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SLUDGE BATCH 4 (SB4) AFTER A TANK 40 DECANT: CANDIDATE FRITS, MAR ASSESSMENTS, AND GLASSES FOR A VARIABILITY STUDY

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Process Science and Engineering Section
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REVIEWS AND APPROVALS

AUTHORS:

K.M. Fox, Materials Science and Technology Section — Date

T.B. Edwards, Statistical Consulting Section — Date

D.K. Peeler, Process Science and Engineering Section — Date

TECHNICAL REVIEWER:

M.E. Smith, Process Science and Engineering Section — Date

APPROVERS:

R.E. Edwards, Manager, Process Science and Engineering Section — Date

C.C. Herman, Manager, Process Engineering Technology Group — Date

J.E. Occhipinti, Manager, DWPF Process Engineering — Date

EXECUTIVE SUMMARY

In early October 2006, the Liquid Waste Organization (LWO) began to consider decanting Tank 40 at the end of Sludge Batch 3 (SB3) processing and transferring the aqueous phase from the decant to Tank 51. This transfer would be done to decrease Tank 51 yield stress and facilitate the transfer of the contents of Tank 51 to Tank 40. The projected composition of Sludge Batch 4 (SB4) was adjusted by LWO to reflect the impact of the Tank 40 decant leading to new projected compositions for SB4, designated as the 10-04-06 and the 10-10-06 compositions. A comparison between these SB4 compositions and those provided in June 2006 indicates that the new compositions are slightly higher in Al_2O_3, Fe_2O_3, and U_3O_8 and slightly lower in SiO_2. The most dramatic change, however, is the new projection's Na_2O concentration, which is more than 4.5 wt% lower than the June 2006 projection.[a] This is a significant change due to the frit development team's approach of aligning the Na_2O concentration in a candidate frit to the Na_2O content of the sludge. This approach enhances the projected operating window and the waste throughput potential for the resulting glass system while eliminating the potential for nepheline crystallization. Nepheline can have a detrimental impact on durability.

Questions surfaced regarding the applicability of Frit 503 to these revised compositions since the Savannah River National Laboratory (SRNL) recommended Frit 503 for use with SB4 based on the June 2006 compositional projection without the Tank 40 decant. Based on the paper study assessments, the change in SB4's expected Na_2O content had a significant, negative impact on the projected operating window for the Frit 503/SB4 glass system. While Frit 418 had slightly smaller waste loading (WL) intervals for the June 2006 SB4 projections as compared to Frit 503 and the Frit 418 glass systems were nepheline limited, Frit 418 had a slightly larger operating window for the 10-04-06 projection (as compared to Frit 503) and the Frit 418/10-04-06 glass system was no longer nepheline limited. Thus, strictly from the perspective of this paper study, Frit 418 was more attractive than Frit 503 for the new SB4 projected compositions. This comparison, however, does not reflect other aspects of interest for the glass systems such as their respective melt rates or the development of alternative frits to balance the projected operating windows, melt rate, waste throughput, and robustness to compositional variation.

In discussions with Waste Solidification Engineering (WS-E) regarding the results being presented in this report, their decision was to utilize Frit 418 for initial processing of SB4. This decision was not only based on the paper study assessments presented in this report, but also on the fact that Frit 418 is currently being used to process SB3 and, perhaps more importantly, frit optimization efforts for SB4 may be premature given the uncertainties in tank transfer and heel volumes associated with the SB4 flowsheet. More specifically, WS-E indicated their plan to initiate processing with Frit 418 with subsequent authorization for the frit development team to optimize a frit based on the measured composition of SB4 after determination of the actual SB4 blend composition (i.e., both the SB3 and SB4 compositions and masses are known).

Given this decision and recognizing that a SB4/Frit 503 variability study had been initiated as part of the qualification process, questions regarding the need for a supplemental variability study to demonstrate applicability of the process control models for a Frit 418 based system surfaced. This report addresses the need for a supplemental study and defines additional glasses to fill the compositional gaps. A total of 13 glasses (based on the 10-10-06 projection) were selected for the supplemental SB4/Frit 418 variability study. These glasses will be batched and melted following standard SRNL procedures, and a suite of characterization testing will be completed to measure the chemical durability of each glass composition.

[a] The most recent composition changes are a result of using the Sludge Receipt and Adjustment Tank (SRAT) and/or updated Tank 51 compositional information based on the SB4 qualification sample and proposed Tank 40 decant. The June 2006 composition was based on the early analyses of SB4 and the WAPS sample analyses of SB3.

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ARP	Actinide Removal Process
DWPF	Defense Waste Processing Facility
EVs	Extreme Vertices
HLW	High Level Waste
LWO	Liquid Waste Organization
MAR	Measurement Acceptability Region
MCU	Modular Caustic Side Solvent Extraction Unit
PCCS	Product Composition Control System
SB3 / SB4	Sludge Batch 3 / Sludge Batch 4
SME	Slurry Mix Evaporator
SRNL	Savannah River National Laboratory
VS	Variability Study
WL	Waste Loading (weight percent)
WS-E	Waste Solidification Engineering

1.0 Introduction

The Defense Waste Processing Facility (DWPF) is preparing for vitrification of Sludge Batch 4 (SB4) in early FY2007. To support this process, the Savannah River National Laboratory (SRNL) has provided a recommendation for the frit compositions to be used in vitrifying this sludge batch.[1] The primary frit recommended for use with SB4 was Frit 503. Frit 418 was identified as a viable frit for the transition from Sludge Batch 3 (SB3) to SB4 (i.e. when the sludge composition is somewhere between that of SB3 and SB4). This frit was recommended primarily to reduce DWPF's inventory of Frit 418 while producing an acceptable glass product. These recommendations were based on composition projections for SB4 that were provided to SRNL in June 2006,[a] assessments of operating windows in terms of waste loading (WL),[2-7] melt rate data,[8] the potential for nepheline formation (a crystalline phase that can be detrimental to product performance) and the chemical durability of test glasses.[9-16] To support the SB4 qualification process, a glass variability study[17, 18] was initiated to confirm the applicability of the durability models,[19] which are used as part of the DWPF's process control strategy, to the SB4/Frit 503 glass system with some coverage of the SB4/Frit 418 glass system. This variability study, which was intended to support the projected composition of SB4 provided in June 2006, will be referred to as the SB4/Frit 503 Variability Study (VS) throughput this report.

As the SB4/Frit 503 VS results were being documented and reviewed in early October 2006, the Liquid Waste Organization (LWO) was exploring the possibility of decanting Tank 40 at the end of SB3 processing to transfer some fraction of the aqueous phase (supernate) to Tank 51 to facilitate the transfer of the contents of that tank back into Tank 40. More specifically, the supernate of Tank 40 would be used to alter rheological properties of the Tank 51 sludge to aid transfer back to Tank 40. The resulting sludge in Tank 40 would then become SB4, and the projected composition for the new version of this sludge was adjusted by LWO to reflect the impact of the Tank 40 decant. This decant would serve an additional benefit to the Tank Farm since the insoluble solids in Tank 40 would be maximized and recycle would be minimized.

Two projected compositions, designated as the 10-04-06 and the 10-10-06 projections, were issued to SRNL[b] by LWO so that the frit development team could:

- add the anticipated sulfate concentration and renormalize the SB4 composition as calcine sludge oxides;
- compare the 10-04-06 and 10-10-06 calcine projections to the projections utilized by SRNL in June 2006 to support the Frit 503 recommendation and the SB4/Frit 503 VS;
- identify candidate frits for use with the new projections for SB4 (including Frit 503 and Frit 418);
- develop the projected operating windows for the candidate frit/sludge glass systems;
- identify a frit or frits for use with the new projections; and

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[a] Personal communication with H. B. Shah, via email, on June 22, 2006 (see WSRC-NB-2006-00017, pp. 51 – 53 for details) for compositions assuming a ~113" heel in Tank 40 and a blend date after meeting canister production goal (mid-November 2006).

