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Frit Optimization for Sludge Batch Processing at the Defense Waste Processing Facility

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1.0 Abstract

The Savannah River National Laboratory (SRNL) Frit Development Team recommends that the Defense Waste Processing Facility (DWPF) utilize Frit 418 for initial processing of high level waste (HLW) Sludge Batch 5 (SB5). The extended SB5 preparation time and need for DWPF feed have necessitated the use of a frit that is already included on the DWPF procurement specification. Frit 418 has been used previously in vitrification of Sludge Batches 3 and 4. Paper study assessments predict that Frit 418 will form an acceptable glass when combined with SB5 over a range of waste loadings (WLs), typically 30-41% based on nominal projected SB5 compositions. Frit 418 has a relatively high degree of robustness with regard to variation in the projected SB5 composition, particularly when the Na_2O concentration is varied. The acceptability (chemical durability) and model applicability of the Frit 418–SB5 system will be verified experimentally through a variability study, to be documented separately. Frit 418 has not been designed to provide an optimal melt rate with SB5, but is recommended for initial processing of SB5 until experimental testing to optimize a frit composition for melt rate can be completed. Melt rate performance can not be predicted at this time and must be determined experimentally. Note that melt rate testing may either identify an improved frit for SB5 processing (one which produces an acceptable glass at a faster rate than Frit 418) or confirm that Frit 418 is the best option.

2.0 Introduction

The objective of this task was to identify a frit for vitrification of high level waste (HLW) Sludge Batch 5 (SB5) at the Defense Waste Processing Facility (DWPF) that:

- is currently listed on the DWPF procurement specification to reduce the time necessary for procurement (due to the short time period available for frit development work),
- will form acceptable (in terms of repository requirements and DWPF processing constraints) glasses with SB5,
- is relatively insensitive (based on projected operating windows) to the uncertainty in the SB5 composition projections.

These objectives were met by:

- identifying the best available composition projections for SB5,
- adding any necessary corrections to the composition projections to account for planned caustic additions and blending operations,
- evaluating the operating windows (the range of waste loadings where acceptable glasses are predicted) projected for Frit 418 with these nominal SB5 projections,
- evaluating the operating windows projected for Frit 418 with variation applied to a bounding SB5 projection.

Each of these steps will be described in further detail in the following sections. This work is performed in response to Technical Task Request HLW-DWPF-TTR-2007-0007[1] following Task Technical and Quality Assurance Plan WSRC-STI-2006-00321.[2]

3.0 SB5 Composition Projections

A series of SB5 composition projections has been received from the Liquid Waste Organization (LWO).[a] SRNL also developed projections[b] for SB5 using a model-based approach.[c] The LWO and SRNL projections included the Tank 40 heel remaining at the end of Sludge Batch 4 (SB4) processing, the Tank 51 SB5 batch prior to the transfer to Tank 40, and the SB5 blend in Tank 40 after the transfer from Tank 51. None of the projections accounted for the planned addition of caustic to Tank 40 to support SB4 processing. The SB5 blend projections did not account for the addition of the Actinide Removal Process (ARP) stream to SB5 at DWPF. In addition, the final blend ratio of the Tank 51 SB5 batch with the Tank 40 heel to constitute the SB5 blend is uncertain due to the estimated sludge usage over the next four months of processing.

To account for these additions and the blending uncertainties, only the LWO and SRNL projected compositions of the Tank 40 heel and the Tank 51 SB5 batch were used to support the frit recommendation. First, projections of the Tank 40 heel composition based on the planned addition of caustic were developed by adding 3 wt% Na_2O to the original Tank 40 heel projections and renormalizing the composition to 100%. The composition projections provided by LWO, along with the 3 wt% Na_2O addition to the Tank 40 heel are listed in Table 3-1.

Table 3-1. Composition Projections (wt% Calcined Oxides) of the Tank 40 Heel and Tank 51 Provided by LWO, as well as a 3 wt% Na_2O addition to the Tank 40 Heel Projection.

