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Revision 0

NEPHELINE FORMATION POTENTIAL IN SLUDGE BATCH 4 (SB4) GLASSES

D.K. Peeler
T.B. Edwards
T.H. Lorier

April 2005

Immobilization Technology Section
Savannah River National Laboratory
Aiken, SC 29808

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Executive Summary

The effect of crystallization on glass durability is complex and depends on several interrelated factors including the change in residual glass composition, the formation of internal stress or microcracks, and the preferential attack at the glass-crystal interface. Perhaps one of the most significant effects is the type and extent (or fraction) of crystallization and the resulting change to the residual glass composition. A strong increase in glass dissolution (or decrease in durability) has been observed in previous studies in glasses that formed aluminum-containing crystals, such as $NaAlSiO_4$ (nepheline) and $LiAlSi_2O_6$, and crystalline SiO_2.

Although the addition of Al_2O_3 to borosilicate glasses enhances the durability of the waste form (through creation of network-forming tetrahedral Na^+-$[AlO_{4/2}]^-$ pairs), the combination of high Al_2O_3 and Na_2O can lead to the formation of nepheline ($NaAlSiO_4$). Given the projected high concentration of Al_2O_3 in SB4 and the potential use of a high Na_2O based glass (as a result of the use of a high Na_2O frit and/or a less washed sludge) to improve melt rate, the potential formation of nepheline in various SB4 systems is being assessed.

Li et al. (2003) indicate that sodium alumino-borosilicate glasses are prone to nepheline crystallization if their compositions projected on the Na_2O-Al_2O_3-SiO_2 ternary fall within the nepheline primary phase field. In particular, durable glasses with $SiO_2/(SiO_2+Na_2O+ Al_2O_3) > 0.62$, where the oxides are expressed as mass fractions in the glass, do not precipitate nepheline as their primary phase.

Twelve SB4-based glasses have been identified or classified as “prone to nepheline formation” using a “less conservative” discriminator value of 0.65. Ten of the 12 glasses are Frit 320 based, and 8 of these 10 target a 40% WL – independent of the SB4 blending scenario used. This is not unexpected due to the higher alkali content of Frit 320 (12% Na_2O) relative to Frit 418 (8% Na_2O) and the fact that as WLs increase, the Na_2O and Al_2O_3 concentrations increase and the SiO_2 concentrations decrease in this series of glasses. Using the “less conservative” value as a guide will not only increase the probability of forming nepheline but will also allow the assessment of several different blending scenarios, both frits, and different WLs which will provide valuable insight into the frit selection process for SB4. More specifically, blending strategies, frit compositions, and WLs that avoid nepheline formation could be used to guide the frit selection process or to make compositional adjustments to the frit. The durability of these 12 glasses (of both quenched and centerline canister cooled versions) will be measured with the results being documented in a subsequent report.

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LIST OF ACRONYMS

ARM	Approved Reference Material
ARP	Actinide Removal Process
ASTM	American Society for Testing and Materials
ccc	centerline canister cooled
CVS	composition variation study
DWPF	Defense Waste Processing Facility
EA	Environmental Assessment
HLW	high-level waste
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectroscopy
LM	lithium metaborate
MCC	Materials Characterization Center
NL [B]	normalized boron release (in g/L)
PCT	Product Consistency Test
PF	peroxide fusion
SB	sludge batch
SRL	Savannah River Laboratory
SRNL-ML	Savannah River National Laboratory – Mobile Lab
T_L	liquidus temperature
η	viscosity
WL	waste loading

1.0 INTRODUCTION

Crystallization (or devitrification) in nuclear waste glasses is an important consideration in terms of processing and product performance (i.e., durability of the final waste form) requirements. With respect to the impacts of crystallization on processing issues, the Defense Waste Processing Facility (DWPF) uses a liquidus temperature (T_L) model (Brown et al. 2001) and an imposed T_L limit for feed acceptability to avoid bulk devitrification within the melter. In terms of product quality or the durability of the waste form, the impacts of devitrification depend on the type and extent of crystallization.

For example, Jantzen and Bickford (1984) assessed the impact of spinel (nominally $NiFe_2O_4$), sodium iron silicate (acmite, $NaFeSi_2O_6$), and alkali silicate phases (Li_2SiO_3 and $NaAlSiO_4$ (nepheline)) on the durability of DWPF-type glasses as a function of heat treatment (quenched versus slow cooled). In that study, crystallization only occurred upon isothermal heat treatments (above 500°C) or slow cooling – the quenched glasses were homogeneous (void of devitrification). The results indicated that the formation of spinel had little or no effect on the durability of Savannah River Laboratory (SRL) 165- or SRL 131-based glasses, while the formation of acmite produced a small but noticeable increase in the rate of dissolution of the matrix glass. The formation of Li_2SiO_3 and $NaAlSiO_4$ (nepheline) only occurred in the SRL 131 glasses which resulted in a 2 – 3X decrease in the durability of the final glass product as compared to their quenched (non-crystallized) counterparts.[1] Jantzen and Bickford (1984) indicated that the more complex devitrification (in terms of the number of phases formed) that was observed in the SRL 131-based glasses was primarily due to the higher alkali content relatively to the SRL 165-based glasses. Given these results, Jantzen and Bickford (1984) concluded that "the effects of devitrification on the durability of the SRL waste glasses demonstrate that devitrification has less of an effect than compositional changes." That is, the differences in durability observed between the SRL 165 and SRL 131 glasses due to their compositional differences were greater than the impacts of devitrification within a specific glass system. With respect to Sludge Batch 4 (SB4), of particular interest is the formation of acmite and nepheline in the higher alkali based SRL 131 glasses (especially when coupled with the high Al_2O_3 content of these glasses similar to that projected for SB4 – the application to SB4 is discussed in Section 2.0).

Cicero et al. (1993) also studied the impact of devitrification on durability of DWPF-type glasses. In that study, seven DWPF glass composition as projected by the DWPF Waste Form Compliance Plan (WCP) were fabricated, heat treated (using isothermal holds at various temperatures and times), and subjected to the PCT.[2] The PCT response was then correlated with the type and extent (vol%) of crystallization as determined by X-ray diffraction (XRD) analysis. Trevorite (spinel), acmite, lithium metasilicate, and nepheline crystals were found by XRD in all seven glass composition (in particular when heat treated between approximately 600 and 900°C). The exception was the lack of lithium metasilicate in the Purex (high iron) glass. No detectable crystallization was found in the quenched (rapidly cooled) glasses. The XRD results were used to construct parabolic curves (i.e., vol% crystallization versus time), sigmoidal fractional ingrowth

[1] Jantzen and Bickford (1984) measured durability using a 24-hour static leach test developed by Corning Glass Works and a 28-day static leach test which (at the time) was suggested by the Materials Characterization Center (MCC) – now referred to as MCC-1.

[2] Four of the seven compositions (referred to as Batch #1 - #4) were based on projection from existing high-level inventories while three were hypothetical compositions (referred to as Blend, high aluminum (HM), and Purex (high iron)). Samples were heat treated at 500, 600, 700, 800, 900, 1000, and 1100°C for times of 0.75, 3, 12, 48, 192 or 768 hours. These times and temperatures are not expected during normal canister cooling or storage.

curves, and ultimately time – temperature – transformation (TTT) diagrams for each of the seven glasses. The TTT diagrams provide a map of the type(s) of crystals expected as a function of time and temperature for each glass composition. Primary phase regions (based on a single crystal type or the co-existence of multiple crystal types) were defined for each glass. In addition, Cicero et al. (1993) superimposed the expected centerline cooling temperature profile onto the TTT diagrams for each glass. Based on a review of how this cooling profile cross-cuts the primary phase regions, the formation of Trevorite, acmite, and/or lithium metasilicate would be expected in all seven glasses. Based on the projected ccc schedule, the formation of nepheline would only be anticipated in the Purex (high iron) glass. Cicero et al. (1993) indicated that the TTT diagram for the Purex glass was different than all other glasses primarily based on the tendency to crystallize nepheline at lower temperatures. This tendency was correlated to the interaction between the glass and the alumina crucibles used and the increase in $(Li_2O + Na_2O) / (SiO_2 + Al_2O_3)$ ratio compared to other compositions. With respect to the impact of crystallization on durability, the data suggested that the type and extent of devitrification ultimately determined the druabilty of the glass.