[b] Site emails communicated from H. B. Shah on October 4 and October 10 of 2006 (see WSRC-NB-2006-00017, pp. 86 – 94 for details). The 10-04-06 SB4 composition was initially used as the technical basis for the nominal stage assessments discussed in this report to identify candidate frits. Based on initial feedback to the LWO and DWPF using the 10-04-06 compositional projections, a decision was made to utilize (at least initially) Frit 418 for processing SB4. This decision was made, in part, due to the uncertainty of the composition for SB4, which may not be well understood until the processing of this sludge actually begins. This decision was made prior to the receipt of the 10-10-06 composition which was ultimately used to support the development of the SB4/Frit 418 supplemental variability study test matrix.

- identify additional glasses that are to be fabricated and tested to complement any existing glasses to serve as a technical basis for a variability study for the anticipated glass system.

It is the purpose of this report to address each of these issues.

2.0 SB4 Projected Composition

The new projected sludge compositions that were considered in this study are provided in the first two columns of Table 2-1. Elemental concentrations for these options were provided to the frit development team by LWO,[20] and these were converted to oxide concentrations by multiplying the values for each element by the gravimetric factor for the corresponding oxide. The compositions submitted to the frit development team did not include estimates of the SO_4^{2-} concentrations. However, LWO personnel did provide information, as part of the washing scenarios and preparation plans, which was used to derive an estimate for the SO_4^{2-} concentration. The concentration was added to the oxide list and the resulting oxide concentrations were then normalized to 100%. It should be noted that the projected sludge compositions presented in Table 2-1 are sludge-only flowsheets and do not account for any potential secondary streams from the Actinide Removal Process (ARP) or the Modular Caustic Side Solvent Extraction Unit (MCU). These auxiliary streams are not considered in this report.

Table 2-1. Nominal SB4 Projected Compositions (wt% calcine basis).

Oxide	10-04-06 SB4 Projection	10-10-06 SB4 Projection	June 2006 SB4 Blend-1 at 12.2 wt% solids, 0.92 M Na^+	June 2006 SB4 Blend-1 at 12.6 wt% solids, 0.912 M Na^+
	Blend 1 Processing	Blend 1 Processing	Processing	Processing
Al_2O_3	25.65	25.490	23.750	23.965
BaO	0.07	0.070	0.124	0.125
CaO	2.79	2.765	2.350	2.371
Ce_2O_3	0.22	0.214	0.150	0.151
Cr_2O_3	0.20	0.198	0.208	0.210
CuO	0.05	0.051	0.060	0.060
Fe_2O_3	29.20	28.989	26.165	26.401
K_2O	0.07	0.068	0.329	0.332
La_2O_3	0.03	0.031	0.106	0.107
MgO	2.79	2.774	2.480	2.502
MnO	5.83	5.783	5.394	5.443
Na_2O	18.22	18.708	23.888	23.261
NiO	1.67	1.660	1.545	1.559
PbO	0.39	0.383	0.091	0.092
SO_4^{2-}	0.79	0.866	1.417	1.368
SiO_2	2.73	2.711	3.963	3.998
ThO_2	0.03	0.031	0.063	0.063
TiO_2	0.04	0.035	0.026	0.026
U_3O_8	9.10	9.031	7.563	7.632
ZnO	0.05	0.000	0.098	0.099
ZrO_2	0.09	0.050	0.233	0.235
SUM	100.00	100.00	100.00	100.00

The last two columns of Table 2-1 reflect the June 2006 SB4 projected compositions that served as the basis for SRNL's Frit 503 recommendation[1] and for the SB4/Frit 503 VS.[17, 18] A comparison between the new projected sludge compositions and those studied previously indicates that the new compositions are slightly higher in Al_2O_3, Fe_2O_3, and U_3O_8 and slightly lower in SiO_2. The most dramatic changes are in the Na_2O and SO_4^{2-} concentrations. The Na_2O is more than 4.5 wt%

lower in the October projections as compared to those used in June assessments.[a] This is a significant change due to the frit development team's approach of aligning the Na_2O concentration in a candidate frit to the Na_2O content of the sludge. This approach is taken to enhance the projected operating window and the waste throughput potential for the resulting glass system while minimizing the possible negative impacts of nepheline formation on durability. This degree of change in SB4's expected Na_2O content may have a detrimental impact on the projected operating window for the SB4/Frit 503 glass system. This issue is addressed in the following sections.

With respect to the SO_4^{2-} concentrations, the revised values are almost a factor of 2 lower than previous projections. These lower values translate into reduced risks of exceeding the SO_4^{2-} solubility limit for the specific frit – SB4 system of interest. More specifically, assuming a 0.6 wt% SO_4^{2-} (in glass) Product Composition Control System (PCCS) limit for the SB4 system, WLs greater than ~70% would be required before either the 10-04-06 or the 10-10-06 systems would become SO_4^{2-} limited. Other process related parameters such as melt rate, liquidus temperature, or nepheline formation will be more restrictive with respect to accessing higher WLs.

[a] The most recent composition changes are a result of using the Sludge Receipt and Adjustment Tank (SRAT) and/or updated Tank 51 compositional information based on the SB4 qualification sample and proposed Tank 40 decant. The June 2006 composition was based on the early analyses of SB4 and the WAPS sample analyses of SB3.

3.0 Candidate Frits

Table 3-1 provides the candidate frits and their nominal compositions (on a wt% basis) that were considered in the assessment of the new SB4 compositions. A closer review of Frits 422 through X1-1 (shaded in Table 3-1) indicates fixed concentrations of B_2O_3 and Li_2O at 8 wt% with only the Na_2O and SiO_2 concentrations varying. In general, these frit compositions reflect an increase in Na_2O by 1% with a corresponding decrease in SiO_2, proceeding from Frit 422 to Frit X1-1. This system has been referred to as a "sliding Na_2O scale," a concept that was developed to accommodate potential sludge Na_2O concentration differences as a result of various washing strategies considered for SB3.[21]

Frits 202 and 200 are historical frits that were developed to support the coupled and sludge-only flowsheets, respectively. They are included in this assessment to provide insight into their potential use with the latest SB4 compositional projection. The "P-series", T1-1, "418-m" series, and the "200-m" series of frits have been developed to minimize the potential for nepheline formation given its impact on durability.[12-14, 16] In general, these frits have lower Na_2O concentrations than the "sliding Na_2O scale" series, with the differences being accounted for by increases in Li_2O, B_2O_3, and/or Fe_2O_3 (individually or in combination). The intent in introducing this series of frits was to find combinations of Na_2O and SiO_2 concentrations that suppressed the potential for nepheline formation to higher WLs with the adjustments in Li_2O, B_2O_3, and/or Fe_2O_3, with the hope of maintaining (or regaining) melt rate, which would presumably be lower for glass systems with lower Na_2O concentrations. In fact, Frit 503 (previously referred to as 418-m10) is one of the "418-m" series frits that was ultimately recommended for SB4 processing based on the June compositional projections.

Table 3-1. Nominal Compositions (in wt%) of Candidate Frits.

