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NEPHELINE FORMATION POTENTIAL IN SLUDGE BATCH 4 (SB4) AND ITS IMPACT ON DURABILITY: SELECTING GLASSES FOR A PHASE 3 STUDY

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Process Science and Engineering Section
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EXECUTIVE SUMMARY

Assessment of the likelihood for nepheline formation in Sludge Batch 4 (SB4) glass systems and the potential impact of nepheline on the durability of these systems are part of the frit development effort for SB4. The effect of crystallization on glass durability is complex and depends on several interrelated factors including the change in residual glass composition, the formation of internal stress or microcracks, and the preferential attack at the glass-crystal interface. Perhaps the most significant effects are the type and extent (or fraction) of crystallization and the change to the residual glass composition. A strong increase in glass dissolution (or decrease in durability) has been observed in previous studies in glasses that formed aluminum-containing crystals, such as $NaAlSiO_4$ (nepheline) and $LiAlSi_2O_6$, and crystalline SiO_2.

Although it is well known that the addition of Al_2O_3 to borosilicate glasses enhances the durability of the waste form (through creation of network-forming tetrahedral Na^+-$[AlO_{4/2}]^-$ pairs), the combination of high Al_2O_3 and Na_2O can lead to the formation of nepheline ($NaAlSiO_4$). Given the projected high concentrations of Al_2O_3 and Na_2O in SB4 and the likely use of a high Na_2O based frit to improve melt rate, the potential for formation of nepheline in various SB4 systems continues to be assessed as part of the frit development effort.

Based upon earlier work by Li et al.,[1] glasses that do not satisfy the constraint:

$$\frac{SiO_2}{SiO_2 + Na_2O + Al_2O_3} > 0.62 \qquad (1)$$

where the oxides are expressed as mass fractions in the glass, will precipitate nepheline as their primary crystalline phase, hindering the durability of the glass. This constraint is referred to as the nepheline discriminator.

The first phase of this study examined the potential for nepheline formation in $SB4^-$ based glasses containing relatively high amounts of Na_2O and Al_2O_3. The glasses produced for Phase 1 were all acceptable in terms of Product Consistency Test (PCT) response regardless of the thermal treatment, with the least durable glass having a normalized release for boron of 2.47 g/L (as compared to the Environmental Assessment (EA) glass at 16.695 g/L). Although the glasses were acceptable, the Phase 1 glasses were not designed to challenge the nepheline discriminator value. More specifically, only two Phase 1 glasses were prone to nepheline formation with discriminator values just below 0.62. These two glasses did show a statistical difference in PCT response between quenched and centerline canister cooled (ccc) glasses, but the difference was of no practical concern.

Phase 2 was then undertaken to fully challenge the nepheline discriminator value of 0.62. Using two updated sludge options from the Closure Business Unit (CBU), 28 glasses were selected to continue the investigation into the ability of the nepheline discriminator to predict nepheline crystallization in SB4 glasses and into the impact of such crystallization on the durability of these glasses. The results of the Phase 2 study suggested that the 0.62 value is a reasonable guide to the potential for nepheline crystallization, particularly for ccc glasses. The study showed that the ccc glasses were provided the kinetic conditions necessary for nepheline crystallization, and that some of these glasses had PCT responses that were above the acceptable limit. The general trend in the Phase 2 data suggested that as waste loading (WL) increased, the value of the nepheline discriminator decreased. Also, the difference in PCT response between quenched and ccc glasses increased.

The most recent compositional projections from the CBU for SB4 have identified Case 15C Blend 1 as the baseline flowsheet for SB4.[2] Four candidate frits have been down-selected for this option via a paper study approach[3] based on operating windows (i.e., waste loading intervals that meet Product Composition Control System (PCCS) Measurement Acceptability Region (MAR) criteria) that are robust to and/or selectively optimal for this sludge option.

For this Phase 3 study, 16 glasses have been selected to complement the earlier work[4-6] by continuing the investigation into the ability of the above constraint to predict the occurrence of a nepheline primary crystalline phase for SB4 glasses and into the impact of such phases on the durability of the SB4 glasses. The Phase 3 study has two primary objectives. The first is to continue to demonstrate the ability of the discriminator value to adequately predict nepheline formation potential for specific glass systems of interest. The second is to generate additional data that have a high probability of supporting the SB4 variability study. To support these two objectives, glasses were selected to cover WLs which tightly bound the nepheline discriminator value of 0.62, with the intent of refining this value to a level of confidence where it can be incorporated into offline administrative controls and/or the PCCS to support Slurry Mix Evaporator (SME) acceptability decisions. In addition, glasses targeting lower WLs (35 and 40%) will be prepared and analyzed to contribute needed data to the ComPro™ database in anticipation of a variability study for SB4.