The impact of devitrification on durability of simulated nuclear waste glasses has also been evaluated by Kim et al. (1995). In that study, the durability response (as measured by the Product Consistency Test – PCT) (ASTM 2002) of over 120 simulated high level waste (HLW) glasses was assessed as a function of thermal heat treatment (quenched versus centerline canister cooled (ccc)). Again, the results of that study indicated that crystallization, depending on the type and extent (or fraction), can have an adverse effect on the chemical durability. More specifically, a strong increase in glass dissolution (or decrease in durability) was observed in glasses that formed aluminum-containing crystals, such as $NaAlSiO_4$ and $LiAlSi_2O_6$, and crystalline SiO_2 during the ccc treatment relative to their quenched counterparts (which were void of devitrification). Figure 1-1 compares the boron releases from quenched and ccc treated glasses as a function of volume fraction and type of crystalline phase formed. Based on the crystallinity of the ccc sample, glasses were classified into three groups: (1) glasses having no crystals, (2) glasses with total crystalline phase volume < 7 vol%, and (3) glasses with ≥ 7 vol% crystallization. Those glasses in which the effect of heat treatment resulted in no change to the PCT response lie along the 45° line in Figure 1-1. If the slow cooling (ccc) had a negative impact on the durability response, the glass lies above the 45° line (which passes through the origin) – the further above the line, the more severe the impact. Consider the set of glasses lying in the upper, left hand quadrant of Figure 1-1. X-ray diffraction results indicate that the formation of nepheline, $LiAlSi_2O_6$, and crystalline SiO_2 (all above the 7 vol% level as denoted by the closed circles) had a negative impact on the durability response as compared to their quenched (crystal-free) counterparts.

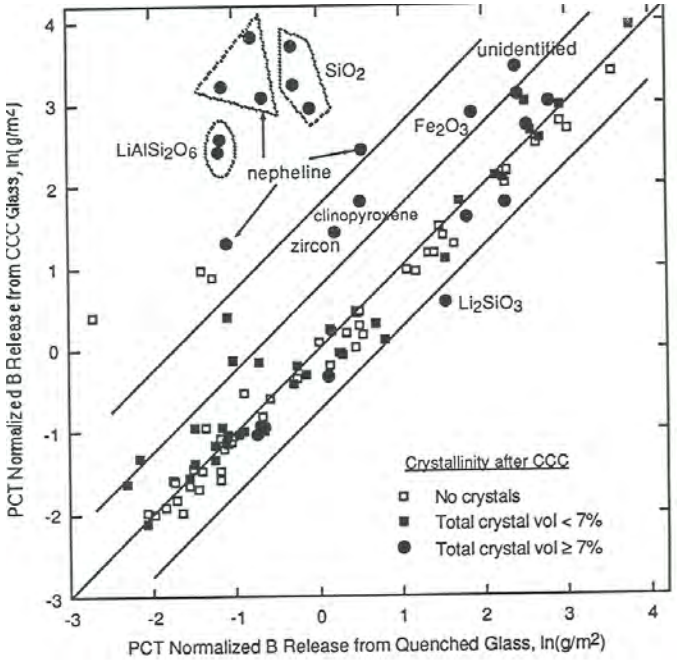

Figure 1-1. Normalized Boron Release (ln (g/m^2)) from Quenched and ccc Treated Glasses.

The effect of crystallization on glass durability is complex and depends on several interrelated factors including the change in residual glass composition, the formation of internal stress or microcracks, and the preferential attack at the glass-crystal interface. Kim et al. (1995) also predicted the impact of both crystal type and extent on the durability of a glass by calculating the change to the residual glass composition followed by model based predictions. Figure 1-2 (from Kim et al. 1995) shows the predicted normalized boron release from a specific simulated HLW glass (CVS1-1) as a function of mass fraction of various primary crystalline phases. The formation of $NaAlSiO_4$, $LiAlSi_2O_6$, and crystalline SiO_2 is predicted to have a detrimental impact on durability which agrees quite well with the experimental data (see Figure 1-1) and those data reported by Jantzen and Bickford (1984).

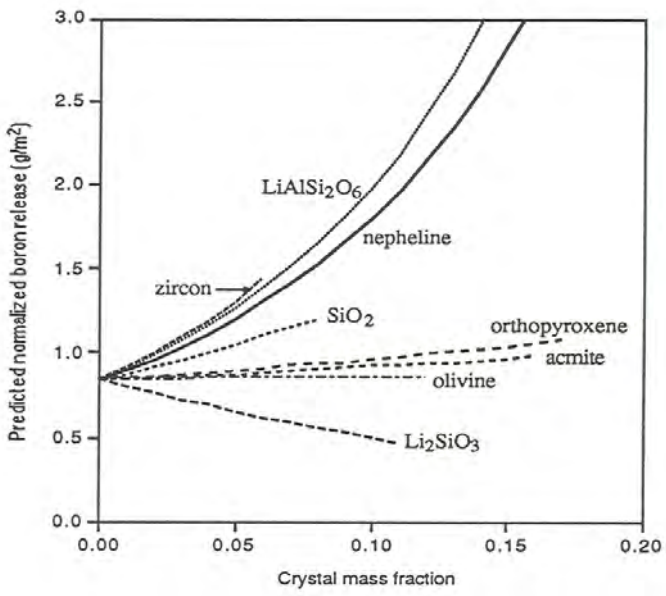

Figure 1-2. Predicted Normalized Boron Release from CVS1-1 Glass as a Function of Mass Fraction of Primary Crystalline Phases.

Although not summarized here, numerous studies (e.g., Bickford and Jantzen (1984), Jantzen et al. (1984), Bickford and Jantzen (1986), Spilman et al. (1986), Marra and Jantzen (1993), Li et al. (1997), and Riley et al. (2001)) have assessed the devitrification potential of HLW glass and its potential impact on durability. In general, these studies agree that the impact of devitrification on durability is dependent upon the type and extent of crystallization. However, there are some differences on the relative impacts (or magnitude) of the interrelated factors that ultimately determine the overall impact including the change in residual glass composition, the formation of internal stress or microcracks, and the preferential attack at the glass-crystal interface.

2.0 APPLICABILITY TO THE SB4 SYSTEM

The potential formation of nepheline and/or other aluminum/silicon-containing crystals is significant to the SB4 system due to the projected compositional views recently evaluated coupled with the frit development strategy. Compositional projections of SB4 by Lilliston (2005) indicate the sludge will be enriched in Al_2O_3 (relative to the Al_2O_3 concentration of previous sludge batches processed through the DWPF). Peeler and Edwards (2005a) have identified candidate frits (ranging in Na_2O concentrations from 8 – 13%) for the SB4 compositional projections, which produce relatively large projected operating windows. This effort was based on the use of a "sliding Na_2O scale" given the historical data linking the alkali content of the glass to melt rate. More specifically, previous research and DWPF processing have indicated that melt rate typically increases as the Na_2O content of the glass increases. The use of the "sliding Na_2O scale" concept was extremely effective in the development of Frit 418 for SB3 (Peeler and Edwards (2003)) and has been used to identify candidate frit compositions (relatively high in Na_2O) for SB4. However, the combination of a high Al_2O_3 sludge stream coupled with a desired high Na_2O based glass (as a result of the use of a high Na_2O frit and/or a less washed sludge) may result in the targeted glass compositions lying in the "phase field" prone to nepheline formation.

Although it is well known that the addition of Al_2O_3 to borosilicate glasses enhances the durability of the waste form (through creation of network-forming tetrahedral Na^+-$[AlO_{4/2}]^-$ pairs (Kim et al. (1995) and Li et al. (2003)), the combination of high Al_2O_3 and Na_2O can lead to the formation of nepheline ($NaAlSiO_4$). Because nepheline removes three moles of glass forming oxides (Al_2O_3 and $2SiO_2$) per each mole of Na_2O, nepheline formation can result in a severe deterioration of the chemical durability of the glass as previously described.