Frit	Oxide Composition					
	B_2O_3	Fe_2O_3	Li_2O	MgO	Na_2O	SiO_2
202	8	0	7	2	6	77
422	8	0	8	0	3	81
d1-1	8	0	8	0	4	80
473	8	0	8	0	5	79
432	8	0	8	0	6	78
460	8	0	8	0	7	77
418	8	0	8	0	8	76
426	8	0	8	0	9	75
425	8	0	8	0	10	74
417	8	0	8	0	11	73
320	8	0	8	0	12	72
431	8	0	8	0	13	71
Y1-1	8	0	8	0	14	70
X1-1	8	0	8	0	15	69
P3-4	8	0	10	0	7	75
P3-1/502	8	0	11	0	5	76
P3-2	8	1	10	0	6	75
P3-3	8	1	10	0	7	74
t1-1	8	2	8	0	5	77
418-m2	8	3	8	0	5	76
418-m6	8	3	8	0	5	76
P2-3	8	3	10	0	6	73
P1-1	8	4	8	0	5	75
P2-1	8	4	10	0	5	73
P2-5	8	5	10	0	7	70
P2-2	8	5	11	0	5	71
P2-4	8	5	11	0	6	70
418-m1/501	9	0	10	0	5	76
418-m3	9	1	9	0	5	76
418-m4	9	2	8	0	5	76
200-m1	10	0	9	0	5	76
418-m7	10	1	9	0	5	75
418-m5	11	0	8	0	5	76
418-m8	11	1	9	0	4	75
200	12	0	5	2	11	70

Frit	Oxide Composition					
	B_2O_3	Fe_2O_3	Li_2O	MgO	Na_2O	SiO_2
418-m11	12	0	8	0	4	76
418-m16	12	0	8	0	5	75
200-m2	12	0	9	0	5	74
418-m9	12	1	9	0	4	74
418-m15	13	0	8	0	5	74
503-m10	14	0	5	0	10	71
503-m9	14	0	6	0	8	72
503-m8	14	0	7	0	6	73
418-m10/503	14	0	8	0	4	74
503-m1	14	0	8	0	5	73
418-m20/505	14	0	8	0	6	72
503-m2	14	0	8	0	7	71
503-m3	14	0	8	0	8	70
503-m4	14	0	8	0	9	69
503-m5	14	0	8	0	10	68
418-m24	14	4	8	0	4	70
418-m23/506	14	4	8	0	6	68
418-m28/507	14	4	10	0	4	68
418-m31	14	4	9	0	5	68
418-m32	14	5	9	0	4	68
418-m25	14	6	8	0	4	68
418-m29	14	6	10	0	4	66
418-m26	14	8	8	0	4	66
418-m30	14	8	10	0	4	64
418-m12	16	0	8	0	4	72
418-m17	16	0	8	0	5	71
418-m21	16	0	8	0	6	70
503-m6	16	0	8	0	8	68
503-m7	16	0	8	0	10	66
418-m13	18	0	8	0	4	70
418-m18	18	0	8	0	5	69
418-m22	18	0	8	0	6	68
418-m14/504	20	0	8	0	4	68
418-m19	20	0	8	0	5	67

4.0 Nominal Stage Assessment – the Approach and the Results

What is the impact of the new SB4 projected composition on the viability of processing this sludge with Frit 503 or with Frit 418? Are there other candidate frits that provide attractive operating windows with the new projected composition for SB4? To answer these questions, a Nominal Stage assessment was conducted using the 10-04-06 SB4 projection. This assessment is a screening tool that is typically applied to a large set of candidate frits to identify those worthy of additional study – specifically, a Variation Stage assessment.[a]

There are 69 frits in Table 3-1, and for the Nominal Stage assessment, all of these frits were considered with the 10-04-06 SB4 projection (i.e., the first column of Table 2-1) and with the two previously studied SB4 projections (i.e., the last two columns of Table 2-1). This allows for comparisons to be readily made between the predicted operating windows for the new and previous SB4 projections. Of particular interest will be the comparisons for Frit 503 and Frit 418 for the different SB4 compositional views, as well as the identification of other frit alternatives that are projected to lead to attractive operating windows with the new SB4 composition.

As in the past, the assessment conducted as part of this effort was strictly a paper study that was driven by predictions from glass property/glass composition models. However, the assessments do provide meaningful insight into the viability of sludge/frit glass systems since the models used in the assessments are the same as the models which will be in DWPF's PCCS during the processing of SB4. The major property models included those for liquidus temperature (T_L), viscosity (η), and durability (as defined by the Product Consistency Test) response in terms of the preliminary glass dissolution estimator (ΔG_P or Del Gp).[19] It should be noted that the proposed durability limits by Edwards *et al.*[22] and the new viscosity model developed by Jantzen[23] were used in this assessment.[b] Jantzen *et al.*,[19] Brown *et al.*,[24] and Brown, Postles, and Edwards[25] provide more detailed discussions on the development of the PCCS models and the constraints imposed on the DWPF operation including a relatively new constraint to limit the potential for the formation of a nepheline primary crystalline phase.[10] This constraint was based on a nepheline discriminator function[c] described by Li *et al*.[26]

For the Nominal Stage assessment, glass compositions were generated to represent combinations of the 10-04-06 SB4 projection with each candidate frit at waste loadings of interest. The acceptability of the model predictions for a particular glass composition for this stage as well as the Variation Stage (to be described later) was judged by employing the same criteria that are used by PCCS in its Slurry Mix Evaporator (SME) acceptability decisions. Acceptable predicted properties for the assessment are based on satisfying their respective Measurement Acceptability

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[a] Based on initial feedback to the LWO and DWPF using the 10-04-06 compositional projections, a decision was made to utilize (at least initially) Frit 418 for processing SB4. This decision was made, in part, due to the uncertainty of the composition for SB4, which may not be well understood until the processing of this sludge actually begins. This decision was made prior to the receipt of the 10-10-06 composition. The latter composition (10-10-06) was ultimately used to support the development of the SB4/Frit 418 supplemental variability study test matrix as will be discussed.

[b] The new durability limits and the new viscosity model were used since both models are currently being implemented in DWPF to support SB4 processing. The durability limits remove excess conservatism in the current model without compromising product quality and provide access to higher alkali compositional regions that may improve melt rate and/or waste loading. The modifications to implement the new viscosity model in PCCS are described by Edwards and Peeler in the memorandum SRNL-SCS-2005-00054.

[c] Sodium alumino-borosilicate glasses are prone to nepheline crystallization if their compositions projected on the Na_2O-Al_2O_3-SiO_2 ternary fall within the nepheline primary phase field. In particular, durable glasses with $SiO_2/(SiO_2+Na_2O+Al_2O_3) > 0.62$, where the oxides are expressed as mass fractions in the glass, do not precipitate nepheline as their primary phase.[26]

Region (MAR) limits. Brown, Postles, and Edwards[25] provide a detailed discussion of how the MAR limits are utilized for SME acceptability decisions in PCCS. Thus, the value of the frit development effort in its assessment of a glass composition is that it mirrors the results that would be generated by the PCCS MAR criteria for the same glass at DWPF. The results of this assessment are provided in Table 4-1.

To aid the interpretation of results presented in Table 4-1, a description of the terminology used and a brief discussion of a specific example are warranted. The first column (labeled "Frit") contains the 69 frits as shown in Table 3-1. The remaining three major column headers (10-04-06 SB4 Projection, SB4 Blend-1 at 12.2 wt% solids, 0.92 M Na^+, and SB4 Blend-1 at 12.6 wt% solids, 0.912 M Na^+) represent the three sludge compositional views. For each frit – sludge combination, there are three sub-columns of information. The middle column represents the WL interval over which glasses are acceptable based on predicted properties as compared to MAR acceptability criteria. The entries to the left and right of this center column indicate the property (or properties) that limit access to lower and higher WLs, respectively. A blank cell indicates that there were no property restrictions below or above 25 and 60% WL, respectively. Nomenclature for specific properties shown in Table 4-1 include: T_L (liquidus temperature), hFrit (high Frit), Neph (nepheline), lvisc (low viscosity), hvisc (high viscosity), and Del Gp (durability).

Consider the 10-04-06 SB4/Frit 200 system as an example. The projected operating window is 25 – 38% WL with predictions of T_L limiting access to higher WLs. There are no restrictions on the lower end of the WL interval of interest (i.e., a blank entry).

Table 4-1. Waste Loadings for the Projected Operating Windows from the Nominal Stage Assessment.

