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The Potential Impacts of Sodium Management on Frit Development for Coupled Operations

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July 2015
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EXECUTIVE SUMMARY

Sodium (Na_2O) management is one of the future challenges facing the Defense Waste Processing Facility (DWPF), Actinide Removal Process (ARP) and Salt Waste Processing Facility (SWPF) operations. Each of these facilities has future projected processing goals that may be compromised if the total alkali of the glass waste form exceeds a critical threshold. The concept of Na_2O management derives from the need to balance the three sources of Na_2O that are introduced into the DWPF flowsheet: (1) sludge from Tank 40, (2) Actinide Removal Process (ARP)/Salt Waste Processing Facility (SWPF) products, and (3) frit. Once the Na_2O contributions from sludge (primarily based on washing strategy) and salt product (based on both volume and composition) are defined, the contribution of Na_2O from frit is essentially fixed. The total alkali content in the glass waste form must remain below a critical value so that Product Composition Control System (PCCS) durability related criteria are not challenged.

For Sludge Batch 8 (SB8), the projected Sludge Receipt and Adjustment Tank (SRAT) Na_2O concentration difference between the sludge-only flowsheet and the coupled operations flowsheet was approximately 5 wt% based on 2000 gallons of ARP product added to the SRAT. This considerable shift in Na_2O concentration between the two flowsheets significantly challenged the ability of the Savannah River National Laboratory (SRNL) frit development team to identify candidate frits that were robust to intermittent sludge-only and coupled operations, while still allowing DWPF to target a nominal 36% waste loading (WL) ± 4 WL points. In order to meet these processing constraints, the SRNL frit development team balanced the Na_2O contributions from the sludge and ARP product streams with that in the frit. Frit 422 was identified as a candidate frit for the 1.75M Na^+ wash endpoint; however, the resulting frit was visually phase separated when fabricated in the laboratory. Based on the unknown impacts of phase separation on downstream unit operations, a decision was made to target a 1.5M Na^+ wash endpoint and use a higher total alkali frit for SB8. Frit 803 was recommended for processing, but its implementation restricted the amount of ARP product that could be processed in a given SRAT batch to 1050 gallons, based upon the supporting paper studies.

Initial SB9 assessments did not identify frits for the 1.5 and 1.25M Na^+ options that provided the operational flexibility and volumes of ARP desired by SRR. Frit 422 was the only frit identified for the 1.0M Na^+ option that would allow DWPF to process over 32 – 40% WL and allow ARP product additions up to 2000 gallons. The unknown potential impacts of a phase separated frit on DWPF operations drove decisions to evaluate increases in the washing strategy. Additional assessments of the SB9 flowsheet for the 0.7 and 0.8M Na^+ options indicated that Frit 553 is a viable candidate; however, this frit is also phase separated, even after being rapidly quenched by the water cooled rollers used by the frit vendor during manufacturing. With the outstanding unknowns related to phase separated frits, DWPF has tentatively elected to continue using Frit 803 for SB9 processing, which restricts the volume of ARP to 750 gallons per SRAT batch based upon supporting paper studies and fixes the wash endpoint to 0.8M Na^+.

If higher volumes of salt product need to be processed in future DWPF operations, then the Na_2O content in the frit must be restricted to produce a final glass waste form with an acceptable durability. Frits containing relatively low total alkali content are prone to phase separation. In order to determine if a phase separated frit is a viable option for future DWPF operations, an experimental program should be implemented to address technical issues for those unit operations that could be adversely affected.

While DWPF may be able to process an extremely low alkali frit through the facility, the manufacturing of low alkali frits may be difficult or not possible. Using frits with more alkali will have a negative impact on the volumes of salt product that can be added to the SRAT and could drive washing strategies to target a lower than initially desired Na^+ molarity. Therefore, SRR system planning should consider the concept of Na_2O management as future flowsheets are developed and as SWPF is brought on-line to ensure a seamless integration.

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LIST OF ABBREVIATIONS

ARP	Actinide Removal Process
DWPF	Defense Waste Processing Facility
M	molarity
MAR	Measurement Acceptability Region
MFT	Melter Feed Tank
MST	monosodium titanate
PCCS	Product Composition Control System
PRFT	Precipitate Reactor Feed Tank
SB	Sludge Batch
SME	Slurry Mix Evaporator
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SWPF	Salt Waste Processing Facility
T_c	Critical temperature
VSL	Vitreous State Laboratory
WAC	Waste Acceptance Criteria
WL	Waste Loading
WTP	Waste Treatment Plant

1.0 Introduction

Since the development of Frit 320 for Sludge Batch 2 (SB2), the Savannah River National Laboratory (SRNL) has worked with Savannah River Remediation (SRR) to balance the alkali between the sludge and frit, particularly the Na_2O concentration. Recognizing that the source of alkali can have impacts on both rheology of the sludge and melt rate, previous formulation efforts have balanced the Tank Farm washing strategy with the Na_2O content in the frit.[1] As the Defense Waste Processing Facility (DWPF) transitioned from SB2 to SB3, the SRR-SRNL team transitioned from Frit 320 to Frit 418 to resolve rheological issues with an over-washed SB2 sludge (0.5 molarity (M) Na^+), while maintaining the ability to target relatively high waste loadings (WLs) and improve melt rate. From a frit development perspective, the shift from Frit 320 to Frit 418 reduced the Na_2O content from 12 wt% to 8 wt% in the frit, which was compensated for by SiO_2. This reduction in frit Na_2O content allowed the Tank Farm to wash less (SB3 targeted a 1.0M Na^+ wash endpoint as compared to 0.5M Na^+ for SB2), which helped to resolve the rheological issues and minimized impacts on Tank Farm working volumes while still meeting DWPF Waste Acceptance Criteria (WAC).

Prior to the Actinide Removal Process (ARP) facility start-up, DWPF processed a sludge-only flowsheet. There were only two sources of alkali entering the facility (sludge and frit), which allowed the SRNL frit development team to work with SRR Tank Farm operations and DWPF to balance the sludge washing strategy with frit development efforts. The implementation of ARP and planned implementation of the Salt Waste Processing Facility (SWPF) have fundamentally changed the approach to frit development efforts. Frit development has transitioned from designing frits capable of targeting WLs of interest for sludge-only processing to identifying frits that are robust to both sludge-only and coupled operations at even higher WLs. Although the ability of DWPF to process both flowsheets with one frit does provide operational flexibility and does not link the two facilities operationally, the SRNL frit development team is challenged to identify a frit that can satisfy both flowsheets, while accounting for various uncertainties and meeting expectations with respect to the ARP processing volume and DWPF WLs.