The Phase 3 glasses are to be batched and fabricated using standard procedures. Visual observations and other analytical techniques are to be used, as needed, to assess the presence of crystals with specific interest in the nepheline primary phase. The durability of these glasses (for both quenched and centerline canister cooled versions) is to be measured using the ASTM PCT Method A. The results from these efforts are to be documented in a subsequent report.

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LIST OF ACRONYMS

ARP	Actinide Removal Process
CBU	Closure Business Unit
ccc	Centerline Canister Cooled
DWPF	Defense Waste Processing Facility
EA	Environment Assessment glass
ComPro™	Composition – Properties database
MAR	Measurement Acceptability Region
PCCS	Product Composition Control System
PCT	Product Consistency Test
SB	Sludge Batch
SME	Slurry Mix Evaporator
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
TT&QA	Task Technical and Quality Assurance (plan)
TTR	Technical Task Request
WL	Waste Loading

1.0 INTRODUCTION

The Defense Waste Processing Facility (DWPF) is currently processing Sludge Batch 3 (SB3) as a "sludge-only" composition by combining SB3 with Frit 418, melting the slurry mix of sludge and frit, and pouring the molten glass in stainless steel canisters to create the final waste form for this high-level waste at the Savannah River Site (SRS). In preparation for the qualification and receipt of the next sludge batch, Sludge Batch 4 (SB4), development and definition of the baseline flowsheet were initiated using options from Lilliston[7] and have progressed to using options provided by Elder[8, 9] and Shah.[2] These options have been and continue to be evaluated for SB4 in an effort to meet critical Closure Business Unit (CBU) objectives including those associated with the durability of the DWPF glass waste form and the efficiency and effectiveness of the DWPF operation. Critical components of DWPF's operational efficiency and effectiveness include sludge/frit processability, melter attainment (the percentage of time DWPF's melter is pouring), melt rate, waste loading, and canister production rates.

An early yet meaningful assessment of the processability of a sludge option and of the durability of the corresponding waste form for candidate frits at various waste loadings is provided by using predictions generated by property/composition models. The models employed are the same as those used by DWPF's Product Composition Control System[10] (PCCS), and the investigation of candidate sludge/frit glass systems may be described as a paper study whose purpose is to identify a viable frit or frits for each sludge option being studied. A frit is deemed viable if its composition allows for economic fabrication and if, when it is combined with a sludge option under consideration, DWPF's property/composition models indicate that the combination has an operating window (a waste loading interval over which the sludge/frit glass system satisfies processability and durability constraints) that allows DWPF to meet its goals for waste loading and canister production.

The Savannah River National Laboratory (SRNL) was asked via technical task requests[11, 12] (TTRs) to provide frit development support for SB4. In response, SRNL issued task technical and quality assurance (TT&QA) plans.[13, 14] Under these plans, subsequent reports were issued that identified candidate frits and assessed their viability for the SB4 options (with and without the actinide removal process (ARP) streams) as provided by Lilliston[7] (see Peeler and Edwards[4, 5]) and by Elder[8, 9] (see Peeler and Edwards[15]). While these assessments were strictly model-based and included no experimental work, experimental work in support of the SB4 program has been planned and is underway.

As part of the qualification of each sludge batch, there is a requirement to demonstrate that the durability/composition models[16] in DWPF's PCCS are applicable for the glass system anticipated by the processing of that sludge. This demonstration of applicability typically takes the form of a variability study that involves the making of glasses and the testing via the Product Consistency Test[17] (PCT) of their durability. The predicted durability is then compared to the measured durability to assess the applicability of the durability/composition models. Another way to assess model applicability involves identifying glasses that are representative of the glass system and that have already been made and tested (i.e., historical data). The model predictions for these glasses could then be compared to the previously recorded PCT results to demonstrate applicability of the durability/composition models. A preliminary assessment of the need for experimental work to support the SB4 variability study has been completed.[18] This assessment used a systematic approach that was developed and utilized to determine whether or not historical glasses contained within the ComPro™ database[19] lie within the projected SB4 compositional region of interest. The results from that assessment suggested that there was a risk of a lack of direct applicability of historical glass/durability data to satisfy the need for a SB4 variability study and reinforced the potential benefit of an experimental program to generate glass compositions and PCT data to complement ComPro™ and to help meet the intent of the SB4 variability study.

