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Revision 0

"Low-Li_2O" Frits: Selecting Glasses that Support the Melt Rate Studies and Challenge the Current Durability Model

D.K. Peeler
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Immobilization Technology Section
Savannah River National Laboratory
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EXECUTIVE SUMMARY

During the progressive development of the cold cap model (as it applies to a potential melt rate predictive tool), the formation of an Al-Li-silicate phase was identified as an intermediate reaction phase that could possibly hinder melt rate for SB4. To test this theory, six glasses were designed (using Frit 320's composition as the baseline) to maintain a constant 20 wt% sum of alkali content (in frit) by varying Na_2O to Li_2O ratios. The Li_2O concentration ranged from 8 wt% down to 0% in either 2% or 1% increments with the differences being accounted for by an increase in Na_2O concentration. Although the primary objective of the "lower Li_2O" frits was to evaluate the potential for melt rate improvements, assessments of durability (as measured by the Product Consistency Test (PCT)) were also performed. The results suggest that durable glasses can be produced with these "lower Li_2O" frits should it be necessary to pursue this option for improving melt rate.

In addition to the series of glasses to support melt rate assessments, a series of frits were also developed to challenge the current durability model based on the limits proposed by Edwards et al. (2004). Although the "new" limits allow access into compositional regions of interest (i.e., higher alkali systems) which can improve melt rate and/or waste loading, there may still be "additional" conservatism. In this report, two series of glasses were developed to challenge the "new" durability limits for the SB4 system. In the first series, the total alkali of the Frit 320-based glasses (designed to support the melt rate program) was increased from 20 wt% to 21 wt% (in the frit), but the series also evaluated the possible impact of various Na_2O and Li_2O mass ratio differences. The second series pushed the alkali limit in the frit even further with frits containing either 22 or 24 wt% total alkali as well as various Na_2O and Li_2O mass ratios.

The results of the PCT evaluation indicated that all of the "higher alkali" glasses are acceptable as defined by their NL [B]'s as compared to the Environmental Assessment (EA) glass (with a 16.695 g/L NL [B]) – regardless of the compositional view (measured or target) or thermal heat treatment (quenched versus centerline canister cooled). The least durable glass (based on NL [B] and target compositions) was Low-Li-7 (quenched) with a NL [B] of 1.11 g/L. With the measured PCT responses being acceptable (i.e., all < 1.11 g/L), the results suggest additional conservatism exists within the current durability model even with the "proposed" limits. More specifically, the "proposed" limits still appear to restrict access to compositional regions of interest (higher alkali glasses) even though their measured PCT responses are acceptable.

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ARM	Approved Reference Material
ASTM	American Society for Testing and Materials
ccc	centerline canister cooled
DOE	Department of Energy
DWPF	Defense Waste Processing Facility
EA	Environmental Assessment
ΔG_P	preliminary glass dissolution estimator
ICP	inductively coupled plasma
MAR	Measurement Acceptability Region
MRF	melt rate furnace
NL [B]	normalized boron release (in g/L)
PCCS	Product Composition Control System
PCT	Product Consistency Test
Q	quenched
REDOX	REDuction/Oxidation
SB	sludge batch
SME	Slurry Mix Evaporator
SRAT	Sludge Receipt and Adjustment Tank
SMRF	slurry fed melt rate furnace
SRNL	Savannah River National Laboratory
SRNL-ML	Savannah River National Laboratory – Mobile Laboratory
T_L	liquidus temperature
η	viscosity
WAPS	Waste Acceptance Product Specifications
WL	waste loading

1.0 INTRODUCTION

In support of the Department of Energy's (DOE's) accelerated clean-up mission, the Savannah River National Laboratory (SRNL) has focused on increasing both waste loading (WL) and melt rate which ultimately play a major role in defining waste throughput for the Defense Waste Processing Facility (DWPF). With respect to melt rate, the general trend has been to increase the total alkali content of the glass by using a high-alkali based frit, a less washed sludge, or a combination of the two. Of particular interest has been the concept of a "Na_2O sliding scale", which has been used to compensate or balance the frit composition with the washing scenario to produce a glass meeting both process and product performance specifications. This approach was very successful as DWPF transitioned from an "over-washed" sludge batch 2 (SB2) to a "less washed" sludge batch 3 (SB3) which, when coupled with a specifically designed frit, improved waste throughput (higher targeted WLs and enhanced melt rates) dramatically.

The strategy for identifying or developing frits for a specific sludge batch is initially based on assessments using predictive models that govern the process control strategy for DWPF. Although candidate frit compositions are identified which satisfy process and product performance requirements over a projected WL range of interest, the paper study assessment does not evaluate melter performance issues related to melt rate and/or waste throughput. Therefore, experimental assessments of melt rate are required to ensure that a specific frit/waste combination that appears attractive on paper (in terms of projected operating windows) does not result in a difficult feed to process through the DWPF.

Over the past few years, the experimental melt rate program has been used as the final screening tool from which recommendations regarding the selection of a specific frit and targeted WL are made to DWPF. The primary experimental melt rate tools currently being used include crucible-scale tests (Stone and Josephs 2001), the dry-fed melt rate furnace (MRF) (Lorier et al. 2002, Lorier and Smith 2004), and the slurry-fed melt rate furnace (SMRF) (Smith et al. (2003), Smith et al. (2004)). Although very effective in terms of ranking various flowsheet options (e.g., different frit compositions or various sludge washing strategies) with respect to melt rate, the experimental melt rate program is both time consuming and labor intensive. Therefore, development of a melt rate model to guide frit development efforts and lessen the dependency on the experimental program would be highly desirable. If successful, such a model would benefit the overall program considerably by allowing more resources to be put on the evaluation of primary flowsheet options.

Choi (2000) describes a 4-stage cold cap model which has been used primarily to assess off-gas flammability issues for DWPF. Recent efforts have been made to extend the utility of this model to assess or rank relative melt rates for various DWPF flowsheet options (Choi et al. 2005). Initial assessments were made to rank or make pair-wise comparisons regarding the impact of frit composition, sludge washing, targeted reduction / oxidation (REDOX expressed as Fe^{+2}/Fe^{total}), and acid addition strategy on melt rate. Based on the success of those comparisons, assessments associated with the impacts of waste loading on melt rate and/or waste throughput for specific systems were made as well as evaluations regarding the impact of alkali addition sources on melt rate. During the progressive development of the cold cap model (as it applies to a potential melt rate predictive tool), the formation of an Al-Li-silicate phase was identified as an intermediate reaction phase that could possibly hinder melt rate for Sludge Batch 4 (SB4). If true, one could potentially adjust the frit composition (given it is the only source of Li in the glass system) to minimize or eliminate the formation of this Li-based phase and thus potentially enhance melt rate. To test this theory, a series of "lower Li_2O" based frits was designed using Frit 320's composition as the baseline (see Section 3.0 for more details). These "lower Li_2O" based frits were then used to assess melt rate with SB4. Although the primary objective of the "lower Li_2O" frits was to

evaluate the potential for melt rate improvements, assessments of durability (as measured by the Product Consistency Test (PCT)) were also performed and are documented in this report. The underlying objective was to provide a preliminary assessment of durability assuming melt rate results suggested that this compositional trend be pursued.