Li et al. (2003) indicate that compositional variation studies have shown that apart from Al_2O_3 and Na_2O, the glass components that significantly affect nepheline formation are B_2O_3 and SiO_2. The results from those studies lead to the following conclusions:

(1) Sodium alumino-borosilicate glasses are prone to nepheline crystallization if their compositions projected on the Na_2O-Al_2O_3-SiO_2 ternary fall within or close to the nepheline primary phase field. In particular, durable glasses with $SiO_2/(SiO_2+Na_2O+Al_2O_3) > 0.62$, where the chemical formula stand for the mass fractions in the glass, do not precipitate nepheline as their primary phase.
(2) Whereas Al_2O_3 and Na_2O tend to enhance nepheline formation, an increased fraction of B_2O_3 tends to suppress its formation.[3]
(3) Nepheline crystallization kinetics is rapid with nearly a zero induction time.

The work performed by Jantzen and Bickford (1984) and Cicero et al. (1993) also found a positive correlation between the temperature of crystallization of alkali silicate phases (e.g., Li_2SiO_3 and $NaAlSiO_4$) and the $(Li_2O+Na_2O)/(SiO_2+Al_2O_3)$ ratio for DWPF-type glasses. To avoid potential formation of these phases, waste glasses are typically formulated outside the nepheline primary phase field given the rapid crystallization kinetics and potential impacts on durability. This can have a negative impact on waste loading as lower waste loadings may minimize the formation potential.

3.0 AN ASSESSMENT OF NEPHELINE FORMATION POTENTIAL

With respect to SB4, Lilliston (2005) provided nominal sludge compositions for twenty SB4 blending scenarios. Based on those projected compositions, Peeler and Edwards (2005a) assessed various frit compositions with respect to model-based, projected operating windows. The primary frits covered Na_2O concentrations ranging from 8 wt% (in Frit 418) to 13% (in Frit 431). In addition to frit development efforts, Peeler and Edwards (2005b) also performed a preliminary assessment on the need to perform a variability study for SB4 using various SB4 compositional blending scenarios when coupled with the range of frit compositions. In that study, 48 glass compositions were identified that would provide the greatest challenge to the process property models in terms of model applicability (the primary objective of a variability study). The four specific blending scenarios used in that study were: (1) 1100 Can Baseline, (2) 1100 Can Max Al, Na; Min Mn, Ni, (3) 1100 Can Max Mg, and (4) 1100 Can Max Ni. Note, the "Max Ti" option as defined by Lilliston (2005) was not included given the TiO_2 concentration is ~ 0.03 wt% without the addition of the Actinide Removal Process (ARP) streams. Issues associated with TiO_2 impacts to the operating windows and/or model applicability were addressed with the addition of ARP Appendix K (referred to as ARP K) to these 4 sludge options (Peeler and Edwards 2005c).

[3] In terms of frit development efforts for SB4, Stone and Joseph (2001) have shown that increased concentrations of B_2O_3 tend to reduce melt rate. Therefore, if nepheline formation is a concern in the SB4 system, alternative frit compositions with increased concentrations of B_2O_3 may be used but perhaps at the expense of melt rate.

Each of the sludge compositions was combined with Frit 320 and with Frit 418 at waste loadings (WLs) of 30%, 35%, and 40%.[4] This led to 48 glass compositions, which are provided in Table 3-1 and Table 3-2. These tables of glass compositions provide a sampling of the glass systems that have been investigated as part of the paper studies supporting the SB4 frit development efforts (Peeler and Edwards 2005a, 2005b, and 2005c). In addition to supporting the assessment of the need for a variability study, the glasses also provided a technical basis for evaluating the potential formation of nepheline for projected SB4 blending scenarios. The use of the 1100 Baseline option provides a central comparison point as this option currently serves as the baseline flowsheet for SB4. The use of these different flowsheets also provides compositional variation from which the formation of nepheline can be evaluated. For example, the 1100 Can Max Al, Na case will be an interesting option as this case increases both Al_2O_3 and Na_2O concentrations in glass as waste loadings are increased. In addition, knowing that the primary source of SiO_2 stems from the frit, as WLs increase the SiO_2 content of the glass decreases – again increasing the probability of nepheline formation according to the discriminator developed by Li et al. (2003). Based on that theory, the probability of nepheline formation should increase as high-alkali frits are used and should further increase with higher WLs for SB4.

[4] Eight sludge compositions resulting from the four 1100 Canister baseline options with and without ARP Appendix K combined with 2 frit compositions (Frit 320 and Frit 418) at three different WLs (30, 35, and 40%) provided 48 glass compositions.

Table 3-1. Compositions of Select Glasses from the SB4 Glass Systems (Part 1: Al_2O_3 through MnO)