Given the projected high concentration of Al_2O_3 in the SB4 options under consideration and the likely targeting of a glass system (i.e., a SB4/frit combination) with high Na_2O content to improve melt rate or waste loading, there is a potential for the formation of nepheline for various SB4 glass systems. Nepheline formation or crystallization raises a concern regarding glass durability.

The effect of crystallization on glass durability is complex and depends on several interrelated factors including the change in residual glass composition, the formation of internal stress or microcracks, and the preferential attack at the glass-crystal interface. Perhaps the most significant effects are the type and extent (or fraction) of crystallization and the resulting change to the residual glass composition. A strong increase in glass dissolution (or decrease in durability) has been observed in previous studies[20-25] in glasses that formed aluminum-containing crystals, such as $NaAlSiO_4$ (nepheline) and $LiAlSi_2O_6$, and crystalline SiO_2.

Li et al.[1] indicate that sodium alumino-borosilicate glasses are prone to nepheline crystallization if their compositions projected on the Na_2O-Al_2O_3-SiO_2 ternary fall within the nepheline primary phase field. In particular, glasses with $SiO_2/(SiO_2+Na_2O+Al_2O_3) > 0.62$, where the oxides are expressed as mass fractions in the glass, do not precipitate nepheline as their primary phase. Using this inequality as a nepheline formation guide or "discriminator," the potential for the formation of this troubling component has been tracked as part of the frit development studies for SB4 and led to the selection of 12 glasses (as Phase 1 of the nepheline study) that were batched and subjected to the PCT.[26] The results from that study[27] suggested that a nepheline discriminator value of 0.62 was a useful guide to predict the formation of this primary crystalline phase for the SB4 glass systems. The results also suggested that the presence of nepheline (or other aluminum-containing crystals) in the SB4 glasses had an impact on the durability of glasses but not to the extent that acceptability or predictability was jeopardized. All of the glasses had acceptable durability as determined by comparisons with the Environmental Assessment (EA) glass.[28] Although the Phase 1 glasses were acceptable, they were not designed to challenge the nepheline discriminator value. More specifically, only two Phase 1 glasses were prone to nepheline formation with discriminator values just below 0.62. These two glasses showed a statistically significant difference in PCT response between quenched and centerline canister cooled (ccc) glasses, but the difference was of no practical concern.

Phase 2 of the nepheline study complemented the first phase of the work by investigating glass compositions that covered WLs over which nepheline was the only criterion restricting access to higher WLs.[6] Phase 2 identified 28 additional glasses for study that intentionally challenged the nepheline discriminator value for two of the updated sludge options from the CBU (1.6M Na, 40" SB3 heel and 1.6M Na, 127" SB3 heel[8, 9]). All 28 glasses were prone to nepheline formation. The results of the Phase 2 study showed that all of the Phase 2 quenched glasses had acceptable normalized boron releases. The quenched glasses showed no sign of nepheline formation (based on PCT response), even at nepheline discriminator values below 0.62. This is consistent with the Phase 1 results. The Phase 2 ccc glasses generally showed an increasing degree of devitrification with increasing WL. This was not unexpected, as the slower cooling provides a thermodynamically favorable glass (i.e., a composition within the nepheline primary phase field) the kinetic opportunity to devitrify. As WL is increased, the concentration of Na_2O and Al_2O_3 in the glass increases, reducing the nepheline discriminator value below the critical level. In addition, Fe, Ni and Cr concentrations also increase, increasing the probability for crystallization of spinels. The PCT showed that the durability of the Phase 2 ccc glasses decreased with increasing WLs. The normalized boron releases for the Phase 2 ccc glasses ranged from 0.89 g/L to 40.11 g/L as WL was increased over a range of approximately 39-59%.[a] Those Phase 2 glasses which were above the benchmark EA glass acceptability limit of 16.695 g/L were primarily higher WL glasses with low nepheline discriminator values. These results highlighted the value of the nepheline discriminator for

[a] Note that the PCT results and the WL used were dependent on the particular glass composition. See Peeler et al.[29] for further detail.

monitoring potential nepheline formation upon ccc, and showed that nepheline formation can indeed raise normalized boron release rates above the acceptable limit in SB4 glasses.