In addition to the series of glasses to support melt rate assessments, frits were also developed to challenge the current durability model based on the limits proposed by Edwards et al. (2004). Previous studies (Peeler and Edwards 2002; Peeler et al. 2004a) have indicated that as higher alkali glass systems are pursued, a transition can occur in which predictions of durability and/or low viscosity begin limiting upper waste loadings rather than predictions of liquidus temperature – the limiting property for current (Frit 418/SB3) and previous DWPF sludge batch processing. Peeler et al. (2001), Cozzi et al. (2003), and Peeler et al. (2004b) have suggested that the current durability model can lead to conservative decisions during the Slurry Mix Evaporator (SME) acceptability process.[1] More specifically, the model (using its original limits) has restricted access to glass composition regions that could potentially enhance melt rate, WL, or waste throughput by classifying a specific glass composition as "unacceptable" whose experimentally determined durability (as defined by the PCT (ASTM 2002)) is "acceptable" relative to the Environmental Assessment (EA) glass (Jantzen et al. 1993). For example, Peeler et al. (2001) found that the Frit 304 – SB2 system was classified as unacceptable (based on model predictions of durability), but when durability was experimentally determined, the results were well below the acceptance limits (e.g., 1.07 g/L compared to 16.695 g/L reported for EA). More recent results (Peeler et al. 2004b) assessed the potential use of Frit 320 with SB3. As with the Frit 304 – SB2 system, the high-alkali content of Frit 320 when coupled with SB3 resulted in predictions of durability restricting its potential recommendation. Experimental determination of durability for two glasses within the Frit 320 – SB3 system (at 35 and 40% WL, ADT-5 and ADT-6, respectively) resulted in normalized boron releases (NL [B]) of ~1.5 g/L and ~2.0 g/L, respectively. Subsequent assessments of melt rate by Smith et al. (2004) indicated that the melt rate for the Frit 320 – SB3 system at 35% WL was higher than the Frit 418 – SB3 system at 35% WL – potentially a second significant opportunity missed to increase melt rate and/or waste throughput strictly due to the conservative decisions made by the current durability model.

To address this issue, an alternative strategy to improve WL and/or melt rate was proposed by Edwards et al. (2004) by establishing "less conservative" SME acceptability limits for durability without compromising product quality. Although the "new" limits allow access into compositional regions of interest (i.e., higher alkali systems) which can improve melt rate and/or waste loading, there may still be "additional" conservatism. In this report, two series of glasses were developed to challenge the "new" durability limits within the SB4 system. In the first series, the total alkali of the Frit 320-based glasses (designed to support the melt rate program) was increased from 20 wt% to 21 wt% (in the frit), and the series also evaluated the possible impact of various Na_2O and Li_2O mass ratio differences. The second series pushed the alkali limit in the frit even further with frits containing either 22 or 24 wt% total alkali as well as various Na_2O and Li_2O mass ratios. Again, the objective of these last two series of glasses was to challenge the durability model (using the less conservative limits as proposed by Edwards et al. (2004)) to assess if there is additional conservatism in the model which may provide further incentive to evaluate other alternative durability approaches.

This report provides a summary of the results associated with frits developed to support both melt rate testing and to challenge the current durability model. The compositional basis of the sludge

[1] Given the conservatism in the original ΔG_P limits, Edwards et al. (2004) provide a detailed discussion of the development of alternative (or less conservative) durability limits within the existing ΔG_P structure. These new ΔG_P limits have been proposed for implementation at DWPF but are not currently being used for the SB3 system.

used to support these tests is defined in Section 2.0. Candidate frits designed to support melt rate assessments and to challenge the durability model are defined in Section 3.0. In Section 4.0, model based assessments are summarized which indicate the projected operating windows (or lack thereof) and the critical property that restricts access to higher WLs or completely eliminates the projected operating window. Based on the model-based assessments, specific glass compositions are defined from which experimental measurements of durability are performed. The specific glass compositions are defined in Section 5.0. Section 6.0 provides the experimental basis for this effort. Section 7.0 summarizes the results of the compositional analysis of the as-fabricated glasses and the measured durability responses. Section 8.0 and 9.0 provide a summary of the work and recommendations for future work, respectively.

2.0 Baseline Sludge Composition

Lilliston (2005) provided 20 different blended scenarios for SB4. The 1100 Canister Baseline option was selected as the baseline sludge composition to support experimental assessments of durability.[2] Table 2-1 summarizes the 1100 Canister Baseline sludge composition (calcined oxide basis in wt%).[3]

Table 2-1. Nominal SB4 Composition Used to Support Testing (from Lilliston 2005).

Oxide	wt%
Al_2O_3	22.675
BaO	0.162
CaO	2.233
Ce_2O_3	0.208
Cr_2O_3	0.252
CuO	0.084
Fe_2O_3	26.009
K_2O	1.025
La_2O_3	0.093
MgO	1.942
MnO	5.838
Na_2O	22.028
NiO	3.715
PbO	0.166
SO_4	1.099
SiO_2	2.732
ThO_2	0.035
TiO_2	0.021
U_3O_8	9.276
ZnO	0.128
ZrO_2	0.279
Total	100.00

[2] It is noted that prior to the issuance of this report, Elder (2005) issued revised SB4 compositions based on a decision not to include Tank 4 in SB4. The primary difference between the 1100 Canister Option provided by Lilliston (2005) and the revised baseline sludge provided by Elder (2005) is the projected Al_2O_3 concentration. Elder (2005) reports the projected Al_2O_3 concentration to be ~ 31% (calcined oxide basis) relative to the 22.65% value shown in Table 3-1. Although differences do exist between the two projections, use of either sludge composition will meet the intent of this study as well as provide additional data to support SB4 flowsheet development activities.

[3] Elementals for the 1100 Canister Baseline option reported by Lilliston (2005) were converted to oxides and normalized to represent the Sludge Receipt and Adjustment Tank (SRAT) product.

3.0 CANDIDATE FRITS

Peeler and Edwards (2005) indicated that Frit 320 was a candidate for the SB4 1100 Canister Baseline option. The projected operating window (based on assessments of predicted properties relative to the SME acceptability criteria) was 25 – 43% WL with predictions of low viscosity (low η) limiting access to higher WLs. It should be noted that the "proposed" durability limits as defined by Edwards et al. (2004) were used in that assessment. If the original durability limits were used, Frit 320 would not be a viable candidate for this sludge option as the high alkali content of the frit coupled with the relatively high alkali content of the sludge would result in predictions of durability limiting its use.

3.1 "20% Total Alkali" Series

As discussed in Section 1.0, there are three primary series of glasses to assess in this study. The first was based on the concept of "lower Li_2O" frits to improve melt rate given the results of thermodynamic modeling efforts. This series of frits is summarized in Table 3-1. Frit 320 is considered to be a "high alkali" based frit with 8 wt% Li_2O and 12 wt% Na_2O. The "low Li_2O" frit series maintains a constant sum of alkali content (on a mass basis) at 20 wt%, but reduces the Li_2O concentration from 8 wt% down to 0 wt% in either 2% or 1% increments with the differences being accounted for by an increase in Na_2O concentration. Although an equivalent sum of alkali mass basis is maintained, this series of Li_2O concentrations transitions from a 1.41:1 molar Na_2O:Li_2O ratio (Frit 320), to a 1:1 molar ratio (Frit 320r), and ultimately to a 1:14:1 molar ratio (Frit 320h). Note Frit 320i has no Li_2O – only 20 wt% Na_2O by mass.

Table 3-1. Frit 320 and the "Low Li_2O" Based Frit Compositions (wt%)

Frit ID	B_2O_3	Li_2O	Na_2O	SiO_2		Σalkali
320	8	8	12	72		20
320f	8	6	14	72		20
320r	8	5	15	72		20
320g	8	4	16	72		20
320h	8	2	18	72		20
320i	8	0	20	72		20

3.2 Challenge to "Proposed" Durability Limits

In the assessments performed by Peeler and Edwards (2005), Frit 320 was viable with the SB4 1100 Canister Baseline option given the use of the "proposed" durability limits. Also in that assessment, a frit containing 13 wt% Na_2O was assessed, which when coupled with the 1100 Canister Baseline option resulted in predictions of durability (even with the "proposed" limits) limiting access to lower WLs. The implication is that Frit 320 appears to be "on the edge" in terms of total alkali content and its impact on projected operating windows of interest.

Table 3-2 summarizes a series of frits developed to "challenge" the proposed durability limits when coupled with SB4 at 35% WL (see Section 4.0 for details regarding the model based assessments) while also evaluating the impact of lower Li_2O concentrations. Consider Frit 320n through Frit 320q in Table 3-2. This series of frits increases the total alkali content from 20 wt% (Frit 320 and the initial melt rate series – see Table 3-1) to 21% as well as partitioning the Na_2O

and Li_2O differently. Frit 320n is based on 15 wt% Na_2O and 6 wt% Li_2O. Subsequent frits are based on a 2% incremental increase in Na_2O (maximum being 21% in Frit 320q) with the difference being accounted for by a reduction in the Li_2O concentration. Note Frit 320 (20 wt% total alkali) is shown in Table 3-2 for comparison purposes.