WL (%)	Frit ID	Sludge Option	Al_2O_3	B_2O_3	BaO	CaO	Ce_2O_3	Cr_2O_3	Cs2O	CuO	Fe_2O_3	K_2O	La_2O_3	Li_2O	MgO	MnO
30	32	1100 Can Baseline	6.80	5.60	0.05	0.67	0.06	0.08	0.00	0.03	7.80	0.31	0.03	5.60	0.58	1.75
35	32	1100 Can Baseline	7.94	5.20	0.06	0.78	0.07	0.09	0.00	0.03	9.10	0.36	0.03	5.20	0.68	2.04
40	32	1100 Can Baseline	9.07	4.80	0.06	0.89	0.08	0.10	0.00	0.03	10.4	0.41	0.04	4.80	0.78	2.34
30	41	1100 Can Baseline	6.80	5.60	0.05	0.67	0.06	0.08	0.00	0.03	7.80	0.31	0.03	5.60	0.58	1.75
35	41	1100 Can Baseline	7.94	5.20	0.06	0.78	0.07	0.09	0.00	0.03	9.10	0.36	0.03	5.20	0.68	2.04
40	41	1100 Can Baseline	9.07	4.80	0.06	0.89	0.08	0.10	0.00	0.03	10.4	0.41	0.04	4.80	0.78	2.34
30	32	1100 Can Max Al, Na; Min Mn, Ni, U	9.46	5.60	0.03	0.66	0.06	0.07	0.00	0.02	6.82	0.51	0.03	5.60	0.55	1.43
35	32	1100 Can Max Al, Na; Min Mn, Ni, U	11.0	5.20	0.04	0.77	0.07	0.08	0.00	0.03	7.95	0.60	0.03	5.20	0.64	1.67
40	32	1100 Can Max Al, Na; Min Mn, Ni, U	12.6	4.80	0.04	0.88	0.08	0.09	0.00	0.03	9.09	0.68	0.03	4.80	0.73	1.91
30	41	1100 Can Max Al, Na; Min Mn, Ni, U	9.46	5.60	0.03	0.66	0.06	0.07	0.00	0.02	6.82	0.51	0.03	5.60	0.55	1.43
35	41	1100 Can Max Al, Na; Min Mn, Ni, U	11.0	5.20	0.04	0.77	0.07	0.08	0.00	0.03	7.95	0.60	0.03	5.20	0.64	1.67
40	41	1100 Can Max Al, Na; Min Mn, Ni, U	12.6	4.80	0.04	0.88	0.08	0.09	0.00	0.03	9.09	0.68	0.03	4.80	0.73	1.91
30	32	1100 Can Max Mg	6.50	5.60	0.05	0.68	0.06	0.07	0.00	0.02	7.96	0.27	0.03	5.60	0.64	1.83
35	32	1100 Can Max Mg	7.58	5.20	0.06	0.79	0.07	0.09	0.00	0.03	9.29	0.32	0.03	5.20	0.75	2.14
40	32	1100 Can Max Mg	8.66	4.80	0.06	0.91	0.08	0.10	0.00	0.03	10.6	0.36	0.04	4.80	0.86	2.44
30	41	1100 Can Max Mg	6.50	5.60	0.05	0.68	0.06	0.07	0.00	0.02	7.96	0.27	0.03	5.60	0.64	1.83
35	41	1100 Can Max Mg	7.58	5.20	0.06	0.79	0.07	0.09	0.00	0.03	9.29	0.32	0.03	5.20	0.75	2.14
40	41	1100 Can Max Mg	8.66	4.80	0.06	0.91	0.08	0.10	0.00	0.03	10.6	0.36	0.04	4.80	0.86	2.44
30	32	1100 Can Max Ni	6.73	5.60	0.06	0.57	0.06	0.08	0.00	0.03	7.26	0.34	0.03	5.60	0.35	1.80
35	32	1100 Can Max Ni	7.85	5.20	0.07	0.66	0.07	0.10	0.00	0.03	8.47	0.40	0.03	5.20	0.40	2.10
40	32	1100 Can Max Ni	8.97	4.80	0.08	0.76	0.08	0.11	0.00	0.03	9.68	0.45	0.03	4.80	0.46	2.40
30	41	1100 Can Max Ni	6.73	5.60	0.06	0.57	0.06	0.08	0.00	0.03	7.26	0.34	0.03	5.60	0.35	1.80
35	41	1100 Can Max Ni	7.85	5.20	0.07	0.66	0.07	0.10	0.00	0.03	8.47	0.40	0.03	5.20	0.40	2.10
40	41	1100 Can Max Ni	8.97	4.80	0.08	0.76	0.08	0.11	0.00	0.03	9.68	0.45	0.03	4.80	0.46	2.40
30	32	SB4 1100 Can Baseline - App. K	6.35	5.60	0.05	0.64	0.06	0.07	0.00	0.02	7.42	0.28	0.03	5.60	0.53	1.72
35	32	SB4 1100 Can Baseline - App. K	7.41	5.20	0.05	0.74	0.07	0.08	0.00	0.03	8.66	0.33	0.03	5.20	0.62	2.00
40	32	SB4 1100 Can Baseline - App. K	8.47	4.80	0.06	0.85	0.08	0.10	0.00	0.03	9.90	0.38	0.04	4.80	0.71	2.29
30	41	SB4 1100 Can Baseline - App. K	6.35	5.60	0.05	0.64	0.06	0.07	0.00	0.02	7.42	0.28	0.03	5.60	0.53	1.72
35	41	SB4 1100 Can Baseline - App. K	7.41	5.20	0.05	0.74	0.07	0.08	0.00	0.03	8.66	0.33	0.03	5.20	0.62	2.00
40	41	SB4 1100 Can Baseline - App. K	8.47	4.80	0.06	0.85	0.08	0.10	0.00	0.03	9.90	0.38	0.04	4.80	0.71	2.29
30	32	SB4 1100 Can Max Al, Na; Min Mn, Ni	8.76	5.60	0.03	0.63	0.06	0.07	0.00	0.02	6.53	0.47	0.03	5.60	0.50	1.43
35	32	SB4 1100 Can Max Al, Na; Min Mn, Ni	10.2	5.20	0.04	0.73	0.07	0.08	0.00	0.02	7.61	0.55	0.03	5.20	0.59	1.67
40	32	SB4 1100 Can Max Al, Na; Min Mn, Ni	11.6	4.80	0.04	0.84	0.08	0.09	0.00	0.03	8.70	0.62	0.03	4.80	0.67	1.91
30	41	SB4 1100 Can Max Al, Na; Min Mn, Ni	8.76	5.60	0.03	0.63	0.06	0.07	0.00	0.02	6.53	0.47	0.03	5.60	0.50	1.43
35	41	SB4 1100 Can Max Al, Na; Min Mn, Ni	10.2	5.20	0.04	0.73	0.07	0.08	0.00	0.02	7.61	0.55	0.03	5.20	0.59	1.67
40	41	SB4 1100 Can Max Al, Na; Min Mn, Ni	11.6	4.80	0.04	0.84	0.08	0.09	0.00	0.03	8.70	0.62	0.03	4.80	0.67	1.91
30	32	SB4 1100 Can Max Mg - App. K	6.07	5.60	0.05	0.64	0.06	0.07	0.00	0.02	7.57	0.25	0.03	5.60	0.59	1.79
35	32	SB4 1100 Can Max Mg - App. K	7.09	5.20	0.05	0.75	0.07	0.08	0.00	0.03	8.83	0.29	0.03	5.20	0.69	2.09
40	32	SB4 1100 Can Max Mg - App. K	8.10	4.80	0.06	0.86	0.08	0.09	0.00	0.03	10.0	0.33	0.04	4.80	0.78	2.39
30	41	SB4 1100 Can Max Mg - App. K	6.07	5.60	0.05	0.64	0.06	0.07	0.00	0.02	7.57	0.25	0.03	5.60	0.59	1.79
35	41	SB4 1100 Can Max Mg - App. K	7.09	5.20	0.05	0.75	0.07	0.08	0.00	0.03	8.83	0.29	0.03	5.20	0.69	2.09
40	41	SB4 1100 Can Max Mg - App. K	8.10	4.80	0.06	0.86	0.08	0.09	0.00	0.03	10.0	0.33	0.04	4.80	0.78	2.39
30	32	SB4 1100 Can Max Ni - App. K	6.28	5.60	0.06	0.54	0.06	0.08	0.00	0.02	6.93	0.31	0.03	5.60	0.32	1.76
35	32	SB4 1100 Can Max Ni - App. K	7.33	5.20	0.07	0.63	0.07	0.09	0.00	0.03	8.09	0.36	0.03	5.20	0.37	2.06
40	32	SB4 1100 Can Max Ni - App. K	8.37	4.80	0.08	0.72	0.08	0.10	0.00	0.03	9.24	0.42	0.03	4.80	0.42	2.35
30	41	SB4 1100 Can Max Ni - App. K	6.28	5.60	0.06	0.54	0.06	0.08	0.00	0.02	6.93	0.31	0.03	5.60	0.32	1.76
35	41	SB4 1100 Can Max Ni - App. K	7.33	5.20	0.07	0.63	0.07	0.09	0.00	0.03	8.09	0.36	0.03	5.20	0.37	2.06
40	41	SB4 1100 Can Max Ni - App. K	8.37	4.80	0.08	0.72	0.08	0.10	0.00	0.03	9.24	0.42	0.03	4.80	0.42	2.35

Table 3-2. Compositions of Select Glasses from the SB4 Glass Systems (Part 2: Na_2O through ZrO_2 and Property Predictions)

