	86
G55	C4-1000-3	12.85	8.2	60.5	78.9	H25	C4-500-768	15.4	10.0	66.4	85.5
G49	C4-1000-3	12.79	7.8	60.7	78.8	H35	C4-500-768	15.7	10.2	67.7	85
G44	C4-1000-384	13.00	9.0	60.8	79.2	H72	C4-500-96	13.1	8.5	61.9	76.8
G56	C4-1000-384	12.72	7.98	61.7	76.7	H39	C4-500-96	13.15	8.4	62.6	77.6
G27	C4-1000-384	12.31	7.6	64.8	80.1	H27	C4-500-96	13.29	8.5	63.5	78.5
G66	C4-1000-48	12.83	8.4	59.2	77.1	F15	C4-600-12	12.35	9.0	56.5	69.0
G39	C4-1000-48	12.83	8.2	60.5	77.8	F04	C4-600-12	11.73	11.2	55.2	70.0
G04	C4-1000-48	12.25	7.7	63.0	77.6	F66	C4-600-12	11.65	8.7	57.1	72.5
G54	C4-1000-6	12.66	8.5	58.8	76.0	F44	C4-600-192	128.5	402.8	999	478
G50	C4-1000-6	12.26	7.5	57.9	74.3	F08	C4-600-192	128.5	403.8	1010	481
G29	C4-1000-6	12.56	7.5	59.4	77.0	F55	C4-600-192	128.8	407.2	1010	494
G43	C4-1000-768	12.23	7.46	56.7	74.4	F06	C4-600-24	13.04	8.4	60.1	77.4
G38	C4-1000-768	12.02	6.94	57.4	73.0	F12	C4-600-24	13.0	10.3	62.6	80.9
G21	C4-1000-768	12.58	6.51	55.8	66.1	F36	C4-600-24	12.26	8.9	60.0	71.7
G10	C4-1000-96	13.0	8.2	60.9	78.5	F41	C4-600-384	140	503	1210	555
G48	C4-1000-96	12.48	7.7	59.3	76.7	F28	C4-600-384	139	499	1210	556
G32	C4-1000-96	12.7	7.8	60.0	79.4	F25	C4-600-384	34	56	94	97

Table A-8. Measured Elemental Release of the PCT Leachates for the C4 – 418 Glass Samples

		Elemental Release from PSAL (mg/L)						Elemental Release from PSAL (mg/L)			
Solution Identifier	Original Sample ID	Li	B	Na	Si	Solution Identifier	Original Sample ID	Li	B	Na	Si
F31	C4-600-48	20.0	17.6	81.8	87.4	H45	C4-700-96	17.6	9.3	76.4	94.1
F14	C4-600-48	19.0	18.3	77.5	87.8	H22	C4-700-96	16.5	8.8	72.6	89.7
F43	C4-600-48	17.9	15.8	76.4	85.2	H44	C4-700-96	17.3	9.1	76.9	92.8
F20	C4-600-768	148	539	1270	589	H41	C4-800-12	13.93	8.4	67.3	82.8
F18	C4-600-768	144	517	1260	568	H62	C4-800-12	13.66	8.31	66.9	82.4
F62	C4-600-768	146	539	1260	595	H43	C4-800-12	13.69	8.33	67.6	82.4
F35	C4-600-96	103.0	196.1	552.5	330.3	H59	C4-800-192	12.60	7.85	62.8	78.8
F59	C4-600-96	102.8	191.7	557.2	315	H31	C4-800-192	13.26	8.18	66.9	83.7
F46	C4-600-96	103.6	194.5	534.8	324.9	H02	C4-800-192	13.23	8.10	65.6	81.2
F24	C4-700-12	13.25	8.7	62.4	78.6	H66	C4-800-24	12.99	7.89	62.3	77.4
F57	C4-700-12	12.72	8.11	63.6	77.0	H33	C4-800-24	13.30	8.11	65.6	79.9
F27	C4-700-12	12.77	10.08	62.9	75.5	H64	C4-800-24	13.81	8.43	68.1	83.1
H26	C4-700-192	54.7	13.0	113.1	160	H32	C4-800-3	13.47	8.16	64.6	80.0
H09	C4-700-192	51.3	12.5	113.2	158.6	H19	C4-800-3	12.94	7.82	61.8	78.4
H16	C4-700-192	53.9	13.4	118.9	166	H34	C4-800-3	13.40	8.23	65.2	80.4
F37	C4-700-24	13.40	8.0	63.0	76.9	H07	C4-800-384	13.48	8.22	67.7	83.2
F72	C4-700-24	12.7	7.6	62.7	77.5	H29	C4-800-384	12.16	7.37	60.7	74.4
F26	C4-700-24	12.69	10.3	64.6	80.4	H47	C4-800-384	12.57	7.77	63.5	77.7
H14	C4-700-384	54.5	13.7	119	164	H70	C4-800-48	13.62	8.19	66.2	81.1
H12	C4-700-384	53.1	13.1	115	160	H42	C4-800-48	13.53	8.20	66.1	81.6
H48	C4-700-384	53.4	13.2	114.1	168	H23	C4-800-48	12.28	7.6	61.6	76.0
H63	C4-700-48	13.68	7.8	66.4	79.5	H51	C4-800-6	13.35	8.21	64.0	79.4
H56	C4-700-48	13.31	7.64	64.4	80.7	H49	C4-800-6	12.73	7.77	62.5	78.8
H60	C4-700-48	13.02	7.50	62.4	75.8	H21	C4-800-6	12.90	7.74	62.9	77.2
F50	C4-700-6	12.93	8.59	59.8	77.0	H58	C4-800-768	12.45	7.49	60.5	76.1
F38	C4-700-6	12.26	8.17	59.5	72.5	H20	C4-800-768	12.15	7.49	59.1	76.3
F67	C4-700-6	12.17	7.88	62.5	75.7	H04	C4-800-768	12.40	7.5	61.2	76.0
H55	C4-700-768	53.7	18.2	150	173	H36	C4-800-96	12.42	7.5	59.8	74.1
H38	C4-700-768	52.0	17.6	142	168	H10	C4-800-96	12.49	7.56	59.9	77.4
H24	C4-700-768	55.0	18.6	140	171	H54	C4-800-96	12.61	7.9	62.3	76.6