Table 3-2. Candidate Frits Based on a 21 wt% Total Alkali Content.

Frit ID	B_2O_3	Li_2O	Na_2O	SiO_2		Σalkali
320	8	8	12	72		20
320n	8	6	15	71		21
320o	8	4	17	71		21
320p	8	2	19	71		21
320q	8	0	21	71		21

Table 3-3 summarizes a series of frit compositions (listed as Frit 320j through Frit 320m) that increase the total alkali content from 21% to either 22 or 24 wt%. Based on previous assessments, this series of frits should result in complete elimination of the projected operating windows due to durability predictions even with the "proposed" limits (see Section 4.0 for more details). This series of frits also increases the Na_2O concentration from 16% up to 22% with Li_2O values decreasing from 6% down to 0%. Frit 320l pushes the total alkali envelope the furthest given it targets a total alkali content of 24%. Again, Frit 320 is shown in Table 3-3 for comparison purposes.

Table 3-3. Candidate Frits Based on a 22 or 24 wt% Total Alkali Content.

Frit ID	B_2O_3	Li_2O	Na_2O	SiO_2		Σalkali
320	8	8	12	72		20
320j	8	6	16	70		22
320k	8	4	18	70		22
320l	8	2	22	68		24
320m	8	0	22	70		22

4.0 MAR ASSESSMENTS

Table 4-1 summarizes the model based Measurement Acceptability Region (MAR) assessments for the various frit – SB4 (1100 Canister Baseline) options over WLs from 25 – 60%. The property predictions assessed in this study included durability (PCT [ASTM 2002] response in terms of the preliminary glass dissolution estimator (ΔG_P) (Jantzen et al. 1995)), viscosity at 1150°C ($\eta_{1150°C}$), liquidus temperature (T_L), and Al_2O_3 and alkali concentrations. Jantzen et al. (1995) and Brown et al. (2001) provide a more detailed discussion on the development of these models. To establish or project operational windows for sludge/frit scenarios of interest, the predicted properties must be assessed relative to established acceptance criteria. Acceptable predicted properties for this assessment were based on the MAR limits. Brown, Postles, and Edwards (2002) provide a detailed discussion of how the MAR limits are utilized in the Product Composition Control System (PCCS). The results of the MAR assessment are discussed separately for each glass series in terms of meeting the task objectives.

Table 4-1. MAR Based Projected Operating Windows.

	20 wt% Total Alkali Series					
	Low-Li-1	**Low-Li-2**	**Low-Li-3**	**Low-Li-4**	**Low-Li-5**	**Low-Li-6**
	Frit 320	**Frit 320f**	**Frit 320g**	**Frit 320h**	**Frit 320i**	**Frit 320r**
1100 Canister Baseline	25 – 43 (low η)	25 – 45 (T_L)	25 – 45 (T_L)	25 – 45 (T_L)	(high η) 30 – 45 (T_L)	25 – 45 (T_L)
Na_2O (wt%)	12	14	16	18	20	15
Li_2O (wt%)	8	6	4	2	0	5
Σalkali	20	20	20	20	20	20
	21 wt% Total Alkali Series					
	Low-Li-11	**Low-Li-12**	**Low-Li-13**	**Low-Li-14**		
	Frit 320n	**Frit 320o**	**Frit 320p**	**Frit 320q**		
1100 Canister Baseline	(ΔG_P) 33 – 44 (low η)	(ΔG_P) 37 – 46 (T_L)	(ΔG_P) 40 – 46 (T_L)	(ΔG_P) 43 – 46 (T_L)		
Na_2O (wt%)	15	17	19	21		
Li_2O (wt%)	6	4	2	0		
Σalkali	21	21	21	21		
	22 and 24 wt% Total Alkali Series					
	Low-Li-7	**Low-Li-8**	**Low-Li-9**	**Low-Li-10**		
	Frit 320j	**Frit 320k**	**Frit 320l**	**Frit 320m**		
1100 Canister Baseline	- (ΔG_P)	- (ΔG_P)	- (ΔG_P)	- (ΔG_P)		
Na_2O (wt%)	16	18	22	22		
Li_2O (wt%)	6	4	2	0		
Σalkali	22	22	24	22		

4.1 "20 wt% Total Alkali" Series

This series of glasses were designed specifically to support assessment of melt rate – not designed to challenge durability predictions. The MAR assessments for the "20 wt% total alkali" series indicate that transitioning to a higher Na_2O content increases the projected operating window relative to the Frit 320 – SB4 system. More specifically, the Frit 320 – SB4 system has a projected operating window of 25 – 43% WL with low viscosity limiting access to higher WLs. Increasing the Na_2O content from 12 wt% to 14 wt% while simultaneously reducing the Li_2O content (Frit 320f) increases the upper WL limit from 43% (low viscosity limited) to 45% (T_L limited). The transition from a low viscosity limited system to a T_L limited system agrees with glass science theory as (in general) Li_2O lowers the viscosity of a glass system more dramatically as compared to Na_2O. Thus, by decreasing the Li_2O content, the predicted viscosities of the glasses at 44 and 45% WL increase and become "acceptable" at the MAR. This opens up the operating window to higher WLs and transitions the limiting property from low viscosity to T_L. However, the increase in Na_2O from 12% to 14 wt% (or reduction in Li_2O from 8 wt% to 6 wt%) appears to be a critical step as further Na_2O increases (or Li_2O reductions) do not have the predicted positive impact (i.e., projected operating windows for 320r, 320g, and 320h are still limited to 45% WL). This is based on the fact that T_L now dictates these systems, and the T_L model is apparently not as sensitive to the varying ratios of Li_2O and Na_2O – but may be driven based on the total alkali content which is being held constant at 20 wt%. At 0% Li_2O (Frit 320i), the projected operating window becomes limited by high viscosity on the low WL side (25 – 29%) while remaining limited at 45% WL on the upper WL side due to T_L predictions.

4.2 "21 wt% Total Alkali" Series

As previously discussed, this series of glasses (Frit 320n through Frit 320q) was developed to "challenge" the proposed durability limits and to begin "pushing the envelope" in terms of Na_2O additions (data that could potentially be used to improve melt rate and/or waste loading for SB4 or future sludge batches). The MAR results suggest that the 1% increase in total alkali content does introduce significant limitations to the projected operating windows via predictions of durability – meeting programmatic objectives for this series. Although projected operating windows do exist for this series of frits, durability (represented by the ΔG_P symbol in Table 4-1) begins to limit access to lower WLs. That is, at lower WLs the model suggests that durability (as measured by the PCT) will be an issue for glasses based on this series of frits.

As the Na_2O concentration (in the frit) increases for this series, the minimum "acceptable" WL also increases (durability becomes more of an issue with the higher Na_2O based frits and/or the partitioning of Na_2O to Li_2O). With lower WLs continuing to be restricted as a function of Na_2O content, the overall window size continually decreases given the upper WL limit is relatively consistent (44 – 46%). It should also be noted that a 1% increase in total alkali content (from 20% to 21 wt%) apparently reduces the predicted T_L values which typically results in access to higher WLs (46% WL for this series as compared to 45% WL for the "20 wt% total alkali" series developed to support melt rate). The Frit 320n system is an exception to this latter statement as this system continues to be low viscosity limited (as is the Frit 320 based system). However, comparing Frit 320n to Frit 320, it appears that although the total alkali content has increased by 1%, the difference in partitioning or ratios does have a positive impact on the upper WL achievable.