WL (%)	Frit ID	Sludge Option	Na_2O	NiO	PbO	SO_4	SiO_2	ThO_2	TiO_2	U_3O_8	ZnO	ZrO_2	alkalis	Viscosity (Poise)	Del G_p	T_L(°C)
30	320	1100 Can Baseline	15.01	1.11	0.05	0.33	51.22	0.01	0.01	2.78	0.04	0.08	20.9	43.7	-	816.9
35	320	1100 Can Baseline	15.51	1.30	0.06	0.38	47.76	0.01	0.01	3.25	0.04	0.10	21.1	36.5	-	884.2
40	320	1100 Can Baseline	16.01	1.49	0.07	0.44	44.29	0.01	0.01	3.71	0.05	0.11	21.2	29.7	-	945.1
30	418	1100 Can Baseline	12.21	1.11	0.05	0.33	54.02	0.01	0.01	2.78	0.04	0.08	18.1	75.8	-	862.7
35	418	1100 Can Baseline	12.91	1.30	0.06	0.38	50.36	0.01	0.01	3.25	0.04	0.10	18.5	63.8	-	928.3
40	418	1100 Can Baseline	13.61	1.49	0.07	0.44	46.69	0.01	0.01	3.71	0.05	0.11	18.8	52.2	-	986.6
30	320	1100 Can Max Al, Na; Min Mn, Ni, U	15.26	0.44	0.06	0.33	51.36	0.01	0.01	1.58	0.03	0.07	21.4	54.7	-	780.5
35	320	1100 Can Max Al, Na; Min Mn, Ni, U	15.80	0.51	0.07	0.39	47.92	0.02	0.01	1.85	0.04	0.08	21.6	48.4	-	837.2
40	320	1100 Can Max Al, Na; Min Mn, Ni, U	16.35	0.58	0.08	0.44	44.48	0.02	0.01	2.11	0.04	0.10	21.8	42.0	-	887.0
30	418	1100 Can Max Al, Na; Min Mn, Ni, U	12.46	0.44	0.06	0.33	54.16	0.01	0.01	1.58	0.03	0.07	18.6	93.6	-9.450	818.1
35	418	1100 Can Max Al, Na; Min Mn, Ni, U	13.20	0.51	0.07	0.39	50.52	0.02	0.01	1.85	0.04	0.08	19.0	83.2	-9.464	872.3
40	418	1100 Can Max Al, Na; Min Mn, Ni, U	13.95	0.58	0.08	0.44	46.88	0.02	0.01	2.11	0.04	0.10	19.4	72.5	-9.478	919.1
30	320	1100 Can Max Mg	14.99	1.14	0.05	0.33	51.23	0.01	0.01	2.81	0.04	0.08	20.9	42.5	-	817.8
35	320	1100 Can Max Mg	15.49	1.32	0.05	0.38	47.76	0.01	0.01	3.28	0.04	0.09	21.0	35.3	-	885.9
40	320	1100 Can Max Mg	15.99	1.51	0.06	0.44	44.30	0.01	0.01	3.75	0.05	0.11	21.1	28.5	-	947.7
30	418	1100 Can Max Mg	12.19	1.14	0.05	0.33	54.03	0.01	0.01	2.81	0.04	0.08	18.1	73.8	-	864.3
35	418	1100 Can Max Mg	12.89	1.32	0.05	0.38	50.36	0.01	0.01	3.28	0.04	0.09	18.4	61.8	-	930.8
40	418	1100 Can Max Mg	13.59	1.51	0.06	0.44	46.70	0.01	0.01	3.75	0.05	0.11	18.7	50.2	-	990.1
30	320	1100 Can Max Ni	14.86	1.82	0.05	0.33	51.09	0.01	0.00	3.22	0.04	0.09	20.8	45.0	-	856.5
35	320	1100 Can Max Ni	15.34	2.12	0.06	0.38	47.60	0.01	0.01	3.75	0.05	0.11	20.9	37.8	-	930.2
40	320	1100 Can Max Ni	15.82	2.43	0.06	0.44	44.11	0.01	0.01	4.29	0.05	0.12	21.1	31.0	-	997.3
30	418	1100 Can Max Ni	12.06	1.82	0.05	0.33	53.89	0.01	0.00	3.22	0.04	0.09	18.0	78.0	-	906.5
35	418	1100 Can Max Ni	12.74	2.12	0.06	0.38	50.20	0.01	0.01	3.75	0.05	0.11	18.3	66.1	-	978.7
40	418	1100 Can Max Ni	13.42	2.43	0.06	0.44	46.51	0.01	0.01	4.29	0.05	0.12	18.7	54.5	-	1043.4
30	320	SB4 1100 Can Baseline - App. K	15.51	1.05	0.05	0.38	51.16	0.01	0.73	2.62	0.04	0.08	21.4	40.1	-	793.2
35	320	SB4 1100 Can Baseline - App. K	16.10	1.22	0.06	0.44	47.69	0.01	0.86	3.05	0.04	0.10	21.6	32.8	-	856.7
40	320	SB4 1100 Can Baseline - App. K	16.68	1.40	0.06	0.51	44.22	0.01	0.98	3.49	0.05	0.11	21.9	26.0	-	913.7
30	418	SB4 1100 Can Baseline - App. K	12.71	1.05	0.05	0.38	53.96	0.01	0.73	2.62	0.04	0.08	18.6	69.8	-	836.9
35	418	SB4 1100 Can Baseline - App. K	13.50	1.22	0.06	0.44	50.29	0.01	0.86	3.05	0.04	0.10	19.0	57.6	-	898.4
40	418	SB4 1100 Can Baseline - App. K	14.28	1.40	0.06	0.51	46.62	0.01	0.98	3.49	0.05	0.11	19.5	46.1	-	952.9
30	320	SB4 1100 Can Max Al, Na; Min Mn, Ni, U	15.74	0.43	0.06	0.38	51.29	0.01	0.73	1.53	0.03	0.07	21.8	49.2	-	764.1
35	320	SB4 1100 Can Max Al, Na; Min Mn, Ni, U	16.36	0.51	0.07	0.44	47.84	0.02	0.86	1.78	0.03	0.08	22.1	42.4	-	818.9
40	320	SB4 1100 Can Max Al, Na; Min Mn, Ni, U	16.99	0.58	0.08	0.51	44.39	0.02	0.98	2.04	0.04	0.09	22.4	35.7	-	867.0
30	418	SB4 1100 Can Max Al, Na; Min Mn, Ni, U	12.94	0.43	0.06	0.38	54.09	0.01	0.73	1.53	0.03	0.07	19.0	84.7	-9.946	800.8
35	418	SB4 1100 Can Max Al, Na; Min Mn, Ni, U	13.76	0.51	0.07	0.44	50.44	0.02	0.86	1.78	0.03	0.08	19.5	73.4	-	853.1
40	418	SB4 1100 Can Max Al, Na; Min Mn, Ni, U	14.59	0.58	0.08	0.51	46.79	0.02	0.98	2.04	0.04	0.09	20.0	62.1	-	898.4
30	320	SB4 1100 Can Max Mg - App. K	15.49	1.07	0.05	0.38	51.17	0.01	0.73	2.65	0.04	0.08	21.3	39.1	-	793.6
35	320	SB4 1100 Can Max Mg - App. K	16.08	1.25	0.05	0.44	47.70	0.01	0.86	3.09	0.04	0.09	21.6	31.8	-	857.7
40	320	SB4 1100 Can Max Mg - App. K	16.66	1.43	0.06	0.51	44.22	0.01	0.98	3.53	0.05	0.10	21.8	25.0	-	915.4
30	418	SB4 1100 Can Max Mg - App. K	12.69	1.07	0.05	0.38	53.97	0.01	0.73	2.65	0.04	0.08	18.5	68.2	-	837.9
35	418	SB4 1100 Can Max Mg - App. K	13.48	1.25	0.05	0.44	50.30	0.01	0.86	3.09	0.04	0.09	19.0	55.9	-	900.1
40	418	SB4 1100 Can Max Mg - App. K	14.26	1.43	0.06	0.51	46.62	0.01	0.98	3.53	0.05	0.10	19.4	44.4	-	955.3
30	320	SB4 1100 Can Max Ni - App. K	15.38	1.69	0.05	0.38	51.04	0.01	0.73	3.01	0.04	0.09	21.3	41.1	-	827.7
35	320	SB4 1100 Can Max Ni - App. K	15.94	1.97	0.05	0.44	47.55	0.01	0.85	3.51	0.04	0.10	21.5	33.8	-	896.5
40	320	SB4 1100 Can Max Ni - App. K	16.50	2.25	0.06	0.50	44.05	0.01	0.97	4.01	0.05	0.12	21.7	27.0	-	958.8
30	418	SB4 1100 Can Max Ni - App. K	12.58	1.69	0.05	0.38	53.84	0.01	0.73	3.01	0.04	0.09	18.5	71.7	-	875.0
35	418	SB4 1100 Can Max Ni - App. K	13.34	1.97	0.05	0.44	50.15	0.01	0.85	3.51	0.04	0.10	18.9	59.5	-	942.0
40	418	SB4 1100 Can Max Ni - App. K	14.10	2.25	0.06	0.50	46.45	0.01	0.97	4.01	0.05	0.12	19.3	47.9	-	1001.8

4.0 THE GLASS SELECTION PROCESS

The 48 compositions were screened using the nepheline discriminator (i.e., SiO_2 / (SiO_2+Na_2O+ Al_2O_3) > 0.62) developed by Li et al. (2003). Table 4-1 summarizes the predicted nepheline ratio for each of the 48 glass compositions identified by Peeler and Edwards (2005b).

Although Li et al. (2003) define the "line of demarcation" between glasses that are prone to nepheline formation from those that are not based on a value of 0.62, that line may be somewhat ill-defined. Therefore, to provide a higher probability of observing the formation of nepheline and the potential negative impact on durability, a value of 0.65 will be used to establish the glasses to be tested in this study. Using the "less conservative" value will not only increase the probability of forming nepheline but will also allow the assessment of several different blending scenarios, both frits (Frit 320 and Frit 418), and different WLs which will provide valuable insight into the frit selection process for SB4. More specifically, blending strategies, frit compositions, and WLs that avoid nepheline formation could be used to guide the frit selection process or to make compositional adjustments to the frit.