Oxide	Tank 40 Heel	Tank 40 Heel plus 3 wt% Na_2O	Tank 51 (SB5 Batch)
Al_2O_3	26.960	26.013	19.673
BaO	0.077	0.075	0.000
CaO	2.969	2.865	2.258
Ce_2O_3	0.070	0.067	0.000
Cr_2O_3	0.174	0.168	0.000
CuO	0.062	0.060	0.000
Fe_2O_3	30.821	29.737	27.594
K_2O	0.000	0.000	0.036
La_2O_3	0.058	0.056	0.000
MgO	2.927	2.824	1.190
MnO	6.184	5.967	5.828
Na_2O	14.649	17.649	29.494
NiO	1.716	1.656	3.512
PbO	0.064	0.062	0.000
SO_4^{2-}	0.831	0.802	0.373
SiO_2	2.906	2.804	2.217
ThO_2	0.000	0.000	0.000
TiO_2	0.050	0.048	0.000
U_3O_8	9.401	9.071	7.825
ZnO	0.000	0.000	0.000
ZrO_2	0.080	0.078	0.000

[a] The most recent SB5 composition projections (those used in this study) were received from LWO via email from D. D. Larsen on June 5, 2008. Washing data used to calculate a SO_4^{2-} concentration were included in a spreadsheet attached to the email, titled 'SB4-5_060408_For Variability Study Comparison.xls.xlsm'. See WSRC-NB-2007-00003 for further detail.
[b] The composition projections developed by SRNL and used in this study were received via email from A. S. Choi on June 12, 2008. See WSRC-NB-2007-00003 for further detail.
[c] For further information on the SRNL model-based approach, see Choi, A. S., "Aluminum Dissolution Flowsheet Modeling in Support of SB5 Frit Development," U.S. Department of Energy Report WSRC-STI-2008-00001, Revision 0, Washington Savannah River Company, Aiken, SC (2008).

The composition projections developed by SRNL, along with the 3 wt% Na_2O addition to the Tank 40 heel are listed in Table 3-2.

Table 3-2. Composition Projections (wt% Calcined Oxides) of the Tank 40 Heel and Tank 51 Developed by SRNL, as well as a 3 wt% Na_2O addition to the Tank 40 Heel Projection.

Oxide	Tank 40 Heel	Tank 40 Heel plus 3 wt% Na_2O	Tank 51 (SB5 Batch)
Ag_2O	0.009	0.009	0.004
Al_2O_3	25.976	25.040	20.874
BaO	0.078	0.075	0.164
CaO	2.868	2.764	2.366
CdO	0.322	0.310	0.027
Ce_2O_3	0.068	0.066	0.000
Cr_2O_3	0.150	0.145	0.088
CuO	0.058	0.055	0.015
Fe_2O_3	33.075	31.883	28.881
Gd_2O_3	0.015	0.014	0.026
K_2O	0.226	0.218	0.101
La_2O_3	0.051	0.049	0.000
Li_2O	0.041	0.040	0.005
MgO	2.820	2.718	1.253
MnO	5.969	5.754	6.106
Na_2O	12.739	15.739	25.090
NiO	1.654	1.594	3.680
P_2O_5	0.989	0.954	0.125
PbO	0.039	0.038	0.004
PdO	0.001	0.001	0.001
PuO_2	0.000	0.000	0.010
Rh_2O_3	0.015	0.015	0.034
RuO_2	0.060	0.058	0.171
SO_4^{2-}	0.899	0.866	0.539
SiO_2	2.795	2.694	2.071
SrO	0.040	0.039	0.080
ThO_2	0.000	0.000	0.000
TiO_2	0.040	0.039	0.000
U_3O_8	9.068	8.742	8.191
ZnO	0.005	0.005	0.012
ZrO_2	0.079	0.076	0.171

Second, two possible blending ratios were considered for constitution of the SB5 blend.[a] Mass ratios of 25:75 and 30:70 (Tank 40 to Tank 51) were used in blending the Tank 40 heel and Tank 51 SB5 batch compositions, both with and without the caustic addition, using both the LWO and SRNL projections. These factors resulted in eight potential compositions for SB5, as listed in Table 3-3.

[a] The final blend ratio is dependent mainly on the rate of SB4 processing, in DWPF.

Table 3-3. Potential Compositions of the SB5 Blend Using the LWO and SRNL Projections at Two Blend Ratios, With and Without Caustic Addition to Tank 40.