4.3 "22 wt% or 24 wt% Total Alkali" Series

The primary purpose of this series of frits (Frit 320j through Frit 320m) was to continue pushing the "total alkali envelope" to the point where durability predictions become a significant issue. Based on the MAR results as shown in Table 4-1, this objective was accomplished given there are no operating windows for any of the "22 wt% or 24 wt% total alkali" frits. The durability model (even with the less conservative durability limits) indicates that "non-durable" products would be produced over the entire 25 – 60% WL range for each of the four frits. An experimental assessment of durability via the PCT will either confirm this prediction or provide data that suggest that there may be additional conservatism in the "proposed" limits.

5.0 CANDIDATE GLASSES

In this section, 14 glasses are identified from which experimental assessments of durability will be evaluated. The 14 glasses will be based on the nominal SB4 1100 Canister Baseline sludge composition (see Table 2-1) coupled with each of the 14 frit compositions. The only input still required to develop specific glass compositions is the targeted WL. The selected WL should be one at which the "low Li_2O" based frits (in support of melt rate) are considered processable (or acceptable), while the higher total alkali frits are considered "unacceptable" from a durability perspective (i.e., challenge the proposed durability limits). A WL of 35% was selected to meet this criterion – the only exception would be the Frit 320n glass at 35% WL (a 21 wt% total alkali frit) that is considered acceptable based on the projected operating window of 33 – 44% WL. However, selecting a WL < 33% may be undesirable given recent DWPF WL targets of 35% or higher. Higher WLs (> 44%) are not feasible given most, if not all, of the systems are either T_L or low viscosity limited at 45 – 46% WL.

Tables 5-1 through 5-3 summarize the targeted compositions for the "20 wt% total alkali" series (labeled Low-Li-1 through Low-Li-6), "21 wt% total alkali" series (labeled Low-Li-7 through Low-Li-10), and the "22 – 24 wt% total alkali" series (labeled Low-Li-11 through Low-Li-14), respectively.

Table 5-1. "20 wt% Total Alkali" Series: Target Glass Compositions.

Glass ID	Low-Li-1	Low-Li-2	Low-Li-3	Low-Li-4	Low-Li-5	Low-Li-6
Frit ID	**320**	**320f**	**320g**	**320h**	**320i**	**320r**
Oxide						
Al_2O_3	8.025	8.025	8.025	8.025	8.025	8.025
B_2O_3	5.200	5.200	5.200	5.200	5.200	5.200
BaO	0.057	0.057	0.057	0.057	0.057	0.057
CaO	0.790	0.790	0.790	0.790	0.790	0.790
Ce_2O_3	0.074	0.074	0.074	0.074	0.074	0.074
Cr_2O_3	0.089	0.089	0.089	0.089	0.089	0.089
CuO	0.030	0.030	0.030	0.030	0.030	0.030
Fe_2O_3	9.204	9.204	9.204	9.204	9.204	9.204
K_2O	0.363	0.363	0.363	0.363	0.363	0.363
La_2O_3	0.033	0.033	0.033	0.033	0.033	0.033
Li_2O	5.200	3.900	2.600	1.300	0.000	3.250
MgO	0.687	0.687	0.687	0.687	0.687	0.687
MnO	2.066	2.066	2.066	2.066	2.066	2.066
Na_2O	15.595	16.895	18.195	19.495	20.795	17.545
NiO	1.315	1.315	1.315	1.315	1.315	1.315
PbO	0.059	0.059	0.059	0.059	0.059	0.059
SiO_2	47.767	47.767	47.767	47.767	47.767	47.767
ThO_2	0.012	0.012	0.012	0.012	0.012	0.012
TiO_2	0.008	0.008	0.008	0.008	0.008	0.008
U_3O_8	3.283	3.283	3.283	3.283	3.283	3.283
ZnO	0.045	0.045	0.045	0.045	0.045	0.045
ZrO_2	0.099	0.099	0.099	0.099	0.099	0.099
Total	100.0	100.0	100.0	100.0	100.0	100.0

Table 5-2. "21 wt% Total Alkali" Series: Target Glass Compositions.

Glass ID	Low-Li-7	Low-Li-8	Low-Li-9	Low-Li-10
Frit ID	**320j**	**320k**	**320l**	**320m**
Oxide				
Al_2O_3	8.025	8.025	8.025	8.025
B_2O_3	5.200	5.200	5.200	5.200
BaO	0.057	0.057	0.057	0.057
CaO	0.790	0.790	0.790	0.790
Ce_2O_3	0.074	0.074	0.074	0.074
Cr_2O_3	0.089	0.089	0.089	0.089
CuO	0.030	0.030	0.030	0.030
Fe_2O_3	9.204	9.204	9.204	9.204
K_2O	0.363	0.363	0.363	0.363
La_2O_3	0.033	0.033	0.033	0.033
Li_2O	3.900	2.600	1.300	0.000
MgO	0.687	0.687	0.687	0.687
MnO	2.066	2.066	2.066	2.066
Na_2O	18.195	19.495	22.095	22.095
NiO	1.315	1.315	1.315	1.315
PbO	0.059	0.059	0.059	0.059
SiO_2	46.467	46.467	45.167	46.467
ThO_2	0.012	0.012	0.012	0.012
TiO_2	0.008	0.008	0.008	0.008
U_3O_8	3.283	3.283	3.283	3.283
ZnO	0.045	0.045	0.045	0.045
ZrO_2	0.099	0.099	0.099	0.099
Total	100.0	100.0	100.0	100.0

Table 5-3. "21 wt% Alkali" Series: Target Glass Compositions.

Glass ID	Low-Li-11	Low-Li-12	Low-Li-13	Low-Li-14
Frit ID	**320n**	**320o**	**320p**	**320q**
Oxide				
Al_2O_3	8.025	8.025	8.025	8.025
B_2O_3	5.200	5.200	5.200	5.200
BaO	0.057	0.057	0.057	0.057
CaO	0.790	0.790	0.790	0.790
Ce_2O_3	0.074	0.074	0.074	0.074
Cr_2O_3	0.089	0.089	0.089	0.089
CuO	0.030	0.030	0.030	0.030
Fe_2O_3	9.204	9.204	9.204	9.204
K_2O	0.363	0.363	0.363	0.363
La_2O_3	0.033	0.033	0.033	0.033
Li_2O	3.900	2.600	1.300	0.000
MgO	0.687	0.687	0.687	0.687
MnO	2.066	2.066	2.066	2.066
Na_2O	17.545	18.845	20.145	21.445
NiO	1.315	1.315	1.315	1.315
PbO	0.059	0.059	0.059	0.059
SiO_2	47.117	47.117	47.117	47.117
ThO_2	0.012	0.012	0.012	0.012
TiO_2	0.008	0.008	0.008	0.008
U_3O_8	3.283	3.283	3.283	3.283
ZnO	0.045	0.045	0.045	0.045
ZrO_2	0.099	0.099	0.099	0.099
Total	100.000	100.000	100.000	100.000

6.0 EXPERIMENTAL

Each glass was prepared from the proper proportions of reagent-grade metal oxides, carbonates, H_3BO_3, and salts in a 150-g batch using the SRNL technical procedure "Glass Batching" (SRNL 2002a). Batch sheets were filled out as the materials were weighed. Once batched, the glasses were melted using SRNL technical procedure "Glass Melting" (SRNL 2002b). The thoroughly mixed raw materials were placed in a 95% Platinum/5% Gold 250-mL crucible and subsequently inserted 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 was removed, and the glass was poured onto a clean stainless steel plate and allowed to air cool.

Approximately 140 g of glass was removed (poured) from the crucible while ~10 g remained in the crucible along the walls. The pour patty was used as a sampling stock for the various chemical and physical property measurements (i.e., chemical composition and durability).

6.1 Chemical Composition Analysis

To confirm that the "as-fabricated" glasses corresponded to the defined target compositions, a representative sample from each glass pour patty was submitted to the SRNL Mobile Laboratory (SRNL-ML) for chemical analysis. Standard dissolutions techniques were used to prepare the samples for Inductively Couple Plasma (ICP) analysis.[4]

6.2 Product Consistency Test (PCT)

The PCT was performed in triplicate on each "quenched" (q) 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 were the EA glass (Jantzen et al. 1993), the Approved Reference Material (ARM) glass, and blanks. Samples were ground, washed, and prepared according to procedure. 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 in an oven at 90 ± 2°C where the samples were maintained for 7 days. The resulting solutions (once cooled) were sampled (filtered and acidified), labeled (according to the analytical plan), and analyzed. Normalized release rates were calculated based on targeted compositions using the average of the logs of the leachate concentrations.