Frit	10-4-06 SB4 Projection			SB4 Blend-1 at 12.2 wt% solids, 0.92 M Na^+			SB4 Blend-1 at 12.6 wt% solids, 0.912 M Na^+		
200		25-38	TL		25-39	Neph		25-40	Neph
200-m1		25-39	TL	hFrit	26-46	Neph	hFrit	26-46	Neph
200-m2		25-39	TL		26-45	Neph	hFrit	26-46	Neph
202		-		hvisc	31-44	TL	hvisc	31-43	TL
320		25-41	Neph	hFrit	26-38	lvisc	hvisc	26-39	lvisc
417		25-43	Neph	hFrit	26-41	lvisc Neph	hFrit	26-41	Neph
418		25-42	TL	hFrit	26-44	Neph	hFrit	26-44	Neph
418-m1/501		25-40	TL	hFrit	26-46	Neph	hFrit	26-46	Neph
503		25-37	TL	hFrit	26-46	TL Neph	hFrit	26-45	TL
418-m11	hvisc	31-37	TL	hFrit	26-46	TL	hFrit	26-45	TL
418-m12		25-36	TL	hFrit	26-45	Neph	hFrit	26-45	TL Neph
418-m13		25-36	TL	hFrit	26-42	lvisc	hFrit	26-43	lvisc
418-m14/504		25-36	TL	hFrit	26-38	lvisc	hFrit	26-39	lvisc
418-m15		25-38	TL	hFrit	26-45	Neph	hFrit	26-46	TL Neph
418-m16		25-38	TL	hFrit	26-46	Neph	hFrit	26-46	TL Neph
418-m17		25-38	TL	hFrit	26-43	lvisc	hFrit	26-44	lvisc Neph
418-m18		25-37	TL	hFrit	26-39	lvisc	hFrit	26-40	lvisc
418-m19		25-37	TL	hFrit	26-35	lvisc Neph	hFrit	26-36	lvisc
418-m2	hvisc	29-35	TL		25-44	TL		25-43	TL
418-m20/505		25-39	TL	hFrit	26-44	lvisc Neph	hFrit	26-44	Neph
418-m21		25-39	TL	hFrit	26-40	lvisc	hFrit	26-41	lvisc
418-m22		25-38	TL	hFrit	26-36	lvisc	hFrit	26-37	lvisc
418-m23/506		25-34	TL		25-37	lvisc		25-37	lvisc
418-m24		25-31	TL		25-41	TL		25-39	TL
418-m25		25-29	TL		25-37	TL		25-36	TL
418-m26		25-26	TL		25-34	TL		25-33	TL
418-m28/507		25-34	TL		25-31	lvisc		25-32	lvisc
418-m29		25-32	TL		25-26	lvisc		25-27	lvisc
418-m3		25-38	TL		25-46	Neph		25-46	Neph
418-m30		25-25	lvisc		-	TL lvisc		-	TL lvisc
418-m31		25-34	TL		25-34	lvisc		25-35	lvisc
418-m32		25-32	TL		25-36	lvisc		25-36	lvisc
418-m4	hvisc	29-36	TL		25-46	TL Neph		25-44	TL
418-m5	hvisc	29-38	TL	hFrit	26-46	Neph	hFrit	26-46	TL Neph
418-m6	hvisc	29-35	TL		25-44	TL		25-43	TL
418-m7		25-38	TL		25-46	Neph		25-46	Neph
418-m8		25-37	TL		25-46	TL Neph		25-45	TL
418-m9		25-37	TL		25-46	TL Neph		25-45	TL
422		-		hvisc	37-46	hvisc	hvisc	38-44	hvisc

Table 4-1. Waste Loadings for the Projected Operating Windows from the Nominal Stage Assessment
(continued)

Frit	10-04-06 SB4 Projection			SB4 Blend-1 at 12.2 wt% solids, 0.92 M Na^+			SB4 Blend-1 at 12.6 wt% solids, 0.912 M Na^+		
425		25-44	TL Neph	hFrit	26-42	Neph	hFrit	26-42	Neph
426		25-43	TL	hFrit	26-43	Neph	hFrit	26-43	Neph
431		25-40	Neph	Del Gp	34-34	Del Gp	hFrit	26-35	lvisc
432	hvisc	33-40	TL	hvisc/hFrit	26-46	Neph	hvisc/hFrit	26-47	Neph
460	hvisc	27-41	TL	hFrit	26-45	Neph	hFrit	26-46	Neph
473	hvisc	38-38	TL	hvisc	30-47	hvisc	hvisc	31-47	hvisc
503-m1		25-38	TL	hFrit	26-45	Neph	hFrit	26-45	Neph
503-m10		25-40	TL	hFrit	26-41	Neph	hFrit	26-41	Neph
503-m2		25-40	TL	hFrit	26-41	lvisc	hFrit	26-42	lvisc Neph
503-m3		25-41	TL	hFrit	26-38	lvisc	hFrit	26-39	lvisc
503-m4		25-42	TL Neph	hFrit	26-35	lvisc	hFrit	26-36	lvisc
503-m5		25-38	lvisc	hFrit	26-31	lvisc	hFrit	26-32	lvisc
503-m6		25-41	TL lvisc	hFrit	26-33	lvisc	hFrit	26-34	lvisc
503-m7		25-31	lvisc		-	lvisc		-	lvisc
503-m8		25-38	TL	hFrit	26-44	Neph	hFrit	26-45	Neph
503-m9		25-39	TL	hFrit	26-43	Neph	hFrit	26-43	Neph
d1-1		-		hvisc	34-47	hvisc	hvisc	34-46	hvisc
P1-1	hvisc	26-34	TL		25-43	TL		25-42	TL
P2-1		25-36	TL		25-42	lvisc		25-43	lvisc
P2-2		25-36	TL		25-34	lvisc		25-35	lvisc
P2-3		25-38	TL		25-41	lvisc		25-42	lvisc
P2-4		25-37	TL lvisc		25-30	lvisc		25-31	lvisc
P2-5		25-37	TL		25-33	lvisc		25-34	lvisc
P3-1/502		25-42	TL	hFrit	26-44	lvisc	hFrit	26-45	lvisc
P3-2		25-41	TL		25-44	lvisc		25-45	lvisc Neph
P3-3		25-42	TL		25-41	lvisc		25-42	lvisc
P3-4		25-43	TL	hFrit	26-43	lvisc	hFrit	26-44	lvisc
t1-1	hvisc	32-36	TL		25-46	TL	hvisc	26-44	TL
X1-1	Del Gp	27-33	lvisc		-	Del Gp		-	Del Gp
Y1-1		25-38	lvisc		-	Del Gp		-	Del Gp

Given a specific interest in Frit 418 and Frit 503, the rows of Table 4-1 showing the results for these two frits are shaded. Prior to assessing their potential use with the 10-04-06 composition, a brief review of the projected operating windows for the June projections is warranted to establish a technical basis for the impact of the recent compositional changes. For the Frit 418 systems, the two previous compositions yielded projected operating windows of 26 – 44% WL with each system being nepheline limited at higher WLs. The high content of Na_2O in both the sludge and the frit drove the system to be nepheline limited – a condition which DWPF may wish to avoid as it relates to a waste form affecting property. For the two Frit 503 systems, the projected operating windows in terms of WL were 26 – 46% and 25 – 45%, with the systems being either T_L

/nepheline or T_L limited. The lower Na_2O content of Frit 503 (relative to Frit 418) for a fixed Na_2O sludge content increased T_L predictions resulting in a shift from a purely nepheline limited system (Frit 418 systems) to one controlled primarily by T_L.

Based on the lower Na_2O and higher Fe_2O_3 concentrations in the 10-04-06 composition (as compared to the June compositions), T_L predictions would be expected to increase for a given frit at a fixed WL. This being the case, for systems that are T_L limited (e.g., the two Frit 503 systems based on previous projections), T_L predictions should further reduce the projected operating windows (assuming a compositional adjustment to the frit is not made). This was indeed the case as the projected operating window for the Frit 503 – 10-04-06 SB4 system was 25 – 37% WL, with the system being T_L limited. Given the lower Na_2O concentration in the 10-04-06 sludge, the Na_2O content could easily be remedied by increasing the Na_2O content in the frit (i.e., 4% in Frit 503 to 8% in Frit 418), which would reduce T_L predictions and provide access to higher WLs. As a result, the projected operating window for the Frit 418 – 10-04-06 SB4 system is 25 – 42% WL with the system still being T_L limited. A continued increase in the Na_2O content of the frit (e.g., 10% in Frit 425) provides a 25 – 44% WL projected operating window – comparable to the previous higher Na_2O-based SB4 sludges when coupled with Frit 503. For the Frit 425 based system, both T_L and nepheline limit access to higher WLs indicating that further increases in Na_2O would drive the system into a nepheline limited situation and upper WLs would decrease from the 44% level.