Tank 40 Source	LWO	LWO	LWO +3 wt% Na_2O	LWO +3 wt% Na_2O	SRNL	SRNL	SRNL +3 wt% Na_2O	SRNL +3 wt% Na_2O
Tank 40 Mass Ratio	25	30	25	30	25	30	25	30
Tank 51 Source	LWO	LWO	LWO	LWO	SRNL	SRNL	SRNL	SRNL
Tank 51 Mass Ratio	75	70	75	70	75	70	75	70
Sludge ID	**BS-01**	**BS-02**	**BS-03**	**BS-04**	**BS-05**	**BS-06**	**BS-07**	**BS-08**
Ag_2O	0.000	0.000	0.000	0.000	0.005	0.005	0.005	0.005
Al_2O_3	21.495	21.859	21.258	21.575	22.149	22.405	21.915	22.124
BaO	0.019	0.023	0.019	0.022	0.142	0.138	0.142	0.137
CaO	2.436	2.472	2.410	2.440	2.491	2.516	2.465	2.485
CdO	0.000	0.000	0.000	0.000	0.101	0.116	0.098	0.112
Ce_2O_3	0.017	0.021	0.017	0.020	0.017	0.020	0.016	0.020
Cr_2O_3	0.043	0.052	0.042	0.050	0.103	0.106	0.102	0.105
CuO	0.016	0.019	0.015	0.018	0.026	0.028	0.025	0.027
Fe_2O_3	28.400	28.562	28.130	28.237	29.930	30.139	29.632	29.782
Gd_2O_3	0.000	0.000	0.000	0.000	0.023	0.023	0.023	0.023
K_2O	0.027	0.025	0.027	0.025	0.132	0.138	0.130	0.136
La_2O_3	0.015	0.017	0.014	0.017	0.013	0.015	0.012	0.015
Li_2O	0.000	0.000	0.000	0.000	0.014	0.016	0.013	0.015
MgO	1.624	1.711	1.598	1.680	1.645	1.723	1.620	1.693
MnO	5.917	5.935	5.863	5.870	6.072	6.065	6.018	6.000
Na_2O	25.783	25.040	26.533	25.940	22.003	21.385	22.753	22.285
NiO	3.063	2.973	3.048	2.955	3.174	3.072	3.159	3.054
P_2O_5	0.000	0.000	0.000	0.000	0.341	0.384	0.332	0.374
PbO	0.016	0.019	0.015	0.019	0.013	0.015	0.013	0.014
PdO	0.000	0.000	0.000	0.000	0.001	0.001	0.001	0.001
Pr_2O_3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
PuO_2	0.000	0.000	0.000	0.000	0.008	0.007	0.008	0.007
Rh_2O_3	0.000	0.000	0.000	0.000	0.030	0.029	0.029	0.028
RuO_2	0.000	0.000	0.000	0.000	0.143	0.137	0.142	0.137
SO_4^{2-}	0.487	0.510	0.480	0.502	0.629	0.647	0.621	0.637
SiO_2	2.389	2.424	2.364	2.393	2.252	2.288	2.227	2.258
SrO	0.000	0.000	0.000	0.000	0.070	0.068	0.069	0.067
ThO_2	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
TiO_2	0.012	0.015	0.012	0.014	0.010	0.012	0.010	0.012
U_3O_8	8.219	8.298	8.137	8.199	8.410	8.454	8.329	8.356
ZnO	0.000	0.000	0.000	0.000	0.010	0.010	0.010	0.010
ZrO_2	0.020	0.024	0.019	0.023	0.148	0.144	0.148	0.143

Third, the addition of the ARP stream was included for each of the above compositions, resulting in eight more potential compositions for SB5 as listed in Table 3-4.

Table 3-4. Potential Compositions of the SB5 Blend Using the LWO and SRNL Projections at Two Blend Ratios, With and Without Caustic Addition, With the ARP Stream Added.