To bound the effects of thermal history on the product performance, approximately 25 g of each glass were 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. This terminology will be used in this report to differentiate samples from different cooling regimes (q versus ccc). PCTs were conducted in triplicate for these glasses.

[4] Two dissolution techniques were used to support the compositional analysis: sodium peroxide fusion and lithium-metaborate. Samples prepared by sodium peroxide fusion dissolution were used to measure elemental concentrations of boron (B), lithium (Li) and nickel (Ni). All other elemental concentrations were obtained using the lithium-metaborate dissolution technique.

7.0 Results and Discussion

7.1 Compositional Analysis

Tables A.1 through A.3 (see Appendix A) summarize the target versus measured compositions for the three series of study glasses ("20 wt% alkali", "21 wt% alkali" and "22 and 2 wt4% alkali" series, respectively).[5] A review of the target versus measured compositions suggests that no significant batching errors were committed during the fabrication of these glasses. This latter statement is based on the use of a ±10% relative difference between target and measured values for the "major" oxides (i.e., those oxides present in the glass at 0.5 wt% or greater). For those oxides < 0.5 wt%, high relative differences are expected and are not a practical concern. The only possible exceptions (based on the ±10% relative difference on the major oxides) are associated with MnO and U_3O_8 for all study glasses and Li_2O for Low-Li-4, Low-Li-9, and Low-Li-13 (which are given in "red" in the appropriate tables in Appendix A). With respect to the MnO values, the analysis of the Batch 1 standard glass (see Table A.4 in Appendix A) suggests that the ICP analysis may be "biased" high as the measured MnO concentration for that glass is 2.13 wt% while the target (or "known") MnO concentration is 1.726 wt% – or a 23.4% relative difference. This relative difference is "consistent" with the % relative differences observed for the "unknown" or study glasses.

The Batch 1 standard glass does not contain U_3O_8; therefore, there is no way to assess whether the measured values for the study glasses are biased "low" as indicated by the % relative difference value (ranging from ~10 to 20 wt% low for the study glasses).

With respect to the three measured Li_2O values that appear to be biased high (when compared to targeted values), the % relative differences range from 10.7% to 13.1% – which are not of practical concern although given the self-imposed definition are classified as being "different." To provide further insight, the target Li_2O values for each of the three glasses is 1.3 wt% with measured values being 1.47, 1.44, and 1.46 wt% for Low-Li-4, -9, and -13, respectively. Again, the values do not represent a significant or practical concern. In addition, the PCT response will be assessed based both on targeted and measured compositions so this impact can be assessed.

7.2 PCT Assessments

Table 7-1 summarizes the normalized release values based on target compositions for the study glasses (both q and ccc versions). Table 7-2 summarizes the normalized release values based on measured compositions for both the quenched and ccc versions of the study glasses. Again, the normalized PCT responses shown are the average values for triplicate analyses.[6]

All of the study glasses are acceptable as defined by their NL [B]'s as compared to the EA glass (with a 16.695 g/L NL [B]) – regardless of the compositional view (measured or target) or thermal heat treatment. Using the targeted values, the most durable glass (based on NL [B]) is Low-Li-2 (ccc) with a 0.59 g/L release. This glass is one of the "20 wt% total alkali" series glasses which "agrees" with the expectations that lower total alkali glasses should (in general) have better durability (i.e., less of a negative impact on durability). Although Low-Li-2 is the most durable, the remaining "20 wt% total alkali" glasses (both q and ccc versions) have NL [B]'s

[5] The chemical composition raw data can be found in WSRC-NB-2004-00134, p. 170. In addition to the target vs. measured compositions, the % relative difference is shown in Tables A.1 – A.3. Table A.4 summarizes the target versus measured compositions for the Batch 1 standard glasses that was analyzed with the study glasses.

[6] The PCT raw data can be found in WSRC-NB-2004-00134, p. 171.

between 0.76 g/L (Low-Li-4 ccc) and 1.02 (Low-Li-1 quenched) – again all very acceptable as compared to EA.

The least durable glass (based on NL [B] and target compositions) is Low-Li-7 (quenched) with a NL [B] of 1.11 g/L. Given the higher concentration of alkali (a glass within the "22 – 24 wt% total alkali" series), it is not surprising that the least durable glass comes out of this grouping. However, the 1.1079 g/L is well below the benchmark of 16.695 g/L for the EA glass. In terms of programmatic objectives, all of the "21 wt% total alkali" and "22 – 24 wt% total alkali" glasses, with the exception of Low-Li-11, fail the MAR criteria for durability. With the measured PCT responses being acceptable (i.e., all < 1.1079 g/L), the results suggest additional conservatism exists within the current durability model even with the "proposed" limits. More specifically, the "proposed" limits still appear to restrict access to compositional regions of interest (higher alkali glasses) even though their measured PCT responses are acceptable.

The information presented in Table 7-2 (based on measured compositions) is in agreement with the statements made above. Although there were some issues associated with MnO for all of the glasses and Li_2O for three, the differences between target and measured normalized releases are not of practical concern and would lead one to the same conclusions.

Table 7-1. Normalized PCT Response for the Study Glasses (g/L). (normalized based on target compositions)[7]

Glass ID	Heat Treatment	Comp View	NL B(g/L)	NL Li (g/L)	NL Na (g/L)	NL Si (g/L)
ARM	-	reference	0.60	0.54	1.01	0.30
EA	-	reference	18.18	10.81	7.67	3.45
Low-Li-1	quenched	target	1.02	0.99	1.32	0.64
Low-Li-2	quenched	target	0.87	0.86	1.21	0.57
Low-Li-3	quenched	target	0.82	0.80	1.20	0.55
Low-Li-4	quenched	target	0.77	0.69	1.17	0.06
Low-Li-5	quenched	target	0.79	-	1.29	0.54
Low-Li-6	quenched	target	0.90	0.88	1.32	0.59
Low-Li-7	quenched	target	1.11	1.05	1.59	0.71
Low-Li-8	quenched	target	0.99	0.89	1.50	0.65
Low-Li-9	quenched	target	1.10	0.84	1.76	0.72
Low-Li-10	quenched	target	0.98	-	1.60	0.65
Low-Li-11	quenched	target	1.03	1.01	1.49	0.67
Low-Li-12	quenched	target	0.92	0.87	1.46	0.62
Low-Li-13	quenched	target	0.88	0.73	1.38	0.59
Low-Li-14	quenched	target	0.88	-	1.51	0.58
Low-Li-1	ccc	target	1.01	1.09	1.29	0.66
Low-Li-2	ccc	target	0.59	0.62	0.78	-
Low-Li-3	ccc	target	0.77	0.81	1.08	0.52
Low-Li-4	ccc	target	0.76	0.74	1.12	0.52
Low-Li-5	ccc	target	0.77	-	1.21	0.52
Low-Li-6	ccc	target	0.83	0.87	1.19	0.56
Low-Li-7	ccc	target	1.00	1.05	1.43	0.67
Low-Li-8	ccc	target	0.94	0.93	1.36	0.63
Low-Li-9	ccc	target	1.05	0.90	1.63	0.70
Low-Li-10	ccc	target	0.93	-	1.50	0.62
Low-Li-11	ccc	target	0.96	1.01	1.36	0.63
Low-Li-12	ccc	target	0.87	0.90	1.34	0.59
Low-Li-13	ccc	target	0.81	0.77	1.26	0.54
Low-Li-14	ccc	target	0.83	-	1.36	0.56

[7] Note that for those glasses based on 0% Li_2O frits, a "-" is shown in the NL [Li] g/L column.