Originally these processing constraints were not an issue as the projected ARP product additions contributed relatively low amounts of Na_2O and the difference between a sludge-only and coupled operations flowsheet was approximately 2 wt% Na_2O.[a,2] This small difference was easily accounted for by reducing the Na_2O content in the frit, and as a result, SRNL essentially placed no restrictions on the Tank Farm washing strategies for the nominal volume of ARP product that could be added directly to the Sludge Receipt and Adjustment Tank (SRAT).[3] Starting with SB8, Precipitate Reactor Feed Tank (PRFT) data were used as the basis for evaluating the coupled flowsheet, which has resulted in significantly higher fractions of Na_2O in the ARP product stream.[4]

As the SB8 flowsheet matured, the projected SRAT Na_2O concentration difference between the sludge-only flowsheet and the coupled operations flowsheet was approximately 5 wt% (based on 2000 gallons of ARP product added to the SRAT).[5] This considerable shift in Na_2O concentration between the two flowsheets significantly challenged the ability of the SRNL frit development team to identify candidate frits that were robust to intermittent sludge-only and coupled operations, while still allowing DWPF to target a nominal 36% WL (± 4 WL points). In order to meet these processing constraints, the SRNL frit development team balanced the Na_2O contributions from the sludge and ARP product streams with that in the frit. Frit 422 was identified as a candidate frit for the 1.75M Na^+ wash endpoint option for SB8 via

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[a] In support of SB7a frit development efforts, the ARP compositions and volumes were based on the Subosits (2004) material balance calculations for ARP. Measurement Acceptability Region (MAR) assessments prior to SB8 were based on the maximum volume of ARP based on Subosits calculations and did not evaluate the impact of incremental additions of ARP product to the Sludge Receipt and Adjustment Tank (SRAT). As documented in SRNL-L3100-2010-00248, the Na_2O difference between sludge-only and coupled operations with the Subosits based composition and volume was less than 1 wt%.

paper Measurement Acceptability Region (MAR) assessments; however, Frit 422 was visually phase separated when fabricated in the laboratory.[b,6] Based on the unknown impacts of phase separation on downstream unit operations, a decision was made to target a 1.5M Na^+ wash endpoint and use a higher total alkali frit for SB8. Frit 803 was recommended for processing, but its implementation restricted the amount of ARP product that could be processed in a given SRAT batch to 1050 gallons based upon supporting paper studies.[c,5]

The desire to minimize washing in the Tank Farms[d] has resulted in a significant shift in the Na_2O difference between sludge-only and coupled operations as the volume of the ARP product increases. Based on this trend, there is a need to reduce the sodium content in the frit in order to compensate for the increased amounts of sodium coming from the ARP product and future SWPF streams, which will likely result in phase separated frits. Currently, the downstream impacts of introducing a phase separated frit to the DWPF operation are unknown.

In this report, Section 2.0 provides a description of sodium management and its impact on the glass waste form, Section 3.0 provides background information on phase separation, Section 4.0 provides the impact of sodium management on SB9 frit development efforts and the results of a limited scoping study investigating phase separation in potential DWPF frits, and Section 5.0 discusses potential technical issues associated with using a phase separated frit for DWPF operations.

2.0 Impact of Na_2O Management on the Glass Waste Form

The three primary sources of Na_2O introduced into the DWPF flowsheet include: (1) sludge from Tank 40, (2) ARP/SWPF products, and (3) frit. As the total[e] alkali content in the glass waste form increases, the durability of the glass waste form decreases. In general, the viscosity and liquidus temperature also decrease. Therefore, when considering the three sources of Na_2O, their sum (dictated by their compositions, volumes, and WL) must be maintained below some upper limit in the final waste form so as not to challenge Product Composition Control System (PCCS) durability related criteria.

A schematic of the Na_2O management concept is shown in Figure 2-1. The sludge composition from Tank 40 is dictated by the tank blending and washing strategy. In general, a higher degree of washing for a given sludge batch will result in a lower Na^+ molarity and vice versa. In addition to sodium concentration, other factors that need to be considered when targeting a washing strategy include, but are not limited to: sulfur concentration, the volume of water and its impacts on tank space and the evaporator system, and the rheology of the sludge.

The second source of Na_2O is the contribution from ARP or SWPF operations. The impact of ARP has been demonstrated in previous MAR assessments in which the composition of the ARP product plays a vital role in determining the maximum volume that could be added to the sludge-only flowsheet prior to failing either PCCS durability or low viscosity constraints.

The third source of Na_2O in the frit is essentially fixed once the Na_2O contributions from sludge washing and salt product are defined. If higher volumes of salt product need to be processed in future DWPF

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[b] The discussion of phase separation in this report is focused on its development in the frit – not in the glass waste form. The DWPF Product Composition Control System (PCCS) has other constraints that eliminate the formation of phase separation in the final waste form.

[c] DWPF operations have been able to add more than 1050 gallons of ARP product to the SB8 flowsheet, which suggests that the ARP product composition used to support the SB8 MAR assessments was conservative with respect to its impact on allowable volumes. It should also be noted that the restriction of 1050 gallons of ARP product was also driven by the requirement that the candidate frit (Frit 803) be robust to both sludge-only and coupled operations in the desired WL range.

[d] Less washing minimizes impacts to the evaporator system and saves working volume in tanks.

[e] Total alkali content is equal to the sum of Cs_2O, K_2O, Li_2O, and Na_2O.

operations, then frits containing a low Na_2O content are required in order to produce a glass waste form with acceptable properties (e.g., durability). Frit compositions containing a low Na_2O content are prone to phase separation as will be discussed in more detail in Section 3.0.