Table A-9. Measured Elemental Release of the PCT Leachates for the C4 – 418 Glass Samples

		Elemental Release from PSAL (mg/L)			
Solution Identifier	**Original Sample ID**	**Li**	**B**	**Na**	**Si**
G14	C4-900-1	12.87	8.0	58.3	76.5
G61	C4-900-1	12.45	7.4	56.7	75.4
G42	C4-900-1	13.07	7.85	59.4	81.2
G09	C4-900-12	12.9	7.8	61.0	77.8
G35	C4-900-12	12.4	7.7	59.3	74.7
G72	C4-900-12	12.46	7.2	58.7	77.0
G60	C4-900-192	12.52	7.8	60.1	76.4
G73	C4-900-192	12.29	7.5	59.2	77.6
G20	C4-900-192	11.86	7.3	63.0	78.7
G63	C4-900-24	12.68	8.03	60.1	76.3
G58	C4-900-24	11.9	7.0	57.5	72.8
G19	C4-900-24	11.96	7.16	63.3	76.7
G11	C4-900-3	13.46	8.46	62.1	80.8
G37	C4-900-3	12.82	7.81	61.1	77.1
G23	C4-900-3	12.81	8.03	64.6	81.8
G18	C4-900-384	11.7	7.3	56.8	72.2
G26	C4-900-384	11.5	7.0	57.0	71.2
G69	C4-900-384	11.9	7.0	58.5	75.4
G70	C4-900-48	12.33	7.7	58.7	75.8
G06	C4-900-48	11.90	7.1	58.1	73.3
G01	C4-900-48	12.00	7.5	64.2	79.7
G25	C4-900-6	12.42	7.8	59.3	73.8
G52	C4-900-6	12.30	7.3	59.7	74.3
G59	C4-900-6	12.09	7.1	58.5	74.9
G64	C4-900-768	11.93	7.3	57.4	72.2
G16	C4-900-768	11.83	7.18	57.6	73.7
G71	C4-900-768	11.29	7.2	55.8	70.7
G13	C4-900-96	12.5	7.8	60.4	75.5
G68	C4-900-96	12.0	7.8	58.6	72.0
G41	C4-900-96	12.08	7.6	58.1	76.3

Distribution:

A. B. Barnes, 999-W
A.R. Shafer, 704-27S
B. A. Hamm, 766-H
B. J. Giddings, 786-5A
C. C. Herman, 999-W
C. J. Bannochie, 773-42A
C. L. Crawford, 773-42A
C. M. Jantzen, 773-A
D. A. Crowley, 773-43A
D. C. Sherburne, 704-S
D. D. Larsen, 766-H
D. H. Miller, 999-W
D. J. McCabe, 773-42A
D. K. Peeler, 999-W
E. W. Holtzscheiter, 704-
F. C. Johnson, 999-W
F. M. Pennebaker, 773-42A
H. B. Shah, 766-H
J. E. Occhipinti, 704-S
J. F. Iaukea, 704-30S
J. M. Bricker, 704-27S
J. M. Gillam, 766-H
J. P. Vaughan, 773-41A
J. W. Ray, 704-S
K. M. Fox, 999-W
M. A. Broome, 704-29S
M. E. Smith, 704-30S
M. E. Stone, 999-W
P.L. Lee, 773-42A
R. N. Hinds, 704-S
R. T. McNew, 704-27S
S. D. Fink, 773-A
S. L. Marra, 773-A
T. B. Edwards, 999-W
T. L. Fellinger, 704-26S
W. R. Wilmarth, 773-A