Table 7-2. Normalized PCT Response for the Study Glasses (g/L). (normalized based on measured compositions)[8]

Glass ID	Heat Treatment	Comp View	NL B(g/L)	NL Li (g/L)	NL Na (g/L)	NL Si (g/L)
ARM	-	reference	0.60	0.54	1.01	0.30
EA	-	reference	18.18	10.81	7.67	3.45
Low-Li-1	quenched	Measured	0.95	0.99	1.29	0.63
Low-Li-2	quenched	Measured	0.84	0.85	1.18	0.57
Low-Li-3	quenched	Measured	0.78	0.77	1.17	0.55
Low-Li-4	quenched	Measured	0.73	0.61	1.14	0.06
Low-Li-5	quenched	Measured	0.76	-	1.23	0.53
Low-Li-6	quenched	Measured	0.83	0.85	1.27	0.58
Low-Li-7	quenched	Measured	1.06	1.04	1.54	0.69
Low-Li-8	quenched	Measured	0.95	0.87	1.47	0.64
Low-Li-9	quenched	Measured	1.04	0.76	1.74	0.71
Low-Li-10	quenched	Measured	0.93	-	1.53	0.64
Low-Li-11	quenched	Measured	0.95	1.00	1.46	0.67
Low-Li-12	quenched	Measured	0.89	0.82	1.38	0.60
Low-Li-13	quenched	Measured	0.85	0.65	1.32	0.57
Low-Li-14	quenched	Measured	0.85	-	1.42	0.57
Low-Li-1	ccc	Measured	0.94	1.09	1.26	0.66
Low-Li-2	ccc	Measured	0.57	0.61	0.76	-
Low-Li-3	ccc	Measured	0.74	0.78	1.06	0.51
Low-Li-4	ccc	Measured	0.73	0.66	1.09	0.51
Low-Li-5	ccc	Measured	0.74	-	1.15	0.52
Low-Li-6	ccc	Measured	0.78	0.84	1.14	0.55
Low-Li-7	ccc	Measured	0.95	1.05	1.39	0.66
Low-Li-8	ccc	Measured	0.90	0.91	1.32	0.62
Low-Li-9	ccc	Measured	1.00	0.81	1.61	0.69
Low-Li-10	ccc	Measured	0.88	-	1.43	0.61
Low-Li-11	ccc	Measured	0.88	1.00	1.32	0.62
Low-Li-12	ccc	Measured	0.84	0.85	1.27	0.57
Low-Li-13	ccc	Measured	0.78	0.68	1.21	0.53
Low-Li-14	ccc	Measured	0.80	-	1.28	0.55

[8] Note that for those glasses based on 0% Li_2O frits, a "-" is shown in the NL [Li] g/L column.

7.3 Quenched Versus CCC

Although not a specific programmatic objective, an assessment of whether or not the thermal heat treatment had an impact on the measured durability response for each glass composition is of interest. Figure 7-3 shows plots of the PCT response of quenched versus ccc glasses in terms of boron (in ppm) release. If the thermal heat treatment had no impact on the measured PCT response for a given glass, their corresponding values would lie directly on the 45° line (shown in Figure 7-3 as a gray line). The log [B] plot suggests that, in general, the quenched version of each glass has a lower durability (higher NL [B]) than their counterpart ccc version. The response of Low-Li-2 is of particular interest; the quenched version has a NL [B] of 0.87 while the ccc version has a release of 0.59. This comparison is statistically significant, but implications in terms of practicality are of little concern.

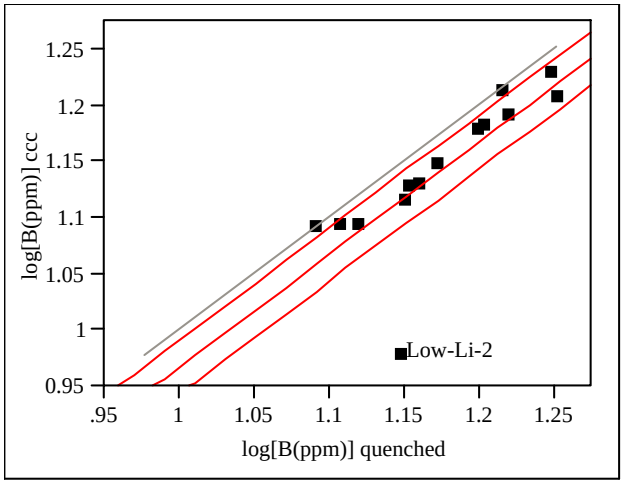

Figure 7-3. Quenched Versus ccc log [B (ppm)] (based on target compositions).

7.4 Predictability of the Durability Model

Although acceptability of the glasses in terms of the normalized PCT response as they compare to the EA glass is a critical measure, predictability or applicability of the model is also an issue that should be addressed. The DWPF models relate the logarithm of the normalized PCT (for each element of interest) to a linear function of a free energy of hydration term (ΔG_p, kcal/100g glass) derived as a function of glass compositional view (Jantzen et al. 1995). If the measured PCT response of the study glasses falls within the prediction limits, at a 95% confidence for an individual PCT result, the model is deemed applicable to the compositional space being assessed. Figure 7-4 shows a plot of log NL [B] versus ΔG_P for the study glasses. The EA (open box in top left corner) and ARM (open box in bottom right hand portion) results are also indicated on these plots. Note that most of the study glasses fall outside the lower 95% confidence band. This suggests that the model is overly conservative with respect to its durability prediction based on composition alone by overestimating the anticipated PCT response. As discussed in the previous section, the experimental results do suggest that even the "proposed" durability limits can potentially limit access to compositional regions that may be of interest to either improve melt rate or waste loading for DWPF. One interesting fact is that there are study glasses with predicted ΔG_P values more negative than that of EA but the measured responses are very acceptable – this is consistent with observations made by Cozzi et al. (2003).

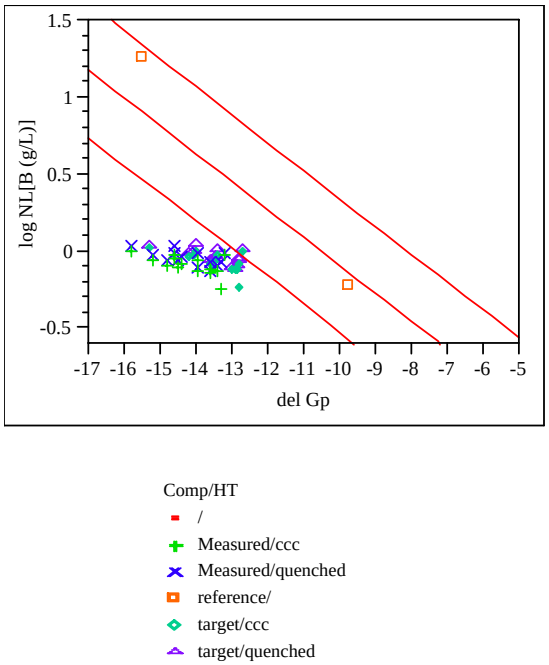

Figure 7-4. log NL [B] Versus ΔG_P.

8.0 SUMMARY

During the progressive development of the cold cap model (as it applies to a potential melt rate predictive tool), the formation of an Al-Li-silicate phase was identified as an intermediate reaction phase that could possibly hinder melt rate for SB4. To test this theory, six glasses were designed (using Frit 320's composition as the baseline) to maintain a constant 20 wt% sum of alkali content (in frit) by varying Na_2O to Li_2O ratios. The Li_2O concentration ranged from 8 wt% down to 0% in either 2% or 1% increments with the differences being accounted for by an increase in Na_2O concentration. Although the primary objective of the "lower Li_2O" frits was to evaluate the potential for melt rate improvements, assessments of durability (as measured by the Product Consistency Test (PCT)) were also performed. The results suggest that durable glasses can be produced with these "lower Li_2O" frits should it be necessary to pursue this option for improving melt rate.