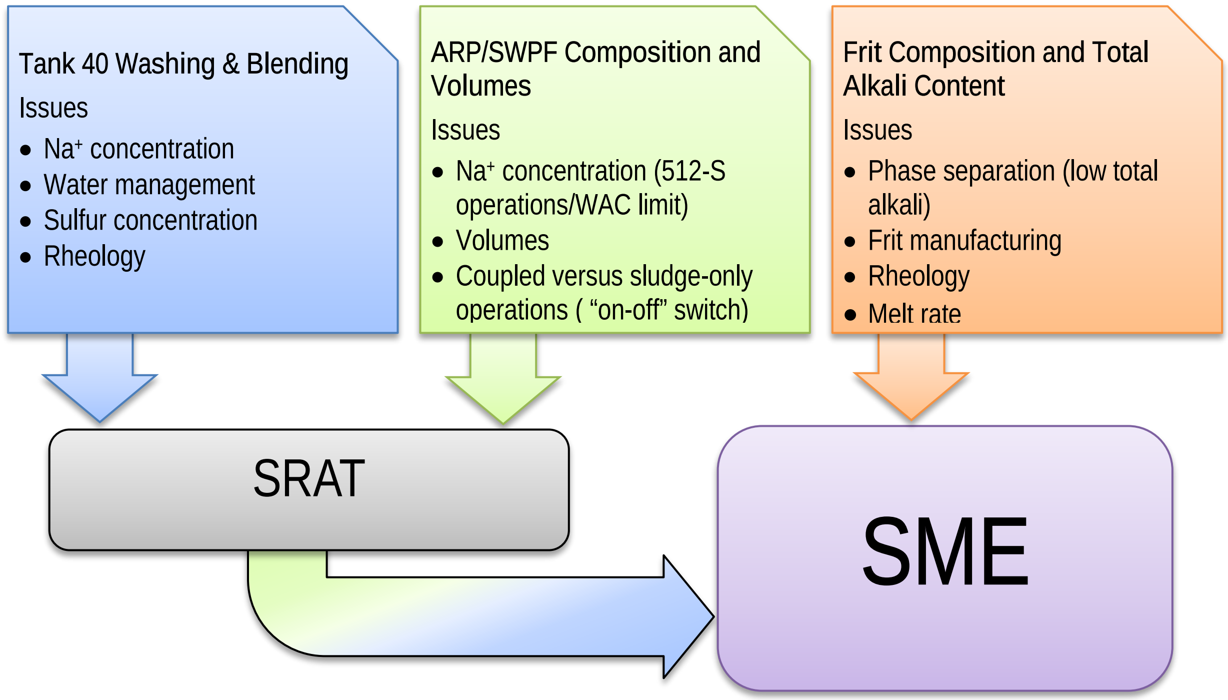
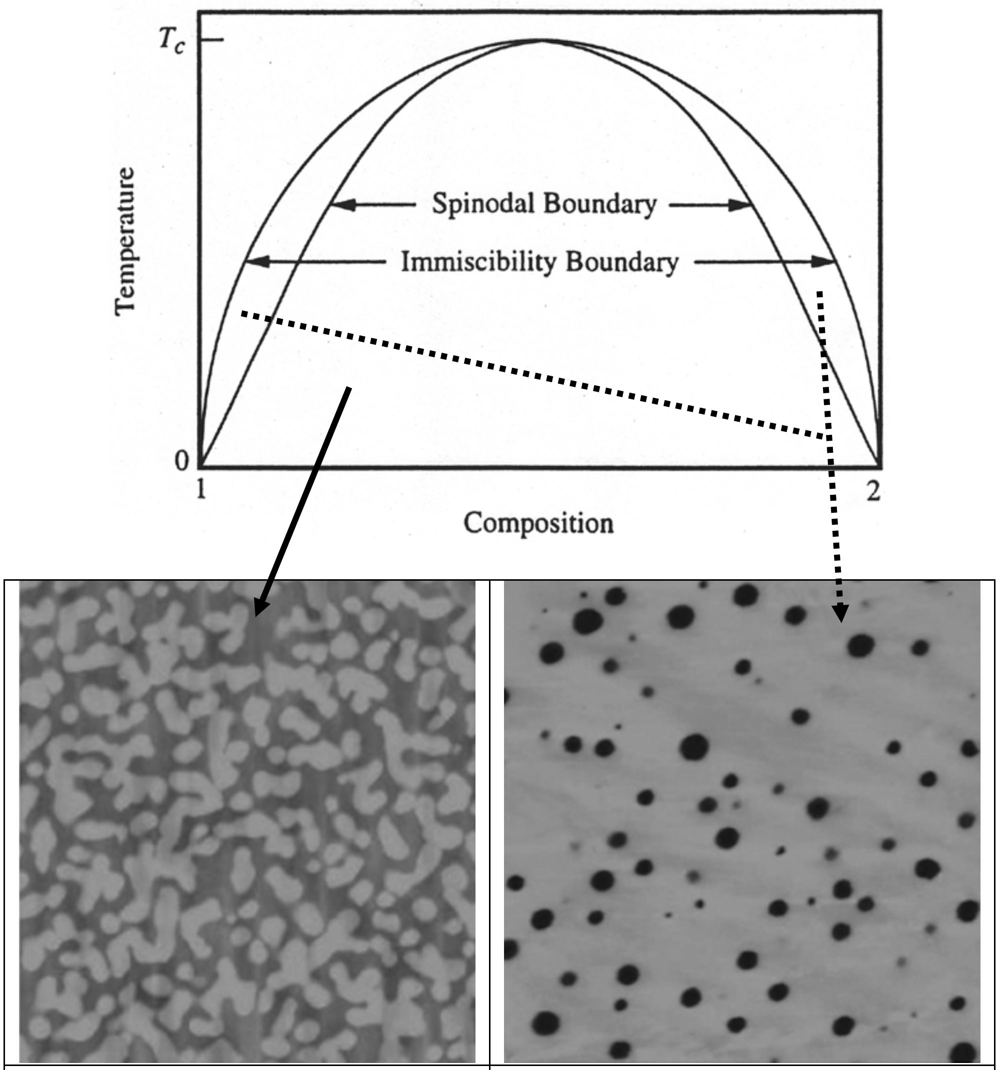


Figure 2-1. Three Primary Sources of Na_2O in the DWPF Flowsheet.

3.0 Phase Separation Background

As the alkali content is reduced in the alkali borosilicate glass system, liquid-liquid immiscibility is exhibited by the glass-forming melt, which is analogous to the behavior of oil in water. Upon cooling, the resulting glass is said to be phase separated and such behavior occurs in alkali borosilicate glass systems within specific compositional regions. In two-component (binary) systems, the region of immiscibility is defined both by temperature and composition as shown in Figure 3-1. For compositions and temperatures above the immiscibility dome, the system is a single phase homogeneous melt. As the composition cools, it crosses the immiscibility boundary and enters the immiscibility dome where phase separation can occur by two mechanisms: spinodal decomposition (Figure 3-1a) and nucleation and growth (Figure 3-1b).

Compositions lying within the spinodal boundary are characterized by two separate phases, with each phase being highly interconnected (Figure 3-1a).[7] For alkali-borosilicate glasses, one phase is SiO_2-rich and the other is B_2O_3-rich. In contrast, compositions between the immiscibility and spinodal boundaries (nucleation and growth region) are characterized by spherical forms of one phase isolated within a continuous matrix of a second glass phase (Figure 3-1b).[7] This behavior leads to either SiO_2-rich droplets isolated in a B_2O_3-rich matrix or vice versa in alkali-borosilicate glasses. Alkali, such as Na_2O and Li_2O, tend to partition with the B_2O_3-rich phase in both the spinodal decomposition region (Figure 3-1a) and the nucleation and growth region (Figure 3-1b). The development of both types of phase separation produces varying degrees of opalescence in the glass depending on the scale of the phase separated microstructure.