Thus, strictly from the perspective of a projected operating window for the nominal composition, Frit 418 is more attractive than Frit 503 for the 10-04-06 SB4 projected composition. However, this comparison does not reflect other aspects of interest for the glass systems such as their respective melt rates. For example, the lower B_2O_3 content of Frit 418 relative to Frit 503 (8% versus 14%) may counter or off-set any positive melt rate impacts of the higher Na_2O concentrations. In fact, Frit 503-m4 (see Table 3-1) was designed specifically for the 10-04-06 SB4 composition with the intent of balancing the Na_2O content as well as maintaining relatively high B_2O_3 concentrations that were effective in terms of nepheline suppression and melt rate enhancements in recent experimental work. Based on the MAR assessments, Frit 503-m4 has a projected operating window of 25 – 42% WL with the system being both T_L and nepheline limited at 43% WL (see Table 4-1).

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5.0 Variation Stage Assessment – the Approach and the Results

Since the Nominal Stage assessment does not account for any anticipated compositional variation in the sludge projection, there is an increased risk with respect to processability or product quality if a decision (i.e., frit selection) were to be based solely on this assessment. The risk is reduced by the Variation Stage assessment, which is used to gain insight into the robustness of candidate frits with respect to sludge compositional variation. For this analysis, a Variation Stage assessment was conducted for the 10-10-06 SB4 projection with Frit 418.[a] Table 5-1 provides the framework for the Variation Stage assessment for the sludge being evaluated. In this assessment, the nominal value for each oxide in the sludge is replaced with an interval, limited by a minimum (min) and maximum (max), of possible values. The second column of this table indicates the types of variation that were introduced to determine the minimums and maximums: a variation of ±7.5% of the nominal value was used to determine the min's and max's for the major oxides (i.e., Al_2O_3, Fe_2O_3, Na_2O, and U_3O_8). A ±0.25 wt% variation was placed around the nominal value for each individually tracked minor oxide (i.e., CaO, MgO, MnO, NiO, and SiO_2, but not SO_4^{2-}) and for "Others." The variation applied to the nominal SO_4^{2-} value was ± 0.10 wt%. The "Others" term was used to allow for the inclusion of the minor oxides that were not tracked individually. The composition of the "Others" component for each of the sludge options considered in this report was the same as used in the SB4/Frit 503 VS[17] and is provided (each oxide is given as a weight percentage of "Others") in Table 5-2.

Table 5-1. Nominal 10-10-06 SB4 Composition Projection and Sludge Composition Space with Traditional Variation Applied.

Oxide Component	Variation to be Applied (Traditional Variation)	10-10-06 Projected SB4 nominal composition	10-10-06 Projected SB4 with variation applied	
		(wt%)	min (wt%)	max (wt%)
Al_2O_3	7.5 %	25.49	23.578	27.402
CaO	0.25 wt%	2.765	2.515	3.015
Fe_2O_3	7.5 %	28.989	26.814	31.163
MgO	0.25 wt%	2.774	2.524	3.024
MnO	0.25 wt%	5.783	5.350	6.217
Na_2O	7.5 %	18.708	17.304	20.111
NiO	0.25 wt%	1.66	1.410	1.910
SO_4	0.1 wt%	0.866	0.766	0.966
SiO_2	0.25 wt%	2.711	2.461	2.961
U_3O_8	7.5 %	9.031	8.354	9.709
Others	0.25 wt%	1.500	1.250	1.750

[a] As previously noted, decisions regarding the use of Frit 418 were made prior to the receipt of the 10-10-06 composition. Therefore, the Variation Stage was performed utilizing only Frit 418 with the 10-10-06 composition.

Table 5-2. Components Making up Others.

Minor Component	Percent of Others
BaO	8.335
Ce_2O_3	10.088
Cr_2O_3	13.975
CuO	4.028
K_2O	22.153
La_2O_3	7.123
PbO	6.099
ThO_2	4.22
TiO_2	1.757
ZnO	6.576
ZrO_2	15.645
Others	100

Table 5-1 and Table 5-2 provide the framework around which the Variation Stage assessment was conducted. A sludge composition is in the region corresponding to the 10-10-06 projection if its concentration for each oxide is within the min and max interval for that oxide (e.g., the Al_2O_3 concentration in the sludge as a wt% is between 23.578 and 27.402) and the sum of the concentrations of all of the oxides in the sludge equals 100%. Such a composition is a mixture of oxides at concentrations that correspond to one of the possible compositions for the sludge projection as defined by Table 5-1. Algorithms are available in statistical software packages such as JMP Version 6.0.2[27] to generate the compositions that are the "corner points" of the bounding sludge region defined by Table 5-1. The bounding "corner-point" compositions generated by JMP are called the extreme vertices (EVs) of the sludge region.

JMP Version 6.0.2[27] was used to generate the EVs or corner points of the sludge regions defined by the information in Table 5-1. For the "Others" component, the concentration for an EV was generated by JMP. This concentration was then exploded into the oxides comprising "Others" using the percentages of Table 5-2. The centroid (or average of the EVs) for the sludge region was also generated so that it may be tracked during the Variation Stage to ensure consistent results with the Nominal Stage assessment.[a]

The EVs of the 10-10-06 SB4 projection that were generated by JMP were combined with Frit 418 at waste loadings from 25 to 60%. The resulting glass compositions were evaluated against the PCCS MAR criteria to determine their respective acceptability. A frit is considered to demonstrate robustness to the variation in a sludge option if 100% of the EVs for the option meet the PCCS MAR criteria over a wide sub-interval of the 25 to 60% WL interval. In addition, where less than 100% of the EVs are acceptable, identification of the constraint or constraints that are not met (i.e., the constraint(s) that limit the operating window) is of interest. The results of this evaluation for the centroid and for the EVs are provided in Table 5-3.

[a] It should be noted that the nominal composition was the 10-04-06 composition and the centroid are not the "exact" composition but will be extremely close. Therefore, the projected operating windows resulting from each should be relatively close in size.

Table 5-3. MAR Results for the Centroid and Percent of EVs that Satisfy the MAR for the 10-10-06 SB4 Projection with Frit 418.

% WL	MAR Status for the Centroid	% of EVs
25		100.0
26		100.0
27		100.0
28		100.0
29		100.0
30		100.0
31		100.0
32		100.0
33		100.0
34		100.0
35		100.0
36		100.0
37		100.0
38		100.0
39		99.8
40		91.8
41		73.9
42		55.4
43	T_L	43.7
44	T_L	31.7
45	T_L	9.3
46	T_L	1.1
47	T_L Neph	
48	T_L Neph	
49	T_L Neph	
50	T_L Neph	
51	T_L Neph	
52	T_L Neph	
53	T_L Neph	
54	T_L Neph	
55	T_L Neph	
56	T_L Neph	
57	T_L lvisc Neph	
58	T_L lvisc Neph	
59	T_L lvisc Neph	
60	T_L lvisc Neph	

As with the Nominal Stage assessment which utilized the 10-04-06 SB4 projection, the 10-10-06 SB4/Frit 418 glass system is T_L limited. The centroid of the Variation Stage assessment is limited to WLs less than 43% (i.e., a projected operating window from 25 – 42% WL – consistent with the Nominal Stage results using the 10-04-06 projection with Frit 418). The yellow shading in Table 5-3 shows the WLs for which the nepheline constraint is not satisfied at the MAR. For the centroid, the nepheline constraint MAR is not satisfied at WLs of 47% and greater. With respect to the EVs, T_L limits some of the EVs (0.2% fail the T_L MAR) at a WL of 39% and some EVs fail the nepheline constraint MAR at a WL of 45%.