In addition to the series of glasses to support melt rate assessments, a series of frits were also developed to challenge the current durability model based on the limits proposed by Edwards et al. (2004). Although the "new" limits allow access into compositional regions of interest (i.e., higher alkali systems) which can improve melt rate and/or waste loading, there may still be "additional" conservatism. In this report, two series of glasses were developed to challenge the "new" durability limits for the SB4 system. In the first series, the total alkali of the Frit 320-based glasses (designed to support the melt rate program) was increased from 20 wt% to 21 wt% (in the frit), but the series also evaluated the possible impact of various Na_2O and Li_2O mass ratio differences. The second series pushed the alkali limit in the frit even further with frits containing either 22 or 24 wt% total alkali as well as various Na_2O and Li_2O mass ratios.

The results of the PCT evaluation indicated that all of the study glasses were acceptable as defined by their NL [B]'s as compared to the EA glass (with a 16.695 g/L NL [B]) – regardless of the compositional view (measured or target) or thermal heat treatment (quenched versus centerline canister cooled). The most durable glass (Low-Li-2 ccc) had a NL [B] of 0.59 g/L. This glass was part of the series supporting melt rate assessment. The least durable glass (based on NL [B] and target compositions) was Low-Li-7 (quenched) with a NL [B] of 1.11 g/L. Given the higher concentration of alkali (a glass within the "22 – 24 wt% total alkali" series), it is not surprising that the least durable glass comes out of this grouping. However, the 1.11 g/L is well below the benchmark of 16.695 g/L for the EA glass. With the measured PCT responses being acceptable (i.e., all < 1.11 g/L) the results suggest additional conservatism exists within the current durability model even with the "proposed" limits. More specifically, the "proposed" limits still appear to restrict access to compositional regions of interest (higher alkali glasses) even though their measured PCT responses are acceptable.

Although acceptability of the glasses in terms of the normalized PCT response as they compare to the EA glass is a critical measure, predictability or applicability of the model was also addressed. The results indicated that most of the study glasses fall outside the lower 95% confidence band which suggests that the model is overly conservative with respect to its durability prediction based on composition alone by overestimating the anticipated PCT response. If "low Li_2O" frits are advantageous to melt rate, the data presented in this report suggest that the resulting glasses (based on the specific frits assessed) are durable (as defined by the PCT.

9.0 RECOMMENDATIONS

Based on the results of this study, the following recommendations are made:

(1) The results of this study indicate that additional conservatism still exists within the durability model even with the "proposed" (less restrictive) durability limits. This being the case, efforts to identify and/or implement alternative durability approaches are warranted assuming those efforts provide incentive for DWPF. Incentive could take the form of allowing access into compositional regions of interest to improve waste loading and/or melt rate for future sludge batches.

(2) Assessments of melt rate should be made with the "low Li_2O" frits to support melt rate modeling efforts. These data could be used to adjust (if warranted) the melt rate indicator currently being used to rank various flowsheets in terms of melt rate. It should be noted that if SB4 is used for this assessment, it is possible that the high Al_2O_3 content may dictate the melt rate and thus a "true" assessment of the impact of lower Li_2O frits may not be realized.

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Appendix A

Target Versus Measured Compositions and % Relative Difference

Table A.1. Target Versus Measured Compositions of the "20 wt% total Alkali" Series.

	Low-Li-1			Low-Li-2			Low-Li-3			Low-Li-4			Low-Li-5			Low-Li-6		
	320, 35% WL			320f, 35% WL			320g, 35% WL			320h, 35% WL			320i, 35% WL			320r, 35% WL		
	Target	Meas	% Diff	Target	Meas	% Diff	Target	Meas	% Diff	Target	Meas	% Diff	Target	Meas	% Diff	Target	Meas	% Diff
Al_2O_3	8.025	8.34	3.93	8.025	8.29	3.30	8.025	8.25	2.80	8.025	8.33	3.80	8.025	8.41	4.80	8.025	8.40	4.67
B_2O_3	5.200	5.60	7.69	5.200	5.40	3.85	5.200	5.43	4.42	5.200	5.47	5.19	5.200	5.41	4.04	5.200	5.59	7.50
BaO	0.057	0.06	5.26	0.057	0.05	-12.28	0.057	0.06	5.26	0.057	0.05	-12.28	0.057	0.05	-12.28	0.057	0.05	-12.28
CaO	0.790	0.79	0.00	0.790	0.80	1.27	0.790	0.79	0.00	0.790	0.76	-3.80	0.790	0.77	-2.53	0.790	0.78	-1.27
Ce_2O_3	0.074	NM	-	0.074	NM	-	0.074	NM	-	0.074	NM	-	0.074	NM	-	0.074	NM	
Cr_2O_3	0.089	0.08	-10.11	0.089	0.08	-10.11	0.089	0.07	-21.35	0.089	0.08	-10.11	0.089	0.07	-21.35	0.089	0.08	-10.11
CuO	0.030	0.04	33.33	0.030	0.04	33.33	0.030	0.04	33.33	0.030	0.04	33.33	0.030	0.04	33.33	0.030	0.04	33.33
Fe_2O_3	9.204	9.42	2.35	9.204	9.17	-0.37	9.204	9.15	-0.59	9.204	9.00	-2.22	9.204	8.92	-3.09	9.204	9.33	1.37
K_2O	0.363	0.41	12.95	0.363	0.41	12.95	0.363	0.41	12.95	0.363	0.44	21.21	0.363	0.45	23.97	0.363	0.44	21.21
La_2O_3	0.033	0.03	-9.09	0.033	0.03	-9.09	0.033	0.03	-9.09	0.033	0.03	-9.09	0.033	0.03	-9.09	0.033	0.03	-9.09
Li_2O	5.200	5.21	0.19	3.900	3.94	1.03	2.600	2.70	3.85	1.300	1.47	13.08	0.000	<1.0	-	3.250	3.37	3.69
MgO	0.687	0.69	0.44	0.687	0.67	-2.47	0.687	0.68	-1.02	0.687	0.65	-5.39	0.687	0.64	-6.84	0.687	0.66	-3.93
MnO	2.066	2.70	30.69	2.066	2.65	28.27	2.066	2.67	29.24	2.066	2.67	29.24	2.066	2.72	31.66	2.066	2.71	31.17
Na_2O	15.595	16.02	2.73	16.895	17.34	2.63	18.195	18.61	2.28	19.495	19.99	2.54	20.795	21.83	4.98	17.545	18.27	4.13
NiO	1.315	1.23	-6.46	1.315	1.23	-6.46	1.315	1.28	-2.66	1.315	1.26	-4.18	1.315	1.23	-6.46	1.315	1.23	-6.46
PbO	0.059	0.06	1.69	0.059	0.06	1.69	0.059	0.06	1.69	0.059	0.05	-15.25	0.059	0.06	1.69	0.059	0.05	-15.25
SiO_2	47.767	48.12	0.74	47.767	48.07	0.63	47.767	48.10	0.70	47.767	48.15	0.80	47.767	48.20	0.91	47.767	48.69	1.93
ThO_2	0.012	< 0.114		0.012	< 0.114	-	0.012	< 0.114	-	0.012	< 0.114	-	0.012	< 0.114	-	0.012	< 0.114	
TiO_2	0.008	0.01	25.00	0.008	0.01	25.00	0.008	0.01	25.00	0.008	0.01	25.00	0.008	0.01	25.00	0.008	0.01	25.00
U_3O_8	3.283	2.91	-11.36	3.283	2.83	-13.80	3.283	2.92	-11.06	3.283	2.71	-17.45	3.283	2.66	-18.98	3.283	2.60	-20.80
ZnO	0.045	0.05	11.11	0.045	0.05	11.11	0.045	0.05	11.11	0.045	0.05	11.11	0.045	0.05	11.11	0.045	0.05	11.11
ZrO_2	0.099	0.08	-19.19	0.099	0.09	-9.09	0.099	0.09	-9.09	0.099	0.09	-9.09	0.099	0.08	-19.19	0.099	0.09	-9.09
Sum	100.00	101.85		100.00	101.22		100.00	101.39		100.00	101.28		100.00	101.65		100.00	102.45	

Table A.2. Target Versus Measured Compositions of the "21 wt% total Alkali" Series.