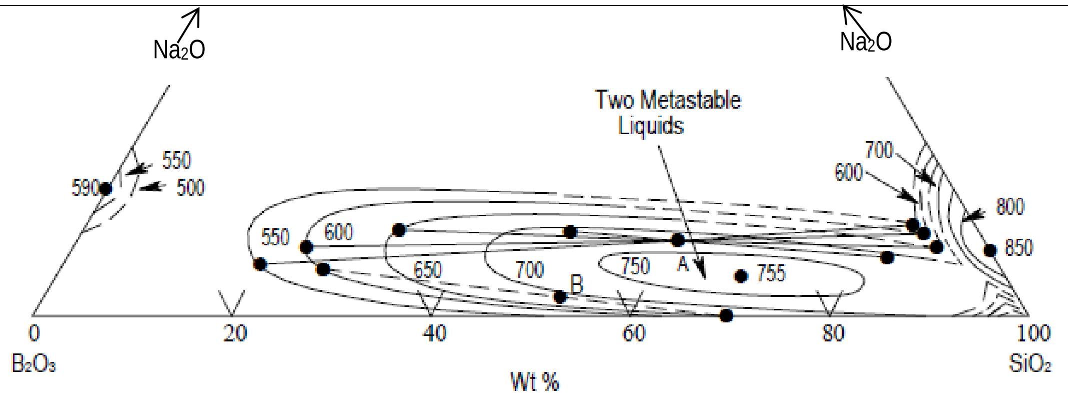
(a) spinodal decomposition

(b) nucleation and growth

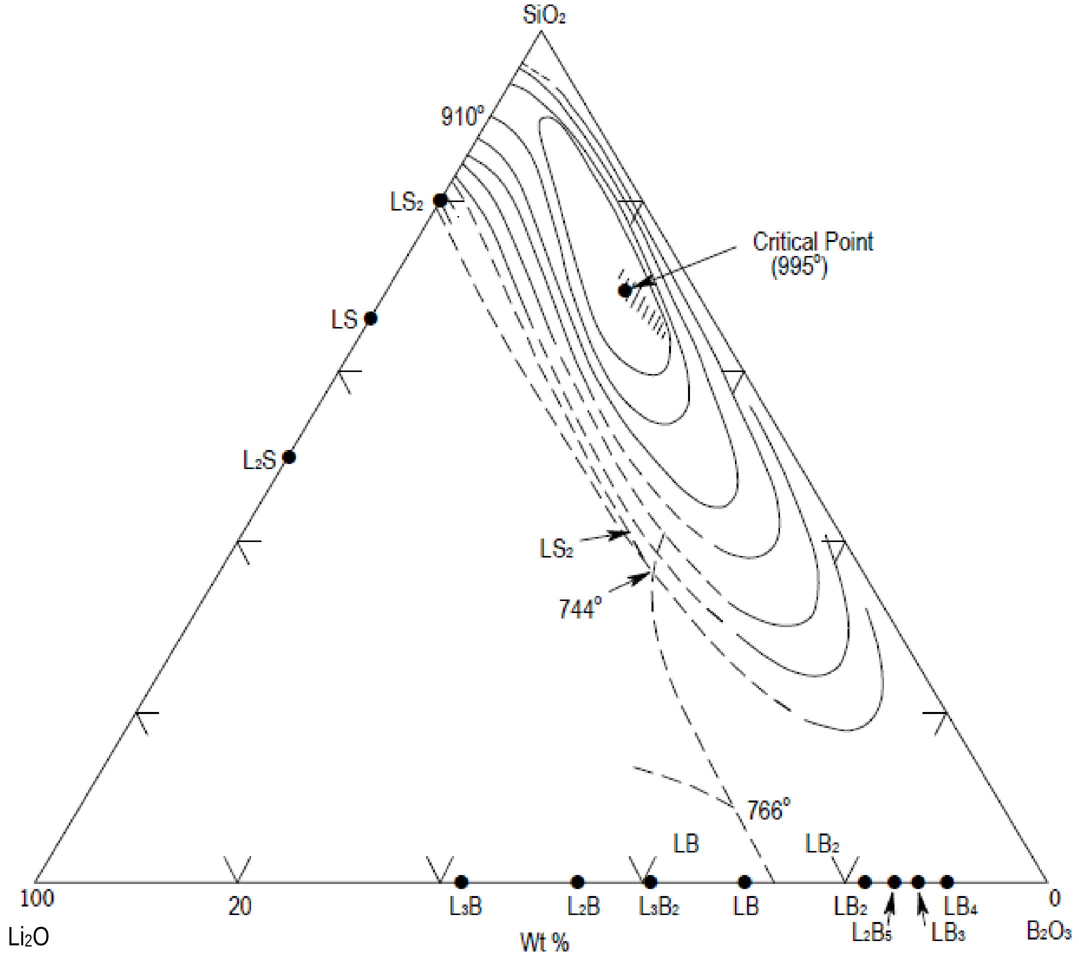
Figure 3-1. Conceptual immiscibility region (dome) in a binary system[8] and corresponding microstructures[7] of (a) spinodal decomposition and (b) nucleation and growth.

The specific mechanism that dictates the final glass microstructure is highly dependent upon composition (location of the composition with respect to the immiscibility boundary) and temperature, which dictates the reaction rate of the process (kinetics). If a composition that is prone to phase separation cools slowly, the resulting glass will be phase separated; however, if such a melt is cooled rapidly (e.g., quenched in water) from a temperature outside of the immiscibility dome, the kinetics for phase separation development are limited and the resulting glass could be homogeneous or the scale of the phase separated microstructure could be of no practical significance.

The simplified view of the immiscibility region for binary systems can be expanded to three-component (ternary) systems as shown in Figure 3-2 for Na_2O-B_2O_3-SiO_2 and Li_2O-B_2O_3-SiO_2.[9]



(a) Na_2O-B_2O_3-SiO_2 ternary diagram



(b) Li_2O-B_2O_3-SiO_2 ternary diagram.

Figure 3-2. Ternary diagrams for the (a) Na_2O-B_2O_3-SiO_2 system and (b) Li_2O-B_2O_3-SiO_2 system.[9]

The contour lines with labeled temperatures correspond to the immiscibility boundary and can be used to conceptualize the degree (or steepness) of the immiscibility region. Due to the complexity of ternary systems, a contour line representing the spinodal boundary is not typically included as it is rarely known.[8] The temperature contours increase and converge at a maximum temperature, which is defined as the critical temperature (T_c) and corresponds to the maximum of the immiscibility dome as shown in Figure 3-2. Above this critical temperature, all melt compositions in the immiscibility region are homogeneous. Kinetically, T_c is the worst case composition for phase separation as it exhibits the largest temperature range over which phase separation could occur when cooled from a melt. For the Na_2O-B_2O_3-SiO_2 system, the immiscibility region is between approximately 550°C and 755°C. Comparatively, the immiscibility region for the Li_2O-B_2O_3-SiO_2 system encompasses a higher temperature region, which is between approximately 744°C and 995°C.

3.1 Phase Separation in DWPF Frits

A phase diagram for the DWPF frit system (Li_2O-Na_2O-B_2O_3-SiO_2) does not exist in the literature, thus the immiscibility region located within the compositional space of frits typically considered for DWPF is not well defined; however, the following assumptions can be made based on the individual ternary diagrams.

1. *Increasing Li_2O content relative to Na_2O would likely produce more favorable conditions for phase separation to occur*. Within the DWPF frit compositional space, the temperature range of the immiscibility region expands with increases in Li_2O content relative to Na_2O; the worst case being for systems containing 0 wt% Na_2O.

2. *Increasing B_2O_3 content and concurrent reductions in alkali content will drive the composition towards T_c (kinetically the worst case for phase separation) in the DWPF frit compositional region of interest as shown in* Figure 3-3.

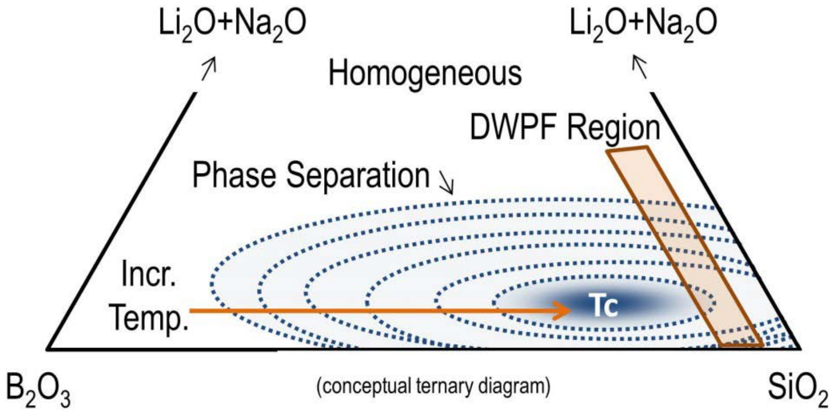


Figure 3-3. Conceptual phase diagram indicating DWPF frit compositional region and T_c.