Based on this assessment using the SB4 projection from 10-10-06, Frit 418 should allow access to WLs of interest (up to 42% based on the centroid composition) and demonstrates a relatively high degree of robustness to potential compositional variation (i.e., all of the EVs are MAR acceptable from 25 – 38% WL). In fact, for those EVs in the 39 – 44% WL interval, only T_L is restrictive which, if encountered during SME acceptability decisions, could be viewed as a management risk based decision. More specifically, nepheline formation and its potential impact to a waste form affecting property (durability) is not an issue at WLs of interest in the system. As previously mentioned, a potential disadvantage of Frit 418 could be associated with melt rate. Previous testing indicated a significantly lower melt rate with Frit 418 as compared to Frit 503, even with the higher Na_2O based SB4 compositional projections received in June 2006.[8]

6.0 Variability Study for the New SB4 Projection

The glass region for the SB4/Frit 503 VS was determined[17] using the June 2006 predictions of the composition of this sludge batch that led to SRNL's frit recommendation report.[1] Variation was introduced into the composition of the sludge for the study to account for some of the uncertainty that may be present in these predictions as well as for process variation that may be experienced at the DWPF during its normal operations. From the frit perspective, the primary focus was on the use of Frit 503, as this frit was recommended for SB4 processing.[1] However, the recommendation report also stated that Frit 418 was a viable option for DWPF processing during the transition from SB3 to SB4 (i.e. an acceptable product can be produced with both SB3 and SB4 when Frit 418 is used).[a] As a result, some glasses from the SB4/Frit 418 system were also included in the variability study.

Do the glasses that were already batched, fabricated, and tested based on the June 2006 composition provide any support for the variability study corresponding to the 10-10-06 SB4/Frit 418 glass system? Table 6-1 was prepared to help address this question.

This table shows the interval of "coverage" for each of the major oxides for the glass system driving the SB4/Frit 503 VS as well as corresponding intervals for the glass system involving the 10-10-06 SB4 projection with Frit 418. For both cases, the intervals are determined for WLs from 25 to 45% (given the T_L limitations shown in Table 5-3). While there is some overlap of select major oxides (Al_2O_3, Fe_2O_3, Na_2O, SiO_2, and U_3O_8), the primary difference is associated with B_2O_3. There is no overlap of the SB4/Frit 503 system with the 10-10-06 SB4/Frit 418 system over the WLs of interest given the significant differences in B_2O_3 content of the frit (8% versus 14%). What does this mean for the need to perform a supplemental variability study for the 10-10-06 SB4/Frit 418 region of interest? Unless there are historical glasses within the current databases that could be used to adequately cover the glass region of interest, a separate matrix would be required.

[a] Frit 503 was recommended for the majority of SB4 processing since this higher B_2O_3-containing frit has advantages over Frit 418 in melt rate and is less prone to nepheline crystallization.

Table 6-1 Projected Glass Space (Mins and Maxs) for the 10-10-06 Projection/Frit Systems (over 25 – 45% WL).

	Al_2O_3	B_2O_3	CaO	Fe_2O_3	Li_2O	MgO	MnO	Na_2O	NiO	SO_4	SiO_2	U_3O_8	
Previous SB4 VS with	0.05250	0.07700	0.00500	0.06000	0.04400	0.00500	0.01250	0.08250	0.00250	0.00250	0.42050	0.01750	Min
Frit 503 (25 - 45 %WL)	0.11700	0.10500	0.01350	0.13050	0.06000	0.01350	0.02700	0.13900	0.00900	0.00900	0.56750	0.03600	Max
Blend 10-10-06 with	0.05895	0.04400	0.00629	0.06704	0.04400	0.00631	0.01383	0.10326	0.00352	0.00192	0.42908	0.02195	Min
Frit 418 (25 - 45 %WL)	0.12331	0.06000	0.01357	0.14023	0.06000	0.01361	0.02715	0.13450	0.00859	0.00435	0.57740	0.04177	Max

Green: complete overlap
Yellow: some overlap exists (varying degrees)
Red: no overlap exists

In looking to the results from previous SB4 glass studies,[12-14, 16] as well as existing glasses within the ComPro[28] and nepheline[29] databases, seven glasses had targeted compositions that reflected sludge contributions (independent of frit composition) at WLs in the interval of 28 to 45%. These glasses are all from Phase 3 of the nepheline study[13] and their targeted compositions are provided in Table 6-2. The durability of each of these glasses was acceptable and predictable.[13] Although within the compositional region of interest, there is inadequate data in hand to technically defend the applicability of the current durability models to the Frit 418 – 10-10-06 SB4 compositional region of interest. More specifically, the seven glasses provide inadequate coverage of the compositional region of interest.

Table 6-2. Historical Glasses with Sludge Compositions Similar to the Revised SB4 projection.

Frit	Frit 418	Frit 501	Frit 501	Frit 501	Frit 502	Frit 502	Frit 502
Glass ID	**NEPH3-41**	**NEPH3-45**	**NEPH3-46**	**NEPH3-47**	**NEPH3-53**	**NEPH3-54**	**NEPH3-55**
Al_2O_3	8.682	8.682	9.922	11.659	8.682	9.922	11.907
B_2O_3	5.200	5.850	5.400	4.770	5.200	4.800	4.160
BaO	0.044	0.044	0.050	0.059	0.044	0.050	0.061
CaO	0.836	0.836	0.955	1.122	0.836	0.955	1.146
Ce_2O_3	0.052	0.052	0.060	0.070	0.052	0.060	0.072
Cr_2O_3	0.074	0.074	0.085	0.100	0.074	0.085	0.102
CuO	0.021	0.021	0.024	0.028	0.021	0.024	0.029
Fe_2O_3	9.298	9.298	10.626	12.486	9.298	10.626	12.751
K_2O	0.120	0.120	0.138	0.162	0.120	0.138	0.165
La_2O_3	0.038	0.038	0.043	0.051	0.038	0.043	0.052
Li_2O	5.200	6.500	6.000	5.300	7.150	6.600	5.720
MgO	0.873	0.873	0.998	1.173	0.873	0.998	1.198
MnO	1.918	1.918	2.192	2.576	1.918	2.192	2.630
Na_2O	12.928	10.978	11.832	13.027	10.978	11.832	13.198
NiO	0.552	0.552	0.631	0.741	0.552	0.631	0.757
PbO	0.032	0.032	0.036	0.043	0.032	0.036	0.043
SO_4^{2-}	0.468	0.468	0.535	0.629	0.468	0.535	0.642
SiO_2	50.840	50.840	47.245	42.213	50.840	47.245	41.494
ThO_2	0.023	0.023	0.026	0.031	0.023	0.026	0.032
TiO_2	0.009	0.009	0.011	0.013	0.009	0.011	0.013
U_3O_8	2.674	2.674	3.056	3.591	2.674	3.056	3.667
ZnO	0.034	0.034	0.039	0.046	0.034	0.039	0.047
ZrO_2	0.083	0.083	0.095	0.111	0.083	0.095	0.114

In discussions with Waste Solidification Engineering (WS-E) of the results being presented in this report, their decision was for SRNL to focus the next phase of the variability study on the use of Frit 418 with the 10-10-06 SB4 composition to reduce the risk associated with processing this glass system. Selecting these glasses is pursued in the next section.