The purpose of this Phase 3 study is to further refine the nepheline discriminator value to a level of confidence where it can be incorporated, if required, into offline administrative controls and/or the PCCS to support Slurry Mix Evaporator (SME) acceptability decisions. The goal is to identify a specific value, or "line in the sand," that identifies the point at which nepheline formation becomes a concern for glass durability. A more fundamental understanding of the nepheline formation phenomenon will allow for advanced prediction of SB4 glass performance and aid in frit development should updates be made to the SB4 flowsheet. Relatively high (>45%) WLs will be included in the study, with the intent of suppressing nepheline crystallization up to WLs that are beyond those expected to be used by DWPF, so that the impact of nepheline formation will no longer be a concern.

All of the Phase 3 glasses will be based on the nominal Case 15C Blend 1 composition, as this currently defines SB4.[2,a] A group of glasses covering a WL range that is likely to be used by DWPF (35 and 40% WL) also will be prepared and analyzed to contribute needed data to the ComPro™ database in anticipation of a variability study for SB4.

There is a discussion of the objectives of this task in Section 2. In Section 3, possible glass systems that are anticipated for SB4 are reviewed, and Section 4 identifies a set of SB4 glass compositions to help support the objectives of this study. The information presented in this report is summarized in Section 5.

2.0 TASK OBJECTIVES

The objectives of this task are threefold: Firstly, to further refine the nepheline discriminator value to a level of confidence where it can be incorporated into offline administrative controls and/or the PCCS to support SME acceptability decisions. Glasses will be prepared with waste loadings tightly bracketing a nepheline discriminator value of 0.62, as this value has been demonstrated in previous reports to be that at which nepheline crystallization can lead to significant differences in durability between quenched and ccc glasses. Secondly, four frit compositions will be included in the testing to provide data for different Na contents in the frit, which will be important should the projected composition of SB4 be revised based on settling or washing strategy changes. Thirdly, a group of glasses covering a somewhat lower waste loading range (35 and 40% WL) will be prepared and analyzed to contribute needed data to the ComPro™ database in anticipation of a variability analysis for SB4. It should be noted that these lower WL glasses are not prone to nepheline formation but will be of significant value in terms of assessing the PCT response in a WL interval of interest to DWPF processing. The results of this study will provide improved guidelines for the avoidance of nepheline crystallization in SB4 glasses and aid in the down-selection of frit compositions.

3.0 SB4 GLASS SYSTEMS

This section investigates the SB4 option that is currently being considered as part of the frit development effort.[2] The nominal composition of Case 15C Blend 1 (or SB4) is presented. No introduction of secondary waste streams (e.g., the ARP) is considered in this Phase 3 study. The compositions of select

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[a] Due to tank settling and washing issues, the strategy outlined by the CBU has evolved into the definition of a SB4 flowsheet and a Sludge Batch 5 (SB5) flowsheet. Typically, four options are provided for a candidate flowsheet which includes Batch 1, Blend 1, Batch 2, and Blend 2. "Batches" refer to projected sludge compositions (prior to blending) that would be qualified. "Blends" refer to projected sludge compositions (after blending with the heel of the previous sludge batch) that would be processed in DWPF.

candidate frits employed during the paper studies are provided,[3] and the discriminator used to predict the potential for the formation of a nepheline primary crystalline phase is discussed.

3.1 The SB4 Composition Under Study

Table 3-1 provides the nominal sludge composition (as mass percents calcine oxides) for Case 15C Blend 1. This composition was selected as it currently defines SB4.[2] Some uncertainty exists with regard to the composition of the stream that will be transferred to DWPF, but this is not seen as having a significant impact on the stated objectives.

Table 3-1. Nominal Composition of SB4 Case 15C Blend 1 as Mass Percents

Al_2O_3	**BaO**	**CaO**	**Ce_2O_3**	**Cr_2O_3**	**CuO**	**Fe_2O_3**
24.806	0.126	2.387	0.150	0.212	0.060	26.565
K_2O	**La_2O_3**	**MgO**	**MnO**	**Na_2O**	**NiO**	**PbO**
0.344	0.108	2.495	5.480	22.080	1.577	0.091
SO_4	**SiO_2**	**ThO_2**	**TiO_2**	**U_3O_8**	**ZnO**	**ZrO_2**
1.338	4.113	0.066	0.027	7.640	0.098	0.237

3.2 Candidate Frits

The compositions of the frits considered in this study, including two frits considered during the earlier frit development efforts[15] are provided in Table 3-2. These frits are currently considered the primary candidates for SB4 based on previous assessments of projected operating windows and melt rate.[3, 30] Frits 418 and 425 have concentrations of B_2O_3 and Li_2O that are fixed at 8 wt%, with only the Na_2O and SiO_2 concentrations varying. These frits stem from the system referred to as a "sliding Na_2O scale," which has been developed to accommodate potential Na_2O concentration differences in the sludge as a result of varying blending and/or washing strategies being considered. A more detailed discussion of the "scaled" approach and of the complete set of candidate frits considered is provided in Peeler and Edwards.[15]