Phase separation in typical four component frits used for DWPF can be avoided by increasing the total alkali concentration, which drives the composition outside of the immiscibility region. For frits within the immiscibility region, the addition of Al_2O_3 could also decrease the immiscibility temperature range so that phase separation is either eliminated or of no practical significance.[10] If the addition of Al_2O_3 to a frit composition is considered to suppress phase separation, then one must ensure that it has no negative impacts on the ability to maintain access to the WL range of interest. That is, the projected WL ranges for a particular flowsheet still have to meet DWPF processing requirements or expectations. Potential impacts to melt rate may also need to be considered.

In addition to the compositional controls (addition of alkali and/or Al_2O_3), the development of phase separation may also be controlled kinetically during frit fabrication by rapidly cooling the molten glass through the immiscibility dome. Techniques such as pouring the molten glass stream into a water bath or between water cooled rollers have the potential to suppress the development of phase separation or significantly reduce the scale of the phase separated microstructure.

4.0 Impact of Na_2O Management on SB9 Frit Development

Additional changes to the projected coupled operations SRAT compositions (based on proposed washing strategies and recent measurements of the ARP product) have led to continued reductions in the total alkali content of candidate frits identified for SB9 processing to allow the DWPF and ARP facilities to meet processing expectations (e.g., WLs and volume of salt processed).[11] Initial SB9 assessments did not identify any frits for the 1.5 and 1.25M Na^+ options that provided the operational flexibility and volumes of ARP desired by SRR. Only one frit (Frit 422) was identified for the 1.0M Na^+ option that would allow DWPF to process over the WL range of interest (32 – 40%) and allow ARP product additions up to 2000 gallons.[12] As stated previously, Frit 422 was visually phase separated when fabricated in the laboratory as part of SB8 frit development efforts. As with SB8, the unknown potential impacts of a phase separated frit on DWPF operations drove decisions to evaluate further increases in the washing strategy for SB9. Further assessments[f] of the SB9 flowsheet for 0.7 and 0.8M Na^+ wash endpoints indicated that Frit 553 is a viable candidate, which prompted a limited experimental scoping study focused on phase separated frits to further support SB9 frit development efforts. The results of the scoping study are presented in the following sections.

4.1 Scoping Study of Phase Separation in DWPF Frits

Since the development of phase separation multi-component glass systems is complex and is influenced by composition and cooling rate of the glass melt, the primary objectives of this limited experimental scoping study were to:

1. Determine the impact of Na_2O and B_2O_3 on phase separation under nominal cooling conditions
2. Determine if phase separation can be suppressed by quenching the glass melt in water (increasing cooling rate)
3. Determine if phase separation can be suppressed by the addition of Al_2O_3
4. Determine if phase separation can be suppressed by the roller quenching manufacturing process[f]

4.1.1 Frit Selection

The compositions of the frits used in the scoping study are shown in Table 4-1. Frits 320, 418, and 803 are provided for reference as these compositions are known to not be phase separated and either have been used or are currently being used by DWPF to process specific sludge batches.

A conceptual phase diagram indicating the location of the frit compositions is shown in Figure 4-1 (see Table 4-1 for color designations). Frit 422 with the 2 wt% Al_2O_3 addition has been omitted from Figure 4-1 for clarity since the composition is only slightly offset from Frit 422 due to the minor change in SiO_2 content.

A brief description of each composition is as follows:

1. *SB9PS-Na6 through -Na0 have the same B_2O_3 and Li_2O content with decreased Na_2O content.* This series of frits (0-6 wt% Na_2O) at a fixed Li_2O content (8 wt%) and B_2O_3 content (8 wt%)) is an initial trial to assess the impact of reducing the Na_2O content on the formation of phase

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[f] D.K. Peeler and T.B. Edwards, "Sludge Batch 9 Frit Development and Melt Rate Concerns," January 27, 2015, presentation to SRR. See laboratory notebook SRNL-NB-2013-00049 page 126-128.

separation on frits that may be considered candidates for future DWPF operations.[g,13]

2. *SB9PS-B12 has the same Li_2O and Na_2O content as Frit 422, but with increased B_2O_3 content.* This frit is designed to verify that the addition of B_2O_3 to a DWPF-like frit pushes the overall frit compositions further into the immiscibility dome (closer to T_c) as theory would suggest.

3. *Frit 422 + 2 wt% Al_2O_3 contains less SiO_2 than Frit 422 to compensate for the Al_2O_3 addition.* This composition is of interest to determine if the addition of 2 wt% Al_2O_3 is sufficient to suppress phase separation strictly from a compositional perspective.

Table 4-1. Frit Compositions (wt%)

Glass ID	Al_2O_3	B_2O_3	Li_2O	Na_2O	SiO_2
Reference Compositions					
Frit 320 ○	---	8	8	12	72
Frit 418 ⚫	---	8	8	8	76
Frit 803 🟡	---	8	6	8	78
Scoping Study Compositions					
Frit 432 (SB9PS-Na6) 🟡	---	8	8	6	78
Frit 553 (SB9PS-Na4) 🔵	---	8	8	4	80
Frit 422 🔴	---	8	8	3	81
SB9PS-Na2 🟢	---	8	8	2	82
SB9PS-Na0 🟠	---	8	8	0	84
SB9PS-B12 🟣	---	12	8	3	77
Frit 422 + 2 wt% Al_2O_3	2	8	8	3	79

Note: Colored symbols are shown on Figure 4-1.

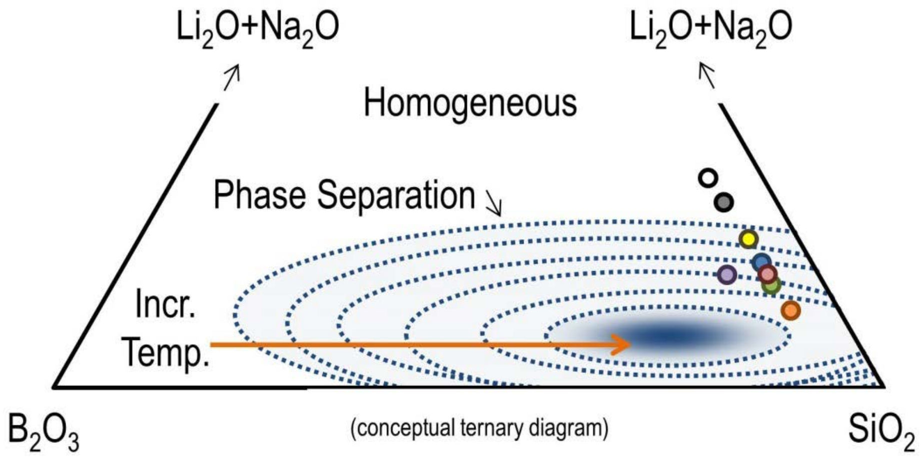

Figure 4-1. Conceptual phase diagram indicating location of frit compositions.