Tank 40 Source	LWO	LWO	LWO +3 wt% Na_2O	LWO +3 wt% Na_2O	SRNL	SRNL	SRNL +3 wt% Na_2O	SRNL +3 wt% Na_2O
Tank 40 Mass Ratio	25	30	25	30	25	30	25	30
Tank 51 Source	LWO	LWO	LWO	LWO	SRNL	SRNL	SRNL	SRNL
Tank 51 Mass Ratio	75	70	75	70	75	70	75	70
Sludge ID	**BS-09**	**BS-10**	**BS-11**	**BS-12**	**BS-13**	**BS-14**	**BS-15**	**BS-16**
Ag_2O	0.003	0.003	0.003	0.003	0.007	0.008	0.007	0.008
Al_2O_3	20.741	21.087	20.516	20.817	21.342	21.584	21.127	21.326
BaO	0.023	0.026	0.022	0.026	0.139	0.135	0.139	0.134
CaO	2.365	2.399	2.340	2.369	2.415	2.439	2.391	2.410
CdO	0.000	0.000	0.000	0.000	0.096	0.110	0.093	0.106
Ce_2O_3	0.025	0.028	0.024	0.027	0.024	0.028	0.024	0.027
Cr_2O_3	0.047	0.055	0.045	0.053	0.103	0.106	0.102	0.105
CuO	0.017	0.020	0.016	0.019	0.027	0.029	0.026	0.028
Fe_2O_3	27.600	27.753	27.342	27.444	29.025	29.223	28.752	28.896
Gd_2O_3	0.000	0.000	0.000	0.000	0.022	0.022	0.022	0.022
K_2O	0.031	0.030	0.031	0.030	0.131	0.137	0.129	0.135
La_2O_3	0.017	0.020	0.017	0.019	0.015	0.018	0.015	0.017
Li_2O	0.000	0.000	0.000	0.000	0.013	0.015	0.013	0.014
MgO	1.549	1.632	1.524	1.602	1.567	1.642	1.544	1.613
MnO	5.850	5.867	5.799	5.805	5.992	5.985	5.943	5.926
Na_2O	26.491	25.786	27.204	26.641	22.875	22.288	23.596	23.152
NiO	2.979	2.894	2.965	2.877	3.081	2.985	3.068	2.969
P_2O_5	0.002	0.002	0.002	0.002	0.326	0.367	0.318	0.357
PbO	0.021	0.024	0.021	0.024	0.018	0.020	0.018	0.020
PdO	0.000	0.000	0.000	0.000	0.001	0.001	0.001	0.001
Pr_2O_3	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.003
PuO_2	0.000	0.000	0.000	0.000	0.007	0.007	0.007	0.007
Rh_2O_3	0.000	0.000	0.000	0.000	0.028	0.027	0.028	0.027
RuO_2	0.006	0.006	0.006	0.006	0.142	0.137	0.142	0.136
SO_4^{2-}	0.606	0.628	0.599	0.619	0.740	0.757	0.732	0.748
SiO_2	2.305	2.338	2.281	2.309	2.172	2.207	2.149	2.179
SrO	0.002	0.002	0.002	0.002	0.068	0.066	0.068	0.066
ThO_2	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
TiO_2	1.311	1.313	1.310	1.312	1.307	1.309	1.307	1.309
U_3O_8	7.973	8.048	7.895	7.954	8.147	8.188	8.072	8.099
ZnO	0.004	0.004	0.004	0.004	0.014	0.013	0.014	0.013
ZrO_2	0.029	0.033	0.028	0.032	0.151	0.146	0.150	0.146

4.0 Assessments of Frit 418 with the Nominal SB5 Compositions

The 16 potential SB5 compositions described in the previous section (referred to as nominal SB5 compositions) were combined with Frit 418 over a WL interval of 25 to 60% and evaluated against the DWPF Product Composition Control System (PCCS) Measurement Acceptability Region (MAR) criteria to identify WLs where acceptable glasses are predicted.[3] The results of the Nominal Stage MAR assessment are given in Table 4-1. In general, the window of available WLs with Frit 418 is quite good, with all of the nominal compositions predicted to form acceptable glasses from 30 to 41% WL (with several of the individual systems having even wider WL windows). Lower WLs are limited by the homogeneity constraint (Homg), which can be relaxed for the compositions that do not include the ARP stream.[4] Upper WLs are limited by predictions of low viscosity (lowv), high liquidus temperature (T_L), or nepheline crystallization (Neph).

Table 4-1. MAR Assessment Results for the Nominal SB5 Compositions with Frit 418.

Sludge ID	Acceptable WLs (%)	Lower Limiting Constraint(s)	Upper Limiting Constraint(s)
BS-01	29-43	Homg	lowv
BS-02	28-44	Homg	lowv, Neph
BS-03	29-42	Homg	lowv
BS-04	29-43	Homg	lowv
BS-05	28-44	Homg	T_L
BS-06	27-43	Homg	T_L
BS-07	28-45	Homg	T_L, Neph
BS-08	28-44	Homg	T_L
BS-09	30-42	Homg	lowv
BS-10	29-43	Homg	lowv
BS-11	30-41	Homg	lowv
BS-12	30-42	Homg	lowv
BS-13	29-46	Homg	T_L, lowv, Neph
BS-14	29-45	Homg	T_L
BS-15	29-45	Homg	lowv, Neph
BS-16	29-45	Homg	Neph

The results of the MAR assessment with the nominal SB5 compositions show that Frit 418 is robust to these variations for the SB5 composition, including differences between the LWO and SRNL projections, the addition of caustic, varying blends of Tank 40 and Tank 51, and the addition of the ARP stream. Frit 418 appears to be particularly robust to a range of Na_2O concentrations for SB5. The WL windows over which the glasses are predicted to be acceptable are generally limited by process-related constraints (lowv and T_L). Five of the WL windows are limited by predictions of nepheline crystallization (which can impact durability of the glass). However, nepheline is only predicted to form at WLs that are significantly higher (>44% WL) than those likely to be targeted by DWPF.