Frits 501 and 502[a] were developed in anticipation of even higher Na_2O contents in SB4 due to reduced washing operations and/or blending. Since nepheline formation becomes a concern as Na_2O is increased, the Na_2O content of these additional frits is reduced. Li_2O is added to help minimize any negative impact the reduction in Na_2O may have on melt rate, as melt rate is related to the total alkali content.[30] These adjustments should move the WL where nepheline crystallization occurs to higher levels.

[a] Please note that Frits 501 and 502 were previously referred to as Frits 418-m1 and P3-1, respectively, in the earlier studies.[3] The names were changed when these frits became primary candidates for SB4 and/or SB5.

Table 3-2. Composition of Candidate Frits
(as mass fractions)

Frit ID	B_2O_3	Li_2O	Na_2O	SiO_2
418	0.08	0.08	0.08	0.76
425	0.08	0.08	0.10	0.74
501	0.09	0.10	0.05	0.76
502	0.08	0.11	0.05	0.76

3.3 Potential for Nepheline Formation

The results of a study by Li et al.[1] indicated that sodium alumino-borosilicate glasses are prone to nepheline crystallization if their compositions projected on the Na_2O-Al_2O_3-SiO_2 ternary fall within the nepheline primary phase field. In particular, glasses that satisfy the constraint:

$$\frac{SiO_2}{SiO_2 + Na_2O + Al_2O_3} > 0.62 \qquad (1)$$

where the oxides are expressed as mass fractions in the glass, do not precipitate nepheline as their primary phase. The impact of the application of this guide or discriminator on the operating windows of the SB4 glass systems studied to date is discussed in previous reports.[15, 29] In those studies, the discriminator was used as defined by Equation 1 (i.e., 0.62 was used as the critical value as established by Li et al.[1] and recommended by Peeler et al.[27] for SB4). The current study will refine and confirm the critical value of the nepheline discriminator.

4.0 SELECTING GLASSES TO REFINE THE NEPHELINE DISCRIMINATOR

In support of SB4 processing, only one sludge option is considered here: Case 15C Blend 1, which is a "sludge-only" (i.e., no additional ARP stream) based flowsheet.[2] This option is seen as providing the most likely representation of SB4. It should be noted that although the primary focus is on SB4, the Phase 3 data will be applicable to other high Al_2O_3 waste streams (i.e., SB5).

This option was combined with the four frits described in Table 3-2 in a paper study where the PCCS measurement acceptability region (MAR) assessments and nepheline discriminator values were determined for a WL range of 25 to 60%.[3] Table 4-1 summarizes the MAR assessments for these glass systems. The limiting factor is indicated in the table for each glass that falls outside of the acceptability criteria. These factors are listed as "Neph" for predicted nepheline formation, "TL" for liquidus temperature, and "lvisc" for low viscosity.

Table 4-1 shows that the Frit 418 and Frit 425 systems are limited by predicted nepheline crystallization at WLs of 47% and 45%, respectively. For the Frit 501 system, liquidus temperature limits access to WLs of 48% and above, with nepheline formation predicted at WLs of 49% and above. Liquidus temperature, viscosity, and predicted nepheline crystallization are all limiting factors for the Frit 502 system at WLs of 49% and above.

To support test objectives, WLs that bounded where the prediction of nepheline was an issue were to be targeted. Given that and the fact that some systems were "non-nepehline" limited, some of the targeted Phase 3 glasses would be selected that would not be acceptable from a PCCS MAR perspective. More specifically, select glasses will be targeted that bound nepheline formation issues, but fail other processing constraints.

Table 4-1. MAR assessments for the SB4 candidate systems of interest.