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[g] On-going frit development efforts for SB9 have identified Frit 422 and Frit 553 as potential candidates for the 1.0M (less washed) and 0.8M (more washed) Na^+ washing endpoints for Tank 51. See laboratory notebook SRNL-NB-2013-00049 for more details. In addition, SRNL has performed an initial assessment of the integration of SWPF into the DWPF flowsheet where all of the candidate frits identified in that study have total alkali contents less than 13 wt% with typical Na_2O concentrations of less than 5 wt%.[13]

4.1.2 Experimental Procedure

4.1.2.1 Frit Fabrication

Each batch was prepared from the proper proportions of reagent-grade chemicals.[14] The raw materials were thoroughly mixed and placed into a uniquely identified platinum alloy crucible. Each crucible was placed into a high-temperature furnace at the desired melt temperature for a set duration as shown in Table 4-2.[15]

Table 4-2. Frit Melting Conditions

Glass ID	Melting Conditions
Frit 432 (SB9PS-Na6)	1350°C for 30 minutes with a loose-fitting lid. Air cooled.
Frit 553 (SB9PS-Na4)	1350°C for 30 minutes with a loose-fitting lid. Air cooled.
Frit 422	1450°C for 30 minutes. Air cooled.
SB9PS-Na2	1450°C for 30 minutes with a loose-fitting lid. Air cooled.
SB9PS-Na0	Batch 1: 1450°C for 30 minutes with a loose-fitting lid. Air cooled. Batch 2: 1500°C for 30 minutes with a loose-fitting lid. Water quenched.
SB9PS-B12	1350°C for 30 minutes with a loose-fitting lid. Air cooled.
Frit 422 + 2 wt% Al_2O_3	1450°C for 30 minutes. Air cooled.

At the end of the isothermal hold, the crucibles were removed and the molten glass was poured onto a clean, stainless steel plate and allowed to air cool.[h] Observations of the resulting pour patty and residual crucible glass were documented. The glass from the pour patty was used as sampling stock for viscosity measurements as needed. A second batch of SB9PS-Na0 was melted at a higher temperature (1500°C) to reduce viscosity so that pouring directly into a chilled[i] water bath was facilitated.

4.1.2.2 Viscosity Measurements

As warranted, the viscosity versus temperature relationship was measured for select glasses using a rotating spindle viscometer in the range of 1250-1500°C.[16] A hysteresis approach was used during data collection to determine if volatility or crystallization was an issue throughout the course of the measurement period.

4.1.2.3 Quality Assurance

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

4.1.3 Results and Discussion

4.1.3.1 Impact of Na_2O

For a fixed B_2O_3 and Li_2O content (both 8 wt%), the degree of phase separation increases as the Na_2O content decreases as shown in Figure 4-2. Note that Frit 803 is shown for comparison. At 6 wt% Na_2O (Frit 432), the glass is transparent and only exhibits slight opalescence (bluish color) primarily near the center of the pour patty, which would have cooled at a slower rate as compared to the edges (kinetic effect). As the Na_2O content decreases to 0 wt%, the glass becomes increasingly more opaque and takes on a milky white appearance, thus demonstrating the compositional effect of Na_2O on phase separation. These visual characteristics (bluish tint to milky white) are primary indicators of the development of

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[h] There was no forced cooling of the glasses except for the second batch of SB9PS-Na0. Visual observations of the air cooled samples were used to define the immiscibility dome (based on a similar cooling profile).

[i] The water bath was initially filled with ice and prior to pouring, the ice cubes were removed.

phase separation in alkali borosilicate glasses. Based on this particular series of glasses (fixed B_2O_3 and Li_2O contents), the immiscibility boundary is between 6-8 wt% Na_2O (14-16 wt% total alkali), since Frit 418 is known to be homogeneous or non-phase separated. Note that these ranges for the immiscibility boundary are only applicable to the air cooled samples, which all underwent a similar cooling profile.

It is interesting to note that Frit 803 and Frit 432 both contain 14 wt% total alkali; however, Frit 803 is not visibly phase separated, while Frit 432 exhibits a slightly bluish coloration. Although the total alkali for these two frits is identical, the relative Na_2O and Li_2O contents are different; Frit 803 contains 6 wt% Li_2O and 8 wt% Na_2O and Frit 432 contains 8 wt% Li_2O and 6 wt% Na_2O. Thus, the relative amount of each alkali is also important in addition to the total alkali content with respect to the potential development of phase separation. More specifically, the higher Li_2O content in Frit 432 broadens the immiscibility dome which results in the formation of phase separation even though the total alkali content is the same as that of the Frit 803 (currently being used to process SB8 in DWPF). The trends between Frit 803 and Frit 432 are supported by the phase separation theory as discussed in Section 3.0.

Frit 803 ●

Frit 432 (SB9PS-Na6) ●
6 wt% Na_2O

Frit 553 (SB9PS-Na4) ●
4 wt% Na_2O

Frit 422 ●
3 wt% Na_2O

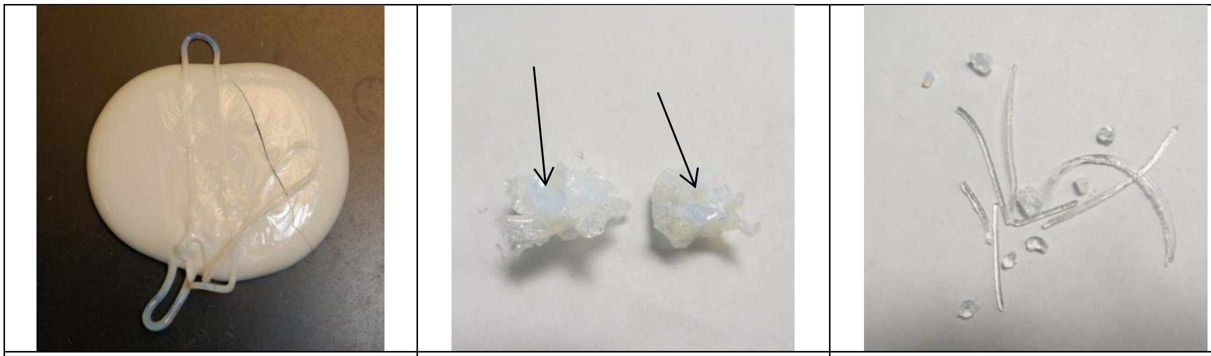
SB9PS-Na2 ●
2 wt% Na_2O

SB9PS-Na0 ●
0 wt% Na_2O

Figure 4-2. Images of as-poured glasses showing a comparison of Na_2O additions.