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7.0 Selecting Target Compositions of Selected Glasses

The information of Table 5-1 was used to define the sludge region from which the glasses for the supplemental SB4/Frit 418 VS were to be selected. Initially, the Design of Experiment platform's Custom Design feature of JMP Version 6.0.2 was used to select 11 sludge compositions satisfying the concentration intervals of Table 5-1. This JMP feature allows the user to specify the form of a model such as a linear model consisting of a term for each of the 11 oxides of Table 5-1 (including "Others"). Then JMP's coordinate exchange algorithm was used to optimally select a specified number of design points, n (where $n \geq 11$), for this model from the region defined by the intervals of Table 5-1, with the intervals being specified in JMP during the design activity. The optimality criterion used in this case was D-optimality, which has the goal of minimizing $|(X^TX)^{-1}|$, where X is the design matrix, X^T indicates the transpose of X, $(X^TX)^{-1}$ indicates the matrix inversion of the product of X^T and X, and $|(X^TX)^{-1}|$ represents the determinant of the matrix $(X^TX)^{-1}$. In the task, the number of design points, n, was taken to be its smallest possible value, 11. The 11 sludge EVs selected by this process are given in Table 7-1.

Table 7-1. D-Optimal Set of 11 Sludge EVs for Projected SB4 Composition with Variation.

Type	EV-01	EV-02	EV-03	EV-04	EV-05	EV-06	EV-07	EV-08	EV-09	EV-10	EV-11
Al_2O_3	23.578	26.917	27.402	27.402	26.945	26.404	23.578	23.578	23.578	27.402	23.578
BaO	0.103	0.103	0.146	0.146	0.146	0.103	0.103	0.146	0.146	0.103	0.146
CaO	3.015	2.515	3.015	2.515	3.015	2.515	3.015	2.515	2.515	3.015	3.015
Ce_2O_3	0.125	0.125	0.177	0.177	0.177	0.125	0.125	0.177	0.177	0.125	0.177
Cr_2O_3	0.173	0.173	0.245	0.245	0.245	0.173	0.173	0.245	0.245	0.173	0.245
CuO	0.050	0.050	0.070	0.070	0.070	0.050	0.050	0.070	0.070	0.050	0.070
Fe_2O_3	30.495	31.163	27.241	26.814	26.814	26.814	28.473	29.613	30.765	27.610	30.932
K2O	0.274	0.274	0.388	0.388	0.388	0.274	0.274	0.388	0.388	0.274	0.388
La_2O_3	0.088	0.088	0.125	0.125	0.125	0.088	0.088	0.125	0.125	0.088	0.125
MgO	3.024	2.524	2.524	3.024	2.524	2.524	2.524	2.524	3.024	3.024	2.524
MnO	5.350	5.350	6.217	5.350	5.350	5.350	6.217	6.217	6.217	6.217	5.350
Na_2O	20.111	17.304	17.304	18.299	20.111	20.111	20.111	20.111	17.304	17.304	17.304
NiO	1.410	1.410	1.410	1.410	1.910	1.910	1.410	1.410	1.910	1.910	1.910
PbO	0.075	0.075	0.107	0.107	0.107	0.075	0.075	0.107	0.107	0.075	0.107
SO_4^{2-}	0.966	0.766	0.966	0.766	0.766	0.966	0.766	0.966	0.766	0.966	0.966
SiO_2	2.461	2.461	2.461	2.961	2.461	2.461	2.961	2.961	2.461	2.961	2.961
ThO_2	0.052	0.052	0.074	0.074	0.074	0.052	0.052	0.074	0.074	0.052	0.074
TiO_2	0.022	0.022	0.031	0.031	0.031	0.022	0.022	0.031	0.031	0.022	0.031
U_3O_8	8.354	8.354	9.709	9.709	8.354	9.709	9.709	8.354	9.709	8.354	9.709
ZnO	0.081	0.081	0.115	0.115	0.115	0.081	0.081	0.115	0.115	0.081	0.115
ZrO_2	0.193	0.193	0.274	0.274	0.274	0.193	0.193	0.274	0.274	0.193	0.274

Each of these sludge EVs was combined with Frit 418 at WLs from 25 to 60% in 1% increments. The resulting glass compositions were assessed against the PCCS MAR criteria, and the outcome is presented in Figure 7-1. The centroid shown in this exhibit was determined by averaging the 11 sludge EVs. The centroid was also combined with Frit 418 at WLs from 25 to 60%.

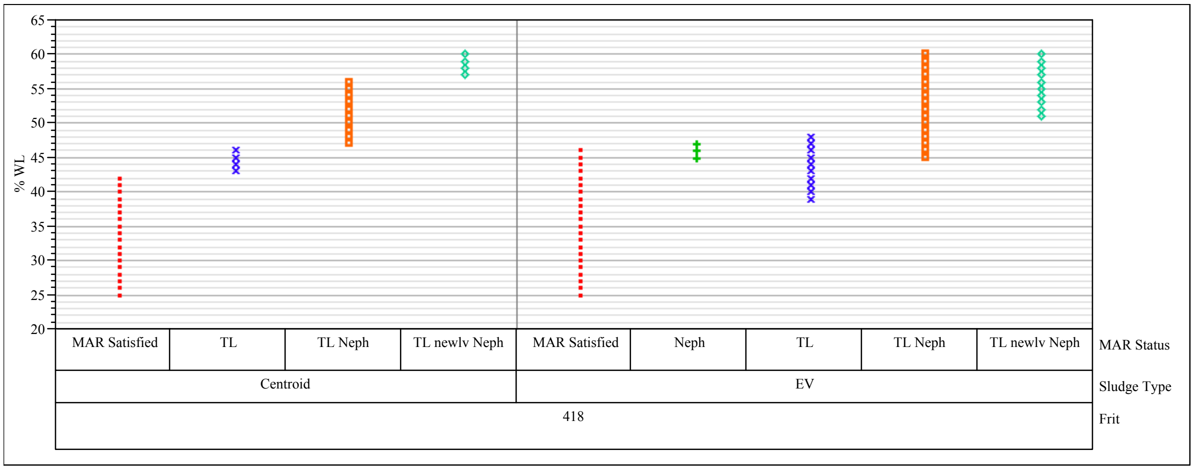

Figure 7-1. Assessment of PCCS MAR Criteria for SB4/Frit 418 Glasses.

All of the glass compositions corresponding to the points shown to meet the MAR criteria in Figure 7-1 (red blocks in the "MAR Satisfied" column) are candidate compositions for the SB4/Frit 418 variability study. Prior to selecting the specific glasses for the supplemental study, a brief review of the projected operating windows for the centroid and EV-based Frit 418 systems is warranted. For the centroid, the projected operating window is 25 – 42% WL with T_L prediction limiting access to higher WLs. All of the EVs can be processed over a WL interval of 25 – 38%. This information is consistent with the results presented in Table 5-3.

A review of the results led to the selection of the combinations for the EVs and their centroid with Frit 418 at the WLs given in Table 7-2. The predictions for several of the processing and quality characteristics of these glasses are also provided in this table.

Table 7-2. Selected Glasses for the SB4/Frit 418 VS with Property Predictions.

WL (wt%)	Frit	Sludge Type	ΔG_p Value (kcal/100 g glass)	NL[B (g/L)]	Liquidus Temperature Prediction (°C)	Viscosity Prediction (P)	Nepheline Discriminator Value
40	418	EV-01	-9.254	0.596	971.3	46.14	0.677
34	418	EV-02	-7.944	0.345	935.2	74.18	0.715
38	418	EV-03	-8.053	0.361	966.5	73.35	0.686
38	418	EV-04	-8.249	0.392	961.1	70.77	0.684
36	418	EV-05	-8.940	0.523	934.0	65.77	0.692
28	418	EV-06	-9.042	0.546	823.7	81.60	0.747
30	418	EV-07	-9.404	0.635	835.3	70.78	0.743
42	418	EV-08	-9.345	0.619	989.2	43.67	0.663
32	418	EV-09	-8.595	0.453	919.4	71.49	0.739
34	418	EV-10	-8.152	0.376	932.2	81.60	0.714
30	418	EV-11	-8.551	0.445	887.7	76.25	0.752
32	418	Centroid	-8.714	0.476	894.6	73.90	0.729
36	418	Centroid	-8.633	0.460	943.8	65.59	0.703

The compositions for the centroid glasses are provided in Table 7-3. This pair of glasses is at WLs of 32 and 36%, the primary WL interval of interest for this glass system.