Sludge Option	Waste Loading (%)	Frit 418	Frit 425	Frit 501	Frit 502
Case 15C Blend 1	25	-	-	-	-
Case 15C Blend 1	26	-	-	-	-
Case 15C Blend 1	27	-	-	-	-
Case 15C Blend 1	28	-	-	-	-
Case 15C Blend 1	29	-	-	-	-
Case 15C Blend 1	30	-	-	-	-
Case 15C Blend 1	31	-	-	-	-
Case 15C Blend 1	32	-	-	-	-
Case 15C Blend 1	33	-	-	-	-
Case 15C Blend 1	34	-	-	-	-
Case 15C Blend 1	35	-	-	-	-
Case 15C Blend 1	36	-	-	-	-
Case 15C Blend 1	37	-	-	-	-
Case 15C Blend 1	38	-	-	-	-
Case 15C Blend 1	39	-	-	-	-
Case 15C Blend 1	40	-	-	-	-
Case 15C Blend 1	41	-	-	-	-
Case 15C Blend 1	42	-	-	-	-
Case 15C Blend 1	43	-	-	-	-
Case 15C Blend 1	44	-	-	-	-
Case 15C Blend 1	45	-	Neph	-	-
Case 15C Blend 1	46	-	Neph	-	-
Case 15C Blend 1	47	Neph	Neph	-	-
Case 15C Blend 1	48	Neph	Neph	TL	-
Case 15C Blend 1	49	TL, Neph	lvisc, Neph	TL, Neph	TL, lvisc, Neph
Case 15C Blend 1	50	TL, Neph	lvisc, Neph	TL, Neph	TL, lvisc, Neph
Case 15C Blend 1	51	TL, Neph	TL, lvisc, Neph	TL, lvisc,Neph	TL, lvisc, Neph
Case 15C Blend 1	52	TL, Neph	TL, lvisc, Neph	TL, lvisc, Neph	TL, lvisc, Neph
Case 15C Blend 1	53	TL, Neph	TL, lvisc, Neph	TL, lvisc, Neph	TL, lvisc, Neph
Case 15C Blend 1	54	TL, lvisc, Neph	TL, lvisc, Neph	TL, lvisc, Neph	TL, lvisc, Neph
Case 15C Blend 1	55	TL, lvisc, Neph	TL, lvisc, Neph	TL, lvisc, Neph	TL, lvisc, Neph
Case 15C Blend 1	56	TL, lvisc, Neph	TL, lvisc, Neph	TL, lvisc, Neph	TL, lvisc, Neph
Case 15C Blend 1	57	TL, lvisc, Neph	TL, lvisc, Neph	TL, lvisc, Neph	TL, lvisc, Neph
Case 15C Blend 1	58	TL, lvisc, Neph	TL, lvisc, Neph	TL, lvisc, Neph	TL, lvisc, Neph
Case 15C Blend 1	59	TL, lvisc, Neph	TL, lvisc, Neph	TL, lvisc, Neph	TL, lvisc, Neph
Case 15C Blend 1	60	TL, lvisc, Neph	TL, lvisc, Neph	TL, lvisc, Neph	TL, lvisc, Neph

In selecting the Phase 3 glasses, a window of nepheline discriminator values was chosen based on the Phase 1 and 2 results. The lower end of the window was set at a value of 0.59, where the glasses should begin to have a measurable difference in PCT response between the quenched and ccc specimens, but will not have unacceptable (EA-like) durability. The upper end of the window was set at 0.62, as the previous phases of the work have shown this value to be a reliable indicator of the potential for nepheline crystallization in ccc glasses.

Table 4-2 lists the nepheline discriminator values for the sludge–frit systems under study, developed through the earlier paper study.[3] WL levels for each of the four frits were chosen at nepheline discriminator values of just above 0.62 and just below 0.60, as described above. These are shaded in Table 4-2. Note that some of the chosen WL levels will produce glasses that have an unacceptable T_L or viscosity based on the PCCS MAR results given in Table 4-1. This was intentionally disregarded in favor of concentrating on the potential for nepheline formation.

In addition, glass specimens at WLs of 35 and 40% (a range more likely to be used by DWPF) will be prepared and analyzed to contribute needed data to the ComPro™ database in anticipation of a variability study for SB4.

The 16 glass compositions generated by this process are given in Table 4-3. Unique identifiers for these glasses are provided in the first row of the table, and the value of the nepheline discriminator for each glass is also included. These glasses are to be batched and fabricated using standard procedures. Visual observations and other analytical techniques are to be used, as needed, to assess the presence of crystals and, specifically, a nepheline phase. The durability of these glasses (for both quenched and ccc treatments) is to be measured using the ASTM PCT Method A.[17] The results from these efforts are to be documented in a subsequent report.

Table 4-2. Nepheline discriminator values over a range of waste loadings for the four frits studied.