Given the use of the 0.65 discriminator value, there are twelve glasses from Table 4-1 (see shaded cells) that fall into the category of being prone to the formation of nepheline. The nominal compositions of these glasses (referred to as Neph-01 through Neph-12) are listed in Table 4-2 and are primarily based on the use of Frit 320 and WLs targeting 40%. In fact, 10 out of the 12 are Frit 320 based, and 8 of these 10 target a 40% WL – independent of the SB4 blending scenario used. This is not unexpected due to the higher alkali content of Frit 320 (12% Na_2O) relative to Frit 418 (8% Na_2O) and the fact that as WLs increase, the Na_2O concentrations increase and the SiO_2 concentrations decrease in this series of glasses. The two Frit 320-based glasses that target a lower WL (35%) are based on the 1100 Canister Max Al, Na case (with and without ARP K). As the nomenclature implies, this SB4 blending option yields the highest Na_2O content which allows lower WLs to be targeted yet still result in the classification of subject to nepheline formation using the "less conservative" 0.65 value.

Two Frit 418 based glasses fall into the "nepheline prone" region using the 0.65 value (i.e., Neph-4 and Neph-8). Again, these two glasses are based on the 1100 Canister Max Al, Na blending option (with and without ARP K) and target the highest WL being evaluated (40%). The lower Na_2O concentration (8%) in Frit 418 is off-set by the maximum Na_2O from the particular blending option driving their discriminator values into the "prone" region using the less conservative 0.65 value.

It should be noted that only two glasses (Neph-01 and Neph-02) would be classified as "prone to nepheline formation" using the guideline or discriminator value (0.62) defined by Li et al. (2003). Again, these glasses are based on Frit 320 and the 1100 Canister Max Al, Na case and target a 40% WL which agree with theory regarding the potential for nepheline formation.

As previously mentioned, opening the assessment of potential nepheline formation issues to a larger matrix than would otherwise be implemented (i.e., using the less conservative 0.65 value) will provide valuable information to the frit selection process. More specifically, if one were to speculate on the experimental results several outcomes are possible. In one extreme case, nepheline formation is either not observed or, if present, it has little or no practical impact on the measured durability response. If these results were realized, then the frit selection process would not have to rule out the possible use of Frit 320 as a candidate for SB4.

Another possible outcome would be that the Frit 320 – 1100 Canister Max Al, Na cases (at 40% and/or 35% WL) did show the development of nepheline and a significant impact on the measured durability of the product. If this were true, then frit development efforts may have to recommend a frit with lower Na_2O content (i.e., Frit 418 or some intermediate frit with 10% Na_2O) to avoid nepheline formation. Another option would be to ensure that the 1100 Canister Max Al, Na blending strategy (or an alternative strategy that resulted in a similar Na_2O concentration) was not realized assuming Frit 320 was used. The response to these possible experimental outcomes is in-line with the "sliding Na_2O scale" presented by Peeler and Edwards (2005a) for SB4. The only added insight into this overall strategy is not only to balance the Na_2O contents from the frit and the sludge to maintain relatively large operating windows and enhanced melt rates, but also to avoid nepheline formation potential. A possible outcome of this balancing act would be that for a given SB4 blending option, the Na_2O content of the frit may have to be lower to avoid nepheline formation which could have a negative impact on melt rate. If needed, further frit development efforts would strive to minimize any negative impacts to melt rate that result from lowering the Na_2O content to avoid nepheline formation issues.

Table 4-1. The 48 SB4 Glasses as a Function of WL, Frit ID, Sludge Type and Nepheline Ratio.

WL (%)	Frit ID	Type	Nepheline Ratio
40	320	1100 Can Max Al, Na; Min Mn, Ni, U	0.606
40	320	SB4 1100 Can Max Al, Na; Min Mn, Ni, U - App. K / ARP Stream	0.608
40	320	SB4 1100 Can Baseline - App. K / ARP Stream	0.637
40	418	1100 Can Max Al, Na; Min Mn, Ni, U	0.638
40	320	1100 Can Baseline	0.638
40	320	SB4 1100 Can Max Ni - App. K / ARP Stream	0.639
40	320	1100 Can Max Ni	0.640
40	418	SB4 1100 Can Max Al, Na; Min Mn, Ni, U - App. K / ARP Stream	0.640
35	320	1100 Can Max Al, Na; Min Mn, Ni, U	0.641
40	320	SB4 1100 Can Max Mg - App. K / ARP Stream	0.641
40	320	1100 Can Max Mg	0.642
35	320	SB4 1100 Can Max Al, Na; Min Mn, Ni, U - App. K / ARP Stream	0.643
35	320	SB4 1100 Can Baseline - App. K / ARP Stream	0.670
35	320	1100 Can Baseline	0.671
35	320	SB4 1100 Can Max Ni - App. K / ARP Stream	0.671
40	418	SB4 1100 Can Baseline - App. K / ARP Stream	0.672
35	320	1100 Can Max Ni	0.672
40	418	1100 Can Baseline	0.673
35	320	SB4 1100 Can Max Mg - App. K / ARP Stream	0.673
40	418	SB4 1100 Can Max Ni - App. K / ARP Stream	0.674
35	320	1100 Can Max Mg	0.674
30	320	1100 Can Max Al, Na; Min Mn, Ni, U	0.675
40	418	1100 Can Max Ni	0.675
35	418	1100 Can Max Al, Na; Min Mn, Ni, U	0.676
40	418	SB4 1100 Can Max Mg - App. K / ARP Stream	0.676
30	320	SB4 1100 Can Max Al, Na; Min Mn, Ni, U - App. K / ARP Stream	0.677

WL (%)	Frit ID	Type	Nepheline Ratio
40	418	1100 Can Max Mg	0.677
35	418	SB4 1100 Can Max Al, Na; Min Mn, Ni, U - App. K / ARP Stream	0.678
30	320	SB4 1100 Can Baseline - App. K / ARP Stream	0.701
30	320	1100 Can Baseline	0.701
30	320	SB4 1100 Can Max Ni - App. K / ARP Stream	0.702
30	320	1100 Can Max Ni	0.703
30	320	SB4 1100 Can Max Mg - App. K / ARP Stream	0.703
30	320	1100 Can Max Mg	0.704
35	418	SB4 1100 Can Baseline - App. K / ARP Stream	0.706
35	418	1100 Can Baseline	0.707
35	418	SB4 1100 Can Max Ni - App. K / ARP Stream	0.708
35	418	1100 Can Max Ni	0.709
35	418	SB4 1100 Can Max Mg - App. K / ARP Stream	0.710
35	418	1100 Can Max Mg	0.711
30	418	1100 Can Max Al, Na; Min Mn, Ni, U	0.712
30	418	SB4 1100 Can Max Al, Na; Min Mn, Ni, U - App. K / ARP Stream	0.714
30	418	SB4 1100 Can Baseline - App. K / ARP Stream	0.739
30	418	1100 Can Baseline	0.740
30	418	SB4 1100 Can Max Ni - App. K / ARP Stream	0.741
30	418	1100 Can Max Ni	0.741
30	418	SB4 1100 Can Max Mg - App. K / ARP Stream	0.742
30	418	1100 Can Max Mg	0.743

Table 4-2. Target Glass Compositions (in wt%) for the Nepheline Formation Study (Neph-01 through Neph-06).