Table 7-3. Target Glass Compositions for Frit 418 with the Centroid SB4 Composition (in wt%).

Glass ID	SB4VS-47	SB4VS-48
WL	**32**	**36**
Al_2O_3	8.134	9.151
B_2O_3	5.440	5.120
BaO	0.040	0.045
CaO	0.885	0.996
Ce_2O_3	0.048	0.054
Cr_2O_3	0.067	0.075
CuO	0.019	0.022
Fe_2O_3	9.247	10.403
K_2O	0.106	0.119
La_2O_3	0.034	0.038
Li_2O	5.440	5.120
MgO	0.888	0.999
MnO	1.851	2.082
Na_2O	11.384	11.807
NiO	0.531	0.598
PbO	0.029	0.033
SO_4^{2-}	0.277	0.312
SiO_2	52.548	49.616
ThO_2	0.020	0.023
TiO_2	0.008	0.009
U_3O_8	2.897	3.259
ZnO	0.031	0.035
ZrO_2	0.075	0.084

The compositions of the glasses derived from the EVs of the sludge region are given in Table 7-4. These glasses cover WLs from 28 to 42% with 8 falling within the WL interval from 30 to 38% (inclusive).

Table 7-4. Target Glass Compositions for Frit 418 with the Inner Layer SB4 EVs (in wt%).

Glass ID	SB4VS-36	SB4VS-37	SB4VS-38	SB4VS-39	SB4VS-40	SB4VS-41	SB4VS-42	SB4VS-43	SB4VS-44	SB4VS-45	SB4VS-46
WL	40	34	38	38	36	28	30	42	32	34	30
Al_2O_3	9.431	9.152	10.413	10.413	9.700	7.393	7.074	9.903	7.545	9.317	7.074
B_2O_3	4.800	5.280	4.960	4.960	5.120	5.760	5.600	4.640	5.440	5.280	5.600
BaO	0.041	0.035	0.055	0.055	0.053	0.029	0.031	0.061	0.047	0.035	0.044
CaO	1.206	0.855	1.146	0.956	1.085	0.704	0.905	1.056	0.805	1.025	0.905
Ce_2O_3	0.050	0.042	0.067	0.067	0.064	0.035	0.037	0.074	0.056	0.042	0.053
Cr_2O_3	0.069	0.059	0.093	0.093	0.088	0.048	0.052	0.103	0.078	0.059	0.073
CuO	0.020	0.017	0.027	0.027	0.025	0.014	0.015	0.030	0.023	0.017	0.021
Fe_2O_3	12.198	10.595	10.352	10.189	9.653	7.508	8.542	12.438	9.845	9.387	9.280
K_2O	0.110	0.093	0.147	0.147	0.140	0.077	0.082	0.163	0.124	0.093	0.116
La_2O_3	0.035	0.030	0.047	0.047	0.045	0.025	0.026	0.052	0.040	0.030	0.037
Li_2O	4.800	5.280	4.960	4.960	5.120	5.760	5.600	4.640	5.440	5.280	5.600
MgO	1.209	0.858	0.959	1.149	0.909	0.707	0.757	1.060	0.968	1.028	0.757
MnO	2.140	1.819	2.363	2.033	1.926	1.498	1.865	2.611	1.989	2.114	1.605
Na_2O	12.844	11.164	11.536	11.914	12.360	11.391	11.633	13.086	10.977	11.164	10.791
NiO	0.564	0.479	0.536	0.536	0.688	0.535	0.423	0.592	0.611	0.649	0.573
PbO	0.030	0.026	0.041	0.041	0.038	0.021	0.023	0.045	0.034	0.026	0.032
SO_4	0.387	0.261	0.367	0.291	0.276	0.271	0.230	0.406	0.245	0.329	0.290
SiO_2	46.585	50.997	48.055	48.245	49.526	55.409	54.088	45.324	52.468	51.167	54.088
ThO_2	0.021	0.018	0.028	0.028	0.027	0.015	0.016	0.031	0.024	0.018	0.022
TiO_2	0.009	0.007	0.012	0.012	0.011	0.006	0.007	0.013	0.010	0.007	0.009
U_3O_8	3.342	2.840	3.689	3.689	3.007	2.718	2.913	3.509	3.107	2.840	2.913
ZnO	0.033	0.028	0.044	0.044	0.041	0.023	0.024	0.048	0.037	0.028	0.035
ZrO_2	0.077	0.066	0.104	0.104	0.099	0.054	0.058	0.115	0.088	0.066	0.082

8.0 Summary

In early October 2006, the LWO began to consider decanting Tank 40 at the end of SB3 processing and transferring the aqueous phase from the decant to Tank 51. This is to facilitate the transfer of the contents of Tank 51 to Tank 40 by adjusting Tank 51 rheology to an acceptable level. The projected composition of SB4 was adjusted by LWO to reflect the impact of the Tank 40 decant leading to new projected compositions for SB4, designated as the 10-04-06 and the 10-10-06 compositions. A comparison between these SB4 compositions and those provided in June 2006 indicates that the new compositions are slightly higher in Al_2O_3, Fe_2O_3, and U_3O_8 and slightly lower in SiO_2. The most dramatic change, however, is the new projection's Na_2O concentration, which is more than 4.5 wt% lower than the earlier projection. This is a significant change due to the frit development team's approach of aligning the Na_2O concentration in a candidate frit to the Na_2O content of the sludge. This approach enhances the projected operating window and the waste throughput potential for the resulting glass system while eliminating the potential for nepheline crystallization. Nepheline has a detrimental impact on durability.

Questions surfaced regarding the applicability of Frit 503 to these revised compositions since SRNL recommended Frit 503 for use with SB4 based on the June 2006 compositional projection. Based on the paper study assessments, the change in SB4's expected Na_2O content had a significant, negative impact on the projected operating window for the Frit 503/SB4 glass system. While Frit 418 had slightly smaller WL intervals for the June 2006 SB4 projections as compared to Frit 503 and the Frit 418 glass systems were nepheline limited, Frit 418 has a slightly larger operating window for the 10-04-06 projection (as compared to Frit 503) and the Frit 418/10-04-06 glass system is no longer nepheline limited. Thus, strictly from the perspective of this paper study, Frit 418 is more attractive than Frit 503 for the new SB4 projected compositions. However, this comparison does not reflect other aspects of interest for the glass systems such as their respective melt rates or the development of alternative frits to balance the projected operating windows, melt rate, waste throughput, and robustness to compositional variation.

In discussions with WS-E of the results being presented in this report, their decision was to utilize Frit 418 for initial processing of SB4. This decision was not only based on the paper study assessments presented in this report, but also on the fact that Frit 418 is currently being used to process SB3 and, perhaps more importantly, frit optimization efforts for SB4 may be premature given the uncertainties in sludge composition compounded by uncertainty in the tank transfer and heel volumes associated with the SB4 flowsheet. More specifically, WS-E plans to initiate processing with Frit 418 and will authorize the frit development team to optimize a frit once SB4 composition projections are more certain (i.e., the transfer volumes and masses are known and updated Tank 40 and Tank 51 compositions are available).

Given this decision and recognizing that a SB4/Frit 503 variability study had been initiated as part of the qualification process, questions regarding the need for a supplemental variability study to demonstrate applicability of the process control models for a Frit 418 based system surfaced. This report addresses the need for a supplemental study and defines additional glasses to fill the compositional gaps. A total of 13 glasses (based on the 10-10-06 projection) were selected for the supplemental SB4/Frit 418 variability study. These glasses will be batched and melted following standard SRNL procedures, and a suite of characterization testing will be completed to measure the chemical durability of each glass composition. A subsequent report will document the results of the experimental portion of the SB4/Frit 418 variability study.

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