Waste Loading (%)	Frit 418	Frit 425	Frit 501	Frit 502
25	0.766	0.746	0.790	0.790
26	0.760	0.740	0.783	0.783
27	0.754	0.734	0.776	0.776
28	0.747	0.728	0.770	0.770
29	0.741	0.722	0.763	0.763
30	0.735	0.716	0.756	0.756
31	0.728	0.709	0.749	0.749
32	0.722	0.703	0.742	0.742
33	0.715	0.697	0.735	0.735
34	0.708	0.690	0.728	0.728
35	0.702	0.684	0.721	0.721
36	0.695	0.677	0.714	0.714
37	0.688	0.671	0.707	0.707
38	0.681	0.664	0.699	0.699
39	0.674	0.657	0.692	0.692
40	0.667	0.650	0.685	0.685
41	0.660	0.643	0.677	0.677
42	0.653	0.637	0.670	0.670
43	0.646	0.630	0.662	0.662
44	0.639	0.622	0.654	0.654
45	0.631	0.615	0.647	0.647
46	0.624	0.608	0.639	0.639
47	0.616	0.601	0.631	0.631
48	0.609	0.594	0.623	0.623
49	0.601	0.586	0.615	0.615
50	0.593	0.579	0.607	0.607
51	0.586	0.571	0.599	0.599
52	0.578	0.563	0.591	0.591
53	0.570	0.556	0.582	0.582
54	0.562	0.548	0.574	0.574
55	0.554	0.540	0.565	0.565
56	0.546	0.532	0.557	0.557
57	0.537	0.524	0.548	0.548
58	0.529	0.516	0.539	0.539
59	0.520	0.508	0.531	0.531
60	0.512	0.500	0.522	0.522

Table 4-3. Compositions of Selected Glasses for SB4 Case 15C Blend 1
(in wt%)

Glass ID	**NEPH 3-41**	**NEPH 3-42**	**NEPH 3-43**	**NEPH 3-44**	**NEPH 3-45**	**NEPH 3-46**	**NEPH 3-47**	**NEPH 3-48**	**NEPH 3-49**	**NEPH 3-50**	**NEPH 3-51**	**NEPH 3-52**	**NEPH 3-53**	**NEPH 3-54**	**NEPH 3-55**	**NEPH 3-56**
Frit ID	418	418	418	418	501	501	501	501	425	425	425	425	502	502	502	502
%WL	35	40	46	50	35	40	47	51	35	40	44	48	35	40	48	51
nepheline discrim.	0.702	0.667	0.624	0.593	0.721	0.685	0.631	0.599	0.684	0.650	0.622	0.594	0.721	0.685	0.623	0.599
Al_2O_3	8.682	9.922	11.411	12.403	8.682	9.922	11.659	12.651	8.682	9.922	10.915	11.907	8.682	9.922	11.907	12.651
B_2O_3	5.200	4.800	4.320	4.000	5.850	5.400	4.770	4.410	5.200	4.800	4.480	4.160	5.200	4.800	4.160	3.920
BaO	0.044	0.050	0.058	0.063	0.044	0.050	0.059	0.064	0.044	0.050	0.056	0.061	0.044	0.050	0.061	0.064
CaO	0.836	0.955	1.098	1.194	0.836	0.955	1.122	1.218	0.836	0.955	1.051	1.146	0.836	0.955	1.146	1.218
Ce_2O_3	0.052	0.060	0.069	0.075	0.052	0.060	0.070	0.076	0.052	0.060	0.066	0.072	0.052	0.060	0.072	0.076
Cr_2O_3	0.074	0.085	0.098	0.106	0.074	0.085	0.100	0.108	0.074	0.085	0.093	0.102	0.074	0.085	0.102	0.108
CuO	0.021	0.024	0.028	0.030	0.021	0.024	0.028	0.031	0.021	0.024	0.026	0.029	0.021	0.024	0.029	0.031
Fe_2O_3	9.298	10.626	12.220	13.283	9.298	10.626	12.486	13.548	9.298	10.626	11.689	12.751	9.298	10.626	12.751	13.548
K_2O	0.120	0.138	0.158	0.172	0.120	0.138	0.162	0.175	0.120	0.138	0.151	0.165	0.120	0.138	0.165	0.175
La_2O_3	0.038	0.043	0.050	0.054	0.038	0.043	0.051	0.055	0.038	0.043	0.048	0.052	0.038	0.043	0.052	0.055
Li_2O	5.200	4.800	4.320	4.000	6.500	6.000	5.300	4.900	5.200	4.800	4.480	4.160	7.150	6.600	5.720	5.390
MgO	0.873	0.998	1.148	1.248	0.873	0.998	1.173	1.273	0.873	0.998	1.098	1.198	0.873	0.998	1.198	1.273
MnO	1.918	2.192	2.521	2.740	1.918	2.192	2.576	2.795	1.918	2.192	2.411	2.630	1.918	2.192	2.630	2.795
Na_2O	12.928	13.632	14.477	15.040	10.978	11.832	13.027	13.711	14.228	14.832	15.315	15.798	10.978	11.832	13.198	13.711
NiO	0.552	0.631	0.726	0.789	0.552	0.631	0.741	0.804	0.552	0.631	0.694	0.757	0.552	0.631	0.757	0.804
PbO	0.032	0.036	0.042	0.045	0.032	0.036	0.043	0.046	0.032	0.036	0.040	0.043	0.032	0.036	0.043	0.046
SO_4	0.468	0.535	0.615	0.669	0.468	0.535	0.629	0.682	0.468	0.535	0.589	0.642	0.468	0.535	0.642	0.682
SiO_2	50.840	47.245	42.932	40.057	50.840	47.245	42.213	39.338	49.540	46.045	43.250	40.454	50.840	47.245	41.494	39.338
ThO_2	0.023	0.026	0.030	0.033	0.023	0.026	0.031	0.034	0.023	0.026	0.029	0.032	0.023	0.026	0.032	0.034
TiO_2	0.009	0.011	0.012	0.013	0.009	0.011	0.013	0.014	0.009	0.011	0.012	0.013	0.009	0.011	0.013	0.014
U_3O_8	2.674	3.056	3.515	3.820	2.674	3.056	3.591	3.897	2.674	3.056	3.362	3.667	2.674	3.056	3.667	3.897
ZnO	0.034	0.039	0.045	0.049	0.034	0.039	0.046	0.050	0.034	0.039	0.043	0.047	0.034	0.039	0.047	0.050
ZrO_2	0.083	0.095	0.109	0.119	0.083	0.095	0.111	0.121	0.083	0.095	0.104	0.114	0.083	0.095	0.114	0.121