Glass ID	Neph-01	Neph-02	Neph-03	Neph-04	Neph-05	Neph-06
WL (%)	40	40	40	40	40	40
Frit ID	320	320	320	418	320	320
Feed Type	1100 Can Max Al, Na; Min Mn, Ni, U	SB4 1100 Can Max Al, Na; Min Mn, Ni, U + ARP K	SB4 1100 Can Baseline + ARP K	1100 Can Max Al, Na; Min Mn, Ni, U	1100 Can Baseline	SB4 1100 Can Max Ni + ARP K
Al_2O_3	12.612	11.683	8.467	12.612	9.070	8.375
B_2O_3	4.800	4.800	4.800	4.800	4.800	4.800
BaO	0.043	0.042	0.062	0.043	0.065	0.076
CaO	0.884	0.839	0.848	0.884	0.893	0.723
Ce_2O_3	0.082	0.081	0.082	0.082	0.083	0.077
Cr_2O_3	0.092	0.087	0.096	0.092	0.101	0.105
CuO	0.029	0.028	0.032	0.029	0.034	0.032
Fe_2O_3	9.087	8.701	9.897	9.087	10.404	9.240
K_2O	0.682	0.624	0.377	0.682	0.410	0.416
La_2O_3	0.034	0.034	0.036	0.034	0.037	0.034
Li_2O	4.800	4.800	4.800	4.800	4.800	4.800
MgO	0.732	0.669	0.710	0.732	0.777	0.424
MnO	1.913	1.905	2.289	1.913	2.335	2.352
Na_2O	16.348	16.987	16.682	13.948	16.011	16.504
NiO	0.583	0.579	1.400	0.583	1.486	2.254
PbO	0.081	0.078	0.065	0.081	0.066	0.063
SO_4	0.442	0.508	0.506	0.442	0.439	0.504
SiO_2	44.482	44.389	44.218	46.882	44.293	44.055
ThO_2	0.020	0.018	0.013	0.020	0.014	0.011
TiO_2	0.010	0.979	0.977	0.010	0.009	0.975
U_3O_8	2.111	2.036	3.489	2.111	3.711	4.013
ZnO	0.040	0.039	0.049	0.040	0.051	0.050
ZrO_2	0.095	0.094	0.109	0.095	0.112	0.120
Nepheline Discriminator	0.606	0.608	0.637	0.638	0.638	0.639

Table 4-2 (continued). Target Glass Compositions (in wt%) for the Nepheline Formation Study (Neph-07 through Neph-12).

Row #	Neph-07	Neph-08	Neph-09	Neph-10	Neph-11	Neph-12
WL (%)	40	40	35	40	40	35
Frit ID	320	418	320	320	320	320
Feed Type	1100 Can Max Ni	SB4 1100 Can Max Al, Na; Min Mn, Ni, U + ARP K	1100 Can Max Al, Na; Min Mn, Ni, U	SB4 1100 Can Max Mg + ARP K	1100 Can Max Mg	SB4 1100 Can Max Al, Na; Min Mn, Ni, U + ARP K
Al_2O_3	8.969	11.683	11.035	8.097	8.664	10.222
B_2O_3	4.800	4.800	5.200	4.800	4.800	5.200
BaO	0.080	0.042	0.038	0.062	0.065	0.037
CaO	0.756	0.839	0.774	0.859	0.905	0.734
Ce_2O_3	0.078	0.081	0.072	0.081	0.083	0.071
Cr_2O_3	0.111	0.087	0.080	0.094	0.100	0.076
CuO	0.034	0.028	0.025	0.032	0.033	0.024
Fe_2O_3	9.680	8.701	7.951	10.088	10.613	7.613
K_2O	0.454	0.624	0.597	0.334	0.363	0.546
La_2O_3	0.035	0.034	0.030	0.036	0.037	0.029
Li_2O	4.800	4.800	5.200	4.800	4.800	5.200
MgO	0.462	0.669	0.641	0.784	0.859	0.585
MnO	2.404	1.905	1.674	2.387	2.443	1.667
Na_2O	15.816	14.587	15.805	16.659	15.987	16.364
NiO	2.426	0.579	0.510	1.425	1.514	0.507
PbO	0.064	0.078	0.071	0.062	0.063	0.068
SO_4	0.438	0.508	0.386	0.506	0.439	0.444
SiO_2	44.114	46.789	47.921	44.225	44.301	47.840
ThO_2	0.012	0.018	0.017	0.012	0.014	0.016
TiO_2	0.006	0.979	0.009	0.978	0.009	0.856
U_3O_8	4.287	2.036	1.847	3.528	3.753	1.781
ZnO	0.052	0.039	0.035	0.048	0.050	0.035
ZrO_2	0.124	0.094	0.083	0.105	0.107	0.082
Nepheline Discriminator	0.64	0.64	0.641	0.641	0.642	0.643

5.0 EXPERIMENTAL

Each glass will be prepared from the proper proportions of reagent-grade metal oxides, carbonates, H_3BO_3, and salts in 150-g batches. Once batched (SRNL 2002a), the glasses will be melted using Savannah River National Laboratory (SRNL) technical procedure "Glass Melting" (SRNL 2002b). In general, the raw materials will be thoroughly mixed and placed into a 95% Platinum/5% Gold 250-mL crucible. The batch will be placed into a high-temperature furnace at the target melt temperature of 1150°C. After an isothermal hold at 1150°C for 1.0 h, the crucible will be removed, and the glass poured onto a clean stainless steel plate and allowed to air cool. The pour patty will be used as a sampling stock for the various property measurements (i.e., chemical composition and durability).

To bound the effects of thermal history on the product performance, approximately 25 g of each glass will be heat treated to simulate cooling along the centerline of a DWPF-type canister (Marra and Jantzen 1993). This cooling regime is commonly referred to as the centerline canister cooled (ccc) curve.

5.1 Compositional Analysis

To confirm that the "as-fabricated" glasses correspond to the defined target compositions, a representative sample from each glass pour patty will be submitted to the SRNL Mobile Laboratory (SRNL-ML) for chemical analysis under the auspices of an analytical plan. The plan will identify the cations to be analyzed and the dissolution techniques (i.e., sodium peroxide fusion [PF] and lithium-metaborate [LM]) to be used. Each glass will be prepared in duplicate for each cation dissolution technique (PF and LM). Concentrations (as mass %) for the cations of interest will be measured by inductively coupled plasma – atomic emission spectroscopy (ICP – AES). The analytical plan will be developed in such a way as to provide the opportunity to evaluate potential sources of error. Glass standards will be intermittently run to assess the performance of the ICP – AES over the course of these analyses.

5.2 Product Consistency Test (PCT)

The PCT will be performed in triplicate on each quenched and ccc "Neph" glass to assess chemical durability using technical procedure "Standard Test Methods for Determining Chemical Durability of Nuclear Waste Glasses: The Product Consistency Test (PCT)" (ASTM 2002). Also included in this experimental test matrix will be the Environmental Assessment (EA) glass (Jantzen et al. 1993), the Approved Reference Material (ARM) glass, and blanks from the sample cleaning batch. Samples will be ground, washed, and prepared according to procedure (ASTM 2002). Fifteen milliliters of Type I American Society for Testing and Materials (ASTM) water will be added to 1.5 g of glass in stainless steel vessels. The vessels will be closed, sealed, and placed in an oven at 90 ± 2°C where the samples will be maintained for 7 days. The resulting solutions (once cooled) will be sampled (filtered and acidified), labeled (according to the analytical plan), and analyzed under the auspices of an analytical plan. The overall philosophy of the plan will be to provide an opportunity to assess the consistency (repeatability) of the PCT and analytical procedures in an effort to evaluate chemical durability of the "Neph" glasses. Normalized release rates will be calculated based on targeted, measured, and bias-corrected compositions using the average of the logs of the leachate concentrations.

6.0 SUMMARY

The effect of crystallization on glass durability is complex and depends on several interrelated factors including the change in residual glass composition, the formation of internal stress or microcracks, and the preferential attack at the glass-crystal interface. Perhaps one of the most significant effects is the type and extent (or fraction) of crystallization and the change to the residual glass composition. A strong increase in glass dissolution (or decrease in durability) has been observed in previous studies in glasses that formed aluminum-containing crystals, such as $NaAlSiO_4$ (nepheline) and $LiAlSi_2O_6$, and crystalline SiO_2.

Although the addition of Al_2O_3 to borosilicate glasses enhances the durability of the waste form (through creation of network-forming tetrahedral Na^+-$[AlO_{4/2}]^-$ pairs), the combination of high Al_2O_3 and Na_2O can lead to the formation of nepheline ($NaAlSiO_4$). Given the projected high concentration of Al_2O_3 in SB4 and the potential use of a high Na_2O based frit to improve melt rate, the potential formation of nepheline in various SB4 systems is being assessed. Li et al. (2003) indicate that sodium alumino-borosilicate glasses are prone to nepheline crystallization if their compositions projected on the Na_2O-Al_2O_3-SiO_2 ternary fall within or close to the nepheline primary phase field in the Na_2O-Al_2O_3-SiO_2 phase diagram. In particular, durable glasses with $SiO_2/(SiO_2+Na_2O+Al_2O_3) > 0.62$, where the chemical formula stand for the mass fractions in the glass, do not precipitate nepheline as their primary phase.