4.1.3.2 Impact of Cooling Rate (Kinetics)

Cooling rate of a glass melt can significantly change the degree of phase separation as shown in Figure 4-3 for the glass containing 0 wt% Na_2O (SB9PS-Na0). As previously mentioned, this glass (Batch 1) was opaque and milky white in color when allowed to cool in air as shown in Figure 4-3a; however, when it was poured directly into water (Batch 2), phase separation was not visible in a majority of the sample (Figure 4-3b1 and Figure 4-3b2). Opalescence was only observed in the larger pieces of glass (Figure 4-3b1) that did not cool as quickly as the thin strands and small pieces (Figure 4-3b2), which demonstrates the role of kinetics in the formation of phase separation.



(a) slow cooled in air (Batch 1) | (b1) water quenched (Batch 2) | (b2) water quenched (Batch 2)

Figure 4-3. Images of SB9PS-Na0 slow cooled in air (a) and rapidly cooled by water quenching (b). Arrows in (b1) are pointing to phase separated areas (light bluish tint).

4.1.3.3 Impacts of Al_2O_3 and B_2O_3

Images of Frit 422 with a 4 wt% B_2O_3 addition and a 2 wt% Al_2O_3 addition are shown in Figure 4-4. The addition of 4 wt% B_2O_3 to Frit 422 increased the degree of phase separation, which resulted in a fully opaque glass. Based on the location of this composition in the phase diagram (●), B_2O_3 additions are not recommended to those compositions along the 8 wt% line (see Figure 4-1) as these additions would drive the composition towards the interior of the immiscibility dome.[j] As expected, the addition of 2 wt% Al_2O_3 to Frit 422 had a positive impact (replacing SiO_2 with Al_2O_3). The pour patty was relatively clear, but a close examination did reveal a bluish hue in the interior of the sample where the pour patty would have cooled the slowest. One could speculate that phase separation could be eliminated in a 3 wt% Al_2O_3 addition (e.g., 3 wt% Al_2O_3, 8 wt% B_2O_3, 8 wt% Li_2O, 3 wt% Na_2O, and 78 wt% SiO_2). It is also possible that phase separation could be further suppressed if the 2 wt% Al_2O_3 based frit was cooled faster.

SB9PS-B12 ● Frit 422 + 4 wt% B_2O_3 | Frit 422 ● | Frit 422 + 2 wt% Al_2O_3

Figure 4-4. Images of as-poured glasses showing a comparison of B_2O_3 and Al_2O_3 additions to Frit 422.

4.1.3.4 Impact of the Frit Vendor's Roller Quenching Manufacturing Process

Based on the presence of phase separation and the potential impacts to DWPF processing, one of the

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[j] At the present time, this recommendation is based on the assumption that a phase separated frit would have a negative impact to processing.

DWPF frit vendors[k] offered to process two compositions from this scoping study using a small melter so that insight related to kinetically suppressing phase separation could be gained for these low alkali borosilicate frits. The pour stream exiting this melter passes through water cooled rollers (the same roller technology that has been used to support fabrication of the DWPF frit for facility operations). In order to select the candidate compositions, the viscosities of the 0 wt% and 2 wt% Na_2O frits were measured (SB9PS-Na0 and SB9PS-Na2), which were the two worst cases for viscosity along the fixed B_2O_3 and Li_2O line. The results are shown in Table 4-3 along with Frit 803 for comparison.

Table 4-3. High Temperature Viscosity Data for Various Frits (Poise)

Temperature (°C)	Frit 803	SB9PS-Na2	SB9PS-Na0
1250	143	>1270	>6300
1300	93	188	335
1350	65	128	189
1400	42	89	126
1450	32	66	95
1500	25	48	69

The frit with 0 wt% Na_2O (SB9PS-Na0) was excluded by the vendor as a candidate for melter testing due to the extremely high viscosity at 1250°C; however, the viscosity of the 2 wt% Na_2O frit (SB9PS-Na2) was deemed acceptable for processing. Frit 553 (4 wt% Na_2O) was also selected as it was an initial candidate for SB9 processing.[l]

Figure 4-5 shows the glass produced by the vendor prior to any grinding or sieving operations. The formation of a thin glass ribbon is a result of the pour stream being forced between the water cooled rollers. Dimensions of the ribbon are approximately 3.8 cm wide with a nominal thickness of 0.65-0.80 mm. Of immediate interest are the white areas down the center of the glass ribbons. Based on feedback from the vendor, this is typically observed on all of the frits produced for DWPF as it is a result of mechanical scuffing by the rollers on the surface of the glass. Despite the rapid cooling by roller quenching both frits exhibited areas of phase separation where the thickness (0.9-1.2 mm) exceeded the nominal thickness, which was typically located at the outer edges of the ribbon as shown by the circled regions in Figure 4-5.

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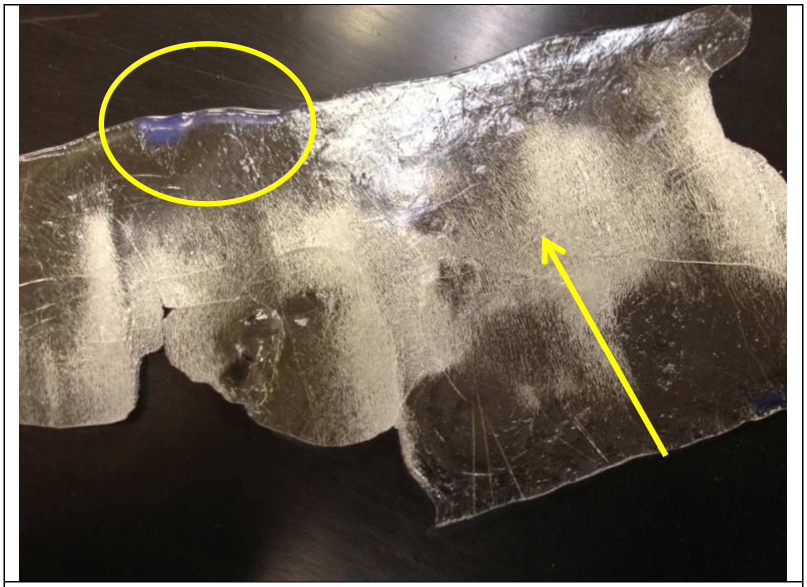
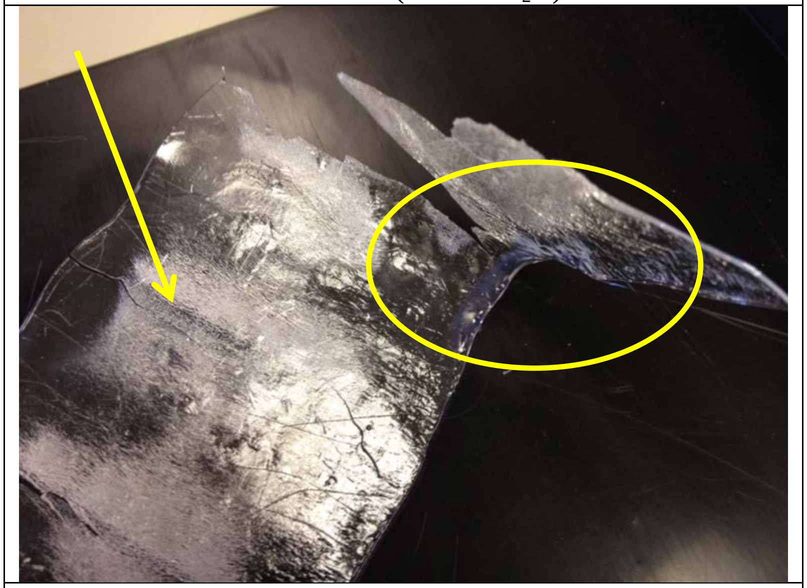
[k] Bekeson Glass, LLC (Flowood, MS).