	Low-Li-7			Low-Li-8			Low-Li-9			Low-Li-10	
	320j, 35% WL			320k, 35% WL			320l, 35% WL			320m, 35% WL	
	Target	Measured	% Diff	Target	Measured	% Diff	Target	Measured	% Diff	Target	Measured
Al_2O_3	8.025	8.20	2.18	8.025	8.29	3.30	8.025	8.19	2.06	8.025	8.35
B_2O_3	5.200	5.46	5.00	5.200	5.42	4.23	5.200	5.47	5.19	5.200	5.50
BaO	0.057	0.05	-12.28	0.057	0.05	-12.28	0.057	0.05	-12.28	0.057	0.05
CaO	0.790	0.75	-5.06	0.790	0.75	-5.06	0.790	0.75	-5.06	0.790	0.77
Ce_2O_3	0.074	NM	-	0.074	NM	-	0.074	NM	-	0.074	NM
Cr_2O_3	0.089	0.08	-10.11	0.089	0.08	-10.11	0.089	0.08	-10.11	0.089	0.08
CuO	0.030	0.04	33.33	0.030	0.04	33.33	0.030	0.04	33.33	0.030	0.04
Fe_2O_3	9.204	9.30	1.04	9.204	9.31	1.15	9.204	9.16	-0.48	9.204	9.08
K_2O	0.363	0.44	21.21	0.363	0.46	26.72	0.363	0.43	18.46	0.363	0.44
La_2O_3	0.033	0.03	-9.09	0.033	0.03	-9.09	0.033	0.03	-9.09	0.033	0.03
Li_2O	3.900	3.92	0.51	2.600	2.66	2.31	1.300	1.44	10.77	0.000	< 1.0
MgO	0.687	0.64	-6.84	0.687	0.64	-6.84	0.687	0.66	-3.93	0.687	0.64
MnO	2.066	2.66	28.75	2.066	2.69	30.20	2.066	2.64	27.78	2.066	2.73
Na_2O	18.195	18.78	3.22	19.495	19.98	2.49	22.095	22.38	1.29	22.095	23.17
NiO	1.315	1.26	-4.18	1.315	1.27	-3.42	1.315	1.25	-4.94	1.315	1.24
PbO	0.059	0.05	-15.25	0.059	0.05	-15.25	0.059	0.05	-15.25	0.059	0.05
SiO_2	46.467	47.32	1.84	46.467	47.29	1.77	45.167	45.44	0.60	46.467	46.99
ThO_2	0.012	< 0.114	-	0.012	< 0.114	-	0.012	< 0.114	-	0.012	< 0.114
TiO_2	0.008	0.01	25.00	0.008	0.01	25.00	0.008	0.01	25.00	0.008	0.01
U_3O_8	3.283	2.74	-16.54	3.283	2.71	-17.45	3.283	2.66	-18.98	3.283	2.83
ZnO	0.045	0.04	-11.11	0.045	0.04	-11.11	0.045	0.05	11.11	0.045	0.05
ZrO_2	0.099	0.07	-29.29	0.099	0.08	-19.19	0.099	0.09	-9.09	0.099	0.09
Sum	100.00	101.86		100.00	101.85		100.00	100.85		100.00	102.13

Table A.3. Target Versus Measured Compositions of the "22 and 24 wt% total Alkali" Series.

	Low-Li-11			Low-Li-12			Low-Li-13			Low-Li-14		
	320n, 35% WL			320o, 35% WL			320p, 35% WL			320q, 35% WL		
	Target	Measured	% Diff	Target	Measured	% Diff	Target	Measured	% Diff	Target	Measured	% Diff
Al_2O_3	8.025	8.20	2.18	8.025	8.43	5.05	8.025	8.39	4.55	8.025	8.40	4.67
B_2O_3	5.200	5.65	8.65	5.200	5.40	3.85	5.200	5.39	3.65	5.200	5.38	3.46
BaO	0.057	0.05	-12.28	0.057	0.05	-12.28	0.057	0.05	-12.28	0.057	0.05	-12.28
CaO	0.790	0.75	-5.06	0.790	0.77	-2.53	0.790	0.75	-5.06	0.790	0.75	-5.06
Ce_2O_3	0.074	NM	-	0.074	NM	-	0.074	NM	-	0.074	NM	-
Cr_2O_3	0.089	0.08	-10.11	0.089	0.08	-10.11	0.089	0.08	-10.11	0.089	0.07	-21.35
CuO	0.030	0.04	33.33	0.030	0.04	33.33	0.030	0.04	33.33	0.030	0.04	33.33
Fe_2O_3	9.204	9.28	0.83	9.204	9.40	2.13	9.204	9.09	-1.24	9.204	9.05	-1.67
K_2O	0.363	0.43	18.46	0.363	0.44	21.21	0.363	0.44	21.21	0.363	0.45	23.97
La_2O_3	0.033	0.03	-9.09	0.033	0.03	-9.09	0.033	0.03	-9.09	0.033	0.03	-9.09
Li_2O	3.900	3.96	1.54	2.600	2.73	5.00	1.300	1.46	12.31	0.000	< 1.0	-
MgO	0.687	0.65	-5.39	0.687	0.66	-3.93	0.687	0.64	-6.84	0.687	0.64	-6.84
MnO	2.066	2.70	30.69	2.066	2.76	33.59	2.066	2.72	31.66	2.066	2.75	33.11
Na_2O	17.545	17.98	2.48	18.845	19.88	5.49	20.145	21.10	4.74	21.445	22.78	6.23
NiO	1.315	1.29	-1.90	1.315	1.21	-7.98	1.315	1.23	-6.46	1.315	1.19	-9.51
PbO	0.059	0.05	-15.25	0.059	0.05	-15.25	0.059	0.05	-15.25	0.059	0.05	-15.25
SiO_2	47.117	47.27	0.32	47.117	48.50	2.94	47.117	48.15	2.19	47.117	47.96	1.79
ThO_2	0.012	< 0.114		0.012	< 0.114	-	0.012	< 0.114		0.012	< 0.114	-
TiO_2	0.008	0.01	25.00	0.008	0.01	25.00	0.008	0.01	25.00	0.008	0.01	25.00
U_3O_8	3.283	2.80	-14.71	3.283	2.62	-20.19	3.283	2.71	-17.45	3.283	2.60	-20.80
ZnO	0.045	0.05	11.11	0.045	0.05	11.11	0.045	0.04	-11.11	0.045	0.05	11.11
ZrO_2	0.099	0.08	-19.19	0.099	0.09	-9.09	0.099	0.08	-19.19	0.099	0.09	-9.09
Sum	100.00	101.37		100.00	103.21		100.00	102.47		100.00	102.32	

Table A.4 Target Versus Measured and % Relative Difference on the Batch 1 Standard Glass.

	Batch 1 Std		
	Target	Measured	% Diff
Al_2O_3	4.877	4.83	-0.964
B_2O_3	7.777	8.44	8.525
BaO	0.151	0.14	-10.596
CaO	1.22	1.13	-7.377
Ce_2O_3	0	NM	-
Cr_2O_3	0.107	0.09	-16.822
CuO	0.399	0.36	-10.526
Fe_2O_3	12.839	12.60	-1.862
K_2O	3.327	3.55	6.703
La_2O_3	0	< .01	-
Li_2O	4.429	4.48	1.152
MgO	1.419	1.28	-9.796
MnO	1.726	2.13	23.407
Na_2O	9.003	9.34	3.743
NiO	0.751	0.72	-4.394
PbO	0	0.00	-
SiO_2	50.22	51.00	1.553
ThO_2	0	< 0.114	-
TiO_2	0.677	0.60	-11.521
U_3O_8	0	< 0.118	-
ZnO	0	0.00	-
ZrO_2	0.098	0.08	-17.347

Total	99.02	101.00	

Distribution:

E. W. Holtzscheiter, 773-A
R.C. Tuckfield, 773-42A
S. L. Marra, 999-W
D. K. Peeler, 999-W
T. B. Edwards, 773-42A
C. C. Herman, 773-42A
M.E. Smith, 999-W