5.0 SUMMARY

Savannah River National Laboratory's frit development effort for SB4 is being driven by the most current CBU option for this sludge, referred to as Case 15C Blend 1. Candidate frits have been identified for this option via a paper study approach developed by Peeler and Edwards[15] with the intent of down-selecting to a set of key frits whose operating windows (i.e., WL intervals that meet PCCS MAR criteria) are robust to and/or selectively optimal for this sludge option. The primary frits that appear attractive on paper (i.e., down-selected via the paper study) are now being incorporated into this experimental study.

The potential for the formation of a nepheline primary crystalline phase is an important factor in frit development for SB4, due to the high Al_2O_3 content of this sludge. Based upon earlier work by Li et al.,[1] glasses that do not satisfy the constraint:

$$\frac{SiO_2}{SiO_2 + Na_2O + Al_2O_3} > 0.62 \qquad (1)$$

where the oxides are expressed as mass fractions in the glass, will precipitate nepheline as their primary crystalline phase, hindering the durability of the glass.

Based on the most recent compositional projection from the CBU for SB4 (Case 15C Blend 1), 16 glasses have been selected to complement the earlier work[4-6] by continuing the investigation into the ability of the above constraint to predict the occurrence of a nepheline primary crystalline phase for SB4 glasses and into the impact of such phases on the durability of the SB4 glasses. Glasses were selected to cover WLs which tightly bound the nepheline discriminator value of 0.62, with the intent of refining this value to a level of confidence where it can be incorporated into offline administrative controls and/or the PCCS to support SME acceptability decisions. In addition, glass specimens at WLs of 35 and 40% will be prepared and analyzed to contribute needed data to the ComPro™ database in anticipation of a variability study for SB4.

The glasses in Table 4-3 are to batched and fabricated using standard procedures. Visual observations and other analytical techniques are to be used, as needed, to assess the presence of crystals with specific interest in the nepheline primary phase. The durability of these glasses (for both quenched and centerline canister cooled versions) is to be measured using the ASTM PCT Method A. The results from these efforts are to be documented in a subsequent report.

The results of this study will provide valuable input for the frit development efforts and subsequent feedback to the CBU regarding the relative viability of the current SB4 option under consideration. The refined nepheline discriminator value will provide a guideline for the avoidance of nepheline crystallization in SB4 glasses and aid in down-selection of frit compositions. These data will be combined with the results of melt rate studies and a paper study of the frits' robustness with regard to variability in the sludge composition to provide an optimized frit recommendation to DWPF for immobilization of SB4.

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