5.0 Variation Stage Assessment of Frit 418 Bounding Potential SB5 Compositions

A Variation Stage assessment was next performed to further demonstrate the ability of Frit 418 to accommodate variation in the composition of SB5. The following strategy was developed to apply variation to the compositional region bounding the series of potential SB5 compositions. First, the minimum and maximum concentrations of each component across all 16 of the potential SB5 compositions were determined. Then, for each of the major components (Al_2O_3, Fe_2O_3, Na_2O and U_3O_8), the minimum concentration was reduced by 7.5% and the maximum concentration was increased by 7.5%. For each of the minor components (CaO, MgO, MnO, NiO, SiO_2 and TiO_2), 0.5 wt% was deducted from the minimum concentration and 0.5 wt% was added to the maximum concentration. The remaining components were grouped into a category called ‘Others’. The sum of the mean concentrations of each of the remaining components over the 16 potential SB5 compositions was taken as the concentration of Others. A variation of +/- 0.5 wt% was then applied to the concentration of Others. The resulting compositional space defined for the Variation Stage assessment is given in Table 5-1.

Table 5-1. Concentration Ranges for Individual Components in the SB5 Composition as Defined for the Variation Stage Assessment.

Oxide	Minimum (wt%)	Maximum (wt%)
Al_2O_3	18.977	24.085
CaO	1.840	3.016
Fe_2O_3	25.292	32.400
MgO	1.024	2.223
MnO	5.299	6.572
Na_2O	19.781	29.245
NiO	2.377	3.674
SO_4^{2-}	0.380	0.857
SiO_2	1.649	2.924
TiO_2	0.000	1.813
U_3O_8	7.302	9.088
Others	0.284	1.284

Table 5-1 provides the framework around which the Variation Stage assessment was conducted. A sludge composition is in the region defined in Table 5-1 if its concentration for each oxide is within the minimum and maximum interval for that oxide (e.g., the Al_2O_3 concentration in the sludge is between 18.98 and 24.09 wt %) 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 SB5 as defined by Table 5-1. Algorithms are available in statistical software packages[a] to generate the compositions that are the bounding "corner points" of the compositional region defined by Table 5-1. The bounding compositions generated by the software are called the extreme vertices (EVs) of the compositional region.

A select set of the Variation Stage MAR assessment results is shown in Table 5-2. For each WL, the number of acceptable and non-acceptable EVs is shown, along with the constraints limiting the non-acceptable EVs.

Table 5-2. Portion of the Variation Stage MAR Assessment Results for SB5 with Frit 418.

WL	No. of Acceptable EVs	No. of Non-Acceptable EVs	Limiting Constraint(s)
28	1833	2087	Homg
29	2374	1546	Homg
30	2674	1246	Homg
31	2838	1082	Homg
32	3174	746	Homg
33	3560	360	Homg
34	3904	16	Homg
35	3920	0	none
36	3920	0	none
37	3920	0	none
38	3902	18	lowv (11) T_L (7)
39	3722	198	lowv (139) T_L (59)

[a] JMP™, Ver. 6.0.3, SAS Institute Inc., Cary, NC (2005).

All of the EVs produced acceptable glasses at WLs of 35 to 37%. Access to lower WLs becomes limited by the homogeneity constraint (which can be relaxed for the sludges without ARP). Access to higher WLs becomes limited by process-related constraints (lowv and T_L) rather than durability-related constraints. As expected, the WL window within which all of the glasses are acceptable is smaller in the Variation Stage than in the Nominal Stage assessment. However, given the large variation applied to the potential SB5 composition and particularly to the Na_2O concentration, the performance of Frit 418 is excellent. Assuming the homogeneity constraint can be relaxed for both sludge-only and coupled operations, all of the EVs could be processed over a 28-37% WL interval with only 18 of the 3920 EVs failing lowv or T_L at 38% WL.

6.0 Conclusions

SRNL recommended that the DWPF utilize Frit 418 for initial processing of SB5. Nominal and Variation Stage assessments predicted that Frit 418 would form an acceptable glass when combined with SB5 over a range of WLs, typically 30-41% based on the nominal projected SB5 compositions. Frit 418 has a relatively high degree of robustness with regard to variation in the projected SB5 composition, particularly when the Na_2O concentration is varied. The acceptability (chemical durability) and model applicability of the Frit 418–SB5 system will be verified experimentally through a variability study. Frit 418 was not designed to provide an optimal melt rate with SB5, but was recommended for initial processing of SB5 until experimental testing to optimize a frit composition for melt rate could be completed.

7.0 References

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