Forty-eight SB4 glass compositions were screened using the nepheline discriminator to assess the potential formation of nepheline. The 48 glasses were based on four specific blending scenarios as defined by Lilliston (2005) [(1) 1100 Can Baseline, (2) 1100 Can Max Al, Na; Min Mn, Ni, (3) 1100 Can Max Mg, and (4) 1100 Can Max Ni] and the use of Frit 418 and Frit 320. The use of the 1100 Can Baseline option provides a central comparison point as this option currently serves as the baseline flowsheet for SB4. The use of these different flowsheets also provides compositional variation from which the formation of nepheline can be evaluated. For example, the 1100 Can Max Al, Na case will be an interesting option as this case increases both Al_2O_3 and Na_2O concentrations in glass as waste loadings are increased. In addition, knowing that the primary source of SiO_2 stems from the frit, as WLs increase the SiO_2 content of the glass decreases – increasing the probability of nepheline formation according to the discriminator developed by Li et al. (2003). Based on that theory, the probability of nepheline formation should increase as high-alkali frits are used and should further increase with higher WLs.

Only two (Neph-01 and Neph-02) of the 48 glasses were classified as “prone to nepheline formation” using the guideline or discriminator value (0.62). These glasses are based on Frit 320 and the 1100 Canister Max Al, Na case and target a 40% WL, which agree with theory regarding the potential for nepheline formation. Although Li et al. (2003) define the “line of demarcation” between glasses that are prone to nepheline formation from those that are not based on a value of 0.62, that line may be somewhat ill-defined. Therefore, to provide a higher probability of observing the formation of nepheline and the potential negative impact on durability, a value of 0.65 was used to establish the glasses to be tested in this study. Twelve glasses were identified or classified as “prone to nepheline” formation using this “less conservative” value which will be fabricated and tested. Using the “less conservative” value will not only increase the probability of forming nepheline but will also allow the assessment of several different blending scenarios, both frits (Frit 320 and Frit 418), and different WLs which will provide valuable insight into the frit selection process for SB4. More specifically, blending strategies, frit compositions, and WLs that avoid nepheline formation could be used to guide the frit selection process or to make compositional adjustments to the frit.

The twelve nepheline glasses will be fabricated using standard procedures. The durability of these 12 glasses (of both quenched and centerline canister cooled versions) will be measured with the results being documented in a subsequent report.

7.0 REFERENCES

ASTM 2002. *Standard Test Methods for Determining Chemical Durability of Nuclear Waste Glasses: The Product Consistency Test (PCT)*, ASTM C-1285-2002.

Bickford, D.F. and CM Jantzen. 1984. "Devitrification of SRL Defense Waste Glass", *Sci. Basis for Nuclear Waste Management*, VII, G.L. McVay (ed). Elsevier Publ., New York, 557-565.

Bickford, D.F. and CM Jantzen. 1986. "Devitrification of Defense Nuclear Waste Glasses: Role of Melt Insolubles", *J. Non-Crystalline Solids*, 84 [1-3] 299-307.

Brown KG, CM Jantzen, and G Ritzhaupt. 2001. *Relating Liquidus Temperature to Composition for Defense Waste Processing Facility (DWPF) Process Control*, WSRC-TR-2001-00520, Westinghouse Savannah River Company, Aiken, South Carolina.

Jantzen, CM, DF Bickford, DG Karraker, and GG Wicks. 1984. "Time-Temperature-Transformation Kinetics in SRL Waste Glass", *Advances in Ceramics*, Volume 8, American Ceramic Society, Westerville, OH, 30-38.

Jantzen, CM, NE Bibler, DC Beam, CL Crawford, and MA Pickett. 1993. *Characterization of the Defense Waste Processing Facility (DWPF) Environmental Assessment (EA) Glass Standard Reference Material*, WSRC-TR-92-346, Revision 1, Westinghouse Savannah River Company, Aiken, South Carolina.

Jantzen, CM and DF Bickford. 1985. "Leaching of Devitrified Glass Containing Simulated SRP Nuclear Waste", *Sci. Basis for Nuclear Waste Management*, VIII, C.M. Jantzen, J.A. Stone and R.C. Ewing (eds.), Materials Research Society, Pittsburgh, PA 135-146.

Kim, DS, DK Peeler, and P Hrma. 1995. "Effect of Crystallization on the Chemical Durability of Simulated Nuclear Waste Glasses", *Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries*, Ceramic Transaction, Volume 61, pp. 177 – 185.

Li, H, JD Vienna, P Hrma, DE Smith, and MJ Schwieger. 1997. "Nepheline Precipitation in High-Level Waste Glasses – Compositional Effects and Impact on the Waste Form Acceptability", *Mat. Res. Soc. Proc.* 465, 261- 268.

Li, H, P Hrma, JD Vienna, M Qian, Y Su, and DE Smith. 2003. "Effects of Al_2O_3, B_2O_3, Na_2O, and SiO_2 on Nepheline Formation in Borosilicate Glasses: Chemical and Physical Correlations", *Journal of Non-Crystalline Solids*, 331 (2003) 202 – 216.

Lilliston, GR. 2005. *Development of Elemental Sludge Compositions for Variations of Sludge Batch 4 (SB4)*, CBU-PIT-2004-00011, Revision 1, Westinghouse Savannah River Company, Aiken, South Carolina.

Marra SL and CM Jantzen. 1993. *Characterization of Projected DWPF Glass Heat Treated to Simulate Canister Centerline Cooling*, WSRC-TR-92-142, Revision 1, Westinghouse Savannah River Company, Aiken, South Carolina.

Peeler, DK and TB Edwards. 2003. *Projected Opeating Windows for Various Sludge Batch 2/3 Blends: A Progression from a PAR to a MAR Assessment*, WSRC-TR-2003-00509, Revision 0, Westinghouse Savannah River Company, Aiken, South Carolina.

Peeler, DK and TB Edwards. 2005a. *Frit Development Efforts for Sludge Batch 4 (SB4): Model-Based Assessments*, WSRC-TR-2005-00103, Revision 0, Westinghouse Savannah River Company, Aiken, South Carolina.

Peeler DK and TB Edwards. 2005b. *A Preliminary Assessment of the Need for a Sludge Batch 4 Variability Study*, WSRC-TR-2005-00122, Revision 0, Westinghouse Savannah River Company, Aiken, South Carolina.

Peeler DK and TB Edwards. 2005c. *The Impact of the Actinide Removal Process (ARP) on the SB4 Projected Operating Windows*, WSRC-TR-2005-00123, Revision 0, Westinghouse Savannah River Company, Aiken, South Carolina.

Riley, BJ, JA Rosario, and P Hrma. 2001. *Impact of HLW Glass Crystallinity on the PCT Response*, PNNL-13491, Pacific Northwest National Laboratory, Richland, Washington.

Spilman, DB, LL Hench, DE Clark. 1986. "Devitrification and Subsequent Effects on the Leach Behavior of a Simulated Borosilicate Nuclear Waste Glass", *Nuclear and Chemical Waste Management*, Vol.6, pp. 107 – 119 (1986).

Savannah River National Laboratory (SRNL). 2002a. "Glass Batching," SRTC Procedure Manual, L29, ITS-0001, Westinghouse Savannah River Company, Aiken, South Carolina.

Savannah River National Laboratory (SRNL). 2002b. "Glass Melting," SRTC Procedure Manual, L29, ITS-0003, Westinghouse Savannah River Company, Aiken, South Carolina.

Stone, ME and JE Josephs. 2001. *Melt Rate Improvement for DWPF MB3: Melt Rate furnace Testing*, WSRC-TR-2001-00146, Revision 0, Westinghouse Savannah River Company, Aiken, South Carolina.

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