[l] SRNL identified Frit 553 as a potential SB9 candidate for the Tank 51 0.8M Na^+ washing endpoint based option. See laboratory notebook SRNL-NB-2013-00049 for more details.



SB9PS-Na2 (2 wt% Na_2O)



Frit 553 (4 wt% Na_2O)

Figure 4-5. Images of as-manufactured glass ribbons by the DWPF frit vendor using a roller quenching process. Phase separated areas are circled and arrows point to the areas scuffed by the rollers during manufacturing.

4.2 SB9 Frit Development Results

While Frit 553 is a viable candidate for SB9, Frit 553 is phase separated, even after being rapidly quenched by the water cooled rollers used by the frit vendor during manufacturing. With the outstanding unknowns related to phase separated frits, DWPF has tentatively elected to continue using Frit 803 for SB9 processing, which potentially reduces the volume of ARP from 2000 gallons to 750 gallons per SRAT batch based upon supporting paper studies and fixes the wash endpoint of SB9 to 0.8M Na^+. The reduction in ARP product volume was deemed satisfactory by SRR given that the upcoming implementation of the ARP option without monosodium titanate (MST) should reduce the volume of ARP product coming to DWPF for immobilization.[17] The "no MST" option is based on the fact that Salt

Batch 8 has a low enough radionuclide content that MST is not needed to absorb radionuclides; thus, the MST can be removed from the ARP process, which is projected to significantly lower the volume of solids transferred to DWPF. If Salt Batch 9 is processed during SB9 and the salt batch requires the re-implementation of MST to absorb radionuclides, then the volumes of ARP product that need to be processed may not be achievable.

Although Frit 803 does provide a technically sound option, the reduction of ARP volumes should not go unnoticed. If the concerns over phase separated frits and their impact on DWPF unit operations are not addressed, then volume limitations of the ARP product will continue resulting in potentially negative impacts on the ability to meet ARP (and ultimately SWPF) processing expectations. A recent assessment of the integration of SWPF into the DWPF flowsheet identified candidate frits that provided access to operational windows of interest to DWPF.[13] Assuming that the current PCCS models apply to the SWPF-based compositional region of interest, the results of that assessment indicated that all of the candidate frits had total alkali contents of 8-13 wt% (Na_2O content ranging from 1-6 wt%). Based on the results discussed in Section 4.1, all of these candidate frits identified for SWPF processing will be phase separated.

The decision to pursue Frit 803 as the primary candidate for SB9 was driven by the unknowns of the potential downstream impacts of a phase separated frit on the DWPF flowsheet. This proposed compromise (i.e., balancing a higher alkali frit with lower volumes of ARP product) is the first of its kind for DWPF and is a prime example of how the unknown impacts of phase separation play a significant role in balancing the three sources of Na_2O. It is this balancing act that the SRNL frit development team is primarily focused on with respect to future decisions regarding DWPF operations and expectations.

5.0 Use of Phase Separated Frits for DWPF Operations

Does the presence of phase separation in a DWPF frit have a practical downstream impact on specific unit operations? Potential technical issues include, but may not be limited to:

1. *Caustic boiling in the SME.* The SME is the process vessel where frit is introduced into the flowsheet. During SME processing, the SRAT product and frit are boiled under caustic conditions to increase the wt% solids of the melter feed prior to transfer to the Melter Feed Tank (MFT) and ultimately the melter. Given the potential for leaching of the high-B_2O_3 portion of the phase separated regions, one must consider the possibility of rheological changes during SME processing, which could have a negative impact on the ability to transfer between DWPF process vessels.

2. *Potential increase in volatility of frit components.* Theoretically, boron and alkali would be in solution if preferential leaching of the frit occurred during SME processing.[m] If there are minimal or no rheological issues and melter feed transfers to the melter are possible, then one must also consider the possibility of increased boron or alkali volatility given their presence in a solution rather than a solid (frit). A glass waste form composition could be produced that is no longer representative of the composition that was used for the determination of SME acceptability. Although potentially an issue for DWPF, the baseline operations for the Waste Treatment Plant (WTP) at Hanford uses boric acid as one of the glass forming chemicals, especially for the high Na_2O-based low activity waste glasses. One could potentially appeal to the results of melter testing at the Vitreous State Laboratory (VSL) to provide more technically defensible insight into volatility (or lack thereof) under melter operating conditions similar to DWPF.

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[m] Na_2O and Li_2O partition with the boron during development of phase separation.

3. *Gelling in the frit decontamination system.* The DWPF flowsheet uses frit to decontaminate canisters via "frit blasting" as each canister exits the melt cell. The frit decontamination system uses a slurry of frit and water to perform the decontamination process. The frit-water slurry mixture is held in a tank until needed. If a phase separated frit were used in this system, then it is possible that the leaching of boron and alkalis would increase the probability of gel formation and blockages in the system.

These potential issues are mentioned to highlight the unknown impacts of a phase separated frit to these DWPF systems. It is possible that there may be no impact at all to DWPF systems, and if so, the use of a phase separated frit to support DWPF processing may be a viable option. The authors are unaware of detailed and specific information to fully address these concerns; thus, an experimental program is recommended.

6.0 Conclusions

The concept of balancing the sources of Na_2O is one of the future challenges facing DWPF, ARP, and SWPF operations. Each of these facilities has future projected processing goals that may be compromised if the total alkali exceeds a critical value in the final glass waste form, which would challenge PCCS durability related criteria. Once the Na_2O contributions from sludge (primarily based on washing strategy) and salt product (based on both volume and composition) are defined, the contribution of Na_2O from frit is essentially fixed. If the Na_2O content in the frit is restricted in order to yield acceptable glass properties in the glass waste form, then the frit could be prone to phase separation. While DWPF may be able to process an extremely low alkali frit through the facility, the manufacturing of low alkali frits may be difficult or not possible. Using frits with more alkali will ultimately have a negative impact on the volumes of salt product that can be added to the SRAT and could drive washing strategies to target a lower than initially desired Na^+ molarity.

7.0 Recommendations

SRNL recommends that SRR system planning consider the concept of Na_2O management as future flowsheets are developed and as SWPF is brought on-line to ensure a seamless integration.

In order to determine if a phase separated frit is a viable option for future DWPF operations, SRNL also recommends that SRR implement an experimental program to determine if there are technical issues related to:

1. Frit manufacturing
2. Rheology changes in the SME associated with potential leaching of boron and alkali from the frit during caustic boiling
3. Volatility of frit components (boron and alkali) during melter processing, which would produce a glass waste form composition that is no longer representative of the composition used for the determination of SME acceptability
4. Melt rate
5. Frit gelling due to enhanced leaching in the frit decontamination system if a phase separated frit is used for the decontamination process

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