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MELT RATE IMPROVEMENT FOR DWPF MB3:

Frit Preparation (U)

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GLOSSARY

CETL	Clemson Environmental Technologies Laboratory
DWPF	Defense Waste Processing Facility
MB2	Macrobatch 2
MB3	Macrobatch 3
PNNL	Pacific Northwest National Laboratory
SRAT	Sludge Receipt and Adjustment Tank
SRTC	Savannah River Technology Center
SRTC-ML	Savannah River Technology Center – Mobile Laboratory
TFA	Tanks Focus Area
TIM	Task Integration Manager

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1.0 Introduction

The objective of this research is to evaluate melt rate of Macrobatch 3 (MB3) for the Defense Waste Processing Facility (DWPF). How quickly feed materials are converted to a liquid melt (the batch-to-glass process) defines melt rate in this case. Formation of a foam layer during processing can impede the melting rate, thus resulting in a reduced throughput and slower canister production by DWPF. The aim is to find the proper frit composition and/or acid addition strategy so that the development of this insulating foam layer is averted.

Formation of a foam layer is the result of two overlapping phenomena – off-gas generation and a highly viscous medium. Acid addition strategies (different combinations of formic and nitric acids), or the addition of other reductants such as sugar, are possible foam mitigation techniques because they can cause shifts in the off-gas evolution interval. The main focus of this study was the frit compositional change though, which can cause shifts in the viscous melt generation interval.

A total of 24 compositionally different frits were tested in this study of melt rate for MB3. While three of these frits were prefabricated by another vendor, the Savannah River Technology Center (SRTC) produced the other 21 frits. Enough frit was produced in order to support all crucible tests (Lorier, 2001) and melt-rate furnace runs (Stone and Josephs, 2001). The further sections of this report discuss said frit production and any issues resulting there of.

2.0 Tested Frits

The frits tested in this study of MB3 melt rate can be divided into two categories: existing frits and alternative frits. The existing frits are Frit 165 (AX667974, containers 3 and 4), Frit 200 (Lot #CS), and Frit 202 (Lot #CN), all of which were originally tested with Macrobatch 2 (MB2). The compositions of these frits are listed in Table I. Variations of Frits 165 and 200 were tested as well: Frits 165 and 200 using batch chemicals, silica deficient Frits 165 and 200, and Frit 165 minus zirconia (the 1% mass fraction of ZrO_2 in Frit 165 was not included and all other components were renormalized). The Frits 165 and 200 using batch chemicals were compositionally the same as those produced by a separate vendor. The batch chemicals method is the separate addition of all individual components (listed in Table I) of the frit, yet producing the same glass compositionally as the original frit. Batch chemicals were suggested since they

generally delay the formation of a liquid phase to a higher temperature at a point where off-gas generation is lower, thus reducing the amount of foaming during melting, which may increase melt rate.

Table I. Frit compositions (in mass percent) of existing frits.

Frit ID	Frit 165	Frit 200	Frit 165 (minus Zr)*	Frit 202
Al_2O_3	0.00	0.00	0.00	0.00
B_2O_3	10.00	12.00	10.10	8.00
Li_2O	7.00	5.00	7.07	7.00
Na_2O	13.00	11.00	13.13	6.00
SiO_2	68.00	70.00	68.69	77.00
ZrO_2	1.00	0.00	0.00	0.00
MgO	1.00	2.00	1.01	2.00

* Not an existing frit, but it is included in this Table since only one component is removed.

Other frits developed were silica deficient Frits 165 and 200, which required leaving out a certain percentage of the SiO_2 from the original frit and adding it as a separate additive. Compositionally, the use of a prefabricated frit, batch chemicals, or SiO_2-deficient frits is the same (i.e., they all target the same frit composition). The “two-component” frit is designed with a low-temperature fraction that would react with the waste and melt first to form a low viscosity glass that will not trap the off-gas produced, combined with a higher temperature melting component (SiO_2). The SiO_2 would be dissolved into the glass pool at a temperature higher than that of peak off-gas production, thus leading to less foam and a higher melt rate.

There were 12 “alternative” frits developed through a joint SRTC/PNNL (Pacific Northwest National Laboratory) that were also tested in this study of melt rate of MB3. The compositions of these frits are listed in Table II.

Table II. Frit compositions (in mass percent) of alternative frits developed by SRTC and PNNL.

Frit ID	Frit 303	Frit 304	Frit 307	Frit 313	Frit 314	Frit 315	Frit 320	Frit 322	Frit 323	Frit 324	Frit 325*	Frit 326
Al_2O_3	2.29	2.29	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
B_2O_3	20.13	6.71	12.08	6.71	20.13	20.13	8.00	8.00	15.00	15.00	8.55	8.00
Li_2O	10.12	5.80	10.74	10.74	5.94	10.03	8.00	5.00	5.19	8.28	7.55	8.00
Na_2O	0.00	18.07	4.67	8.75	6.12	0.00	12.00	10.00	8.28	5.19	9.10	11.00
SiO_2	67.46	67.13	72.51	73.80	65.79	69.84	72.00	77.00	71.53	71.53	72.80	72.00
ZrO_2	0.00	0.00	0.00	0.00	2.01	0.00	0.00	0.00	0.00	0.00	0.50	0.00
MgO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.50	1.00

* Testing of Frit 325 was conducted as a 50/50 blend with Frit 202 when mixed with Macrobatch 3 simulant. The composition listed for Frit 325 is for this 50/50 combination.

3.0 Frit Production

To fabricate frit at SRTC, the chemicals were batched to target a specified amount of frit and composition, added to a 600 mL platinum crucible with a lid, inserted in the furnace at temperature (1150°C), held at temperature for approximately one hour, and then poured on a stainless-steel plate and air-quenched (see WSRC-NB-2000-00144).

Once the final melting was complete, the frit was ground and sieved to a particle size of -80, +200 mesh. Recovery of this correct particle size was approximately 50% - i.e., had to produce 500g of glass to acquire ~250g of the desired size fraction. The -80, +200 mesh-sized material was then mixed with the simulated SRAT product for each crucible and melt-rate furnace test.

When small amounts of the frits were being made, the grinding was performed at SRTC using Tekmar grinders, and this frit was used for the crucible tests (Lorier, 2001). Larger amounts of frit were required for the melt-rate furnace runs, so a larger grinder was used to save time. A disc-mill grinder with carbon-steel plates at Clemson Environmental Technologies Laboratory (CETL) was utilized for this purpose. This grinder was capable of grinding larger amounts of glass more quickly, but an issue with contamination (specifically iron, nickel, and chrome) from the grinding plates arose. After grinding, the frit had a grayish tint rather than the usual white

appearance, due to the iron that came off the plates. In order to "clean" the frit, a magnet was run over the frit and it was discovered that a significant amount of metal shavings could be removed from the frit. This decontamination process was performed prior to these frits being utilized in either the crucible-scale or melt rate furnace tests. To ensure target compositions were obtained (i.e., no batching errors and/or volatilization issues), samples of each frit (after decontamination) were submitted to the SRTC Mobile Laboratory (SRTC-ML) for chemical composition analysis. The results of those analyses, as compared to target, are listed in Tables III and IV for the frits ground at CETL and those ground at SRTC, respectively.

Table III. Chemical composition analysis results of frit ground at CETL after as much contamination as possible was removed. (Chemical compositions given in mass percent; analysis performed by the SRTC-ML).

	Frit 303		Frit 304		Frit 307		Frit 313		Frit 314		Frit 315	
	Target	Measured	Target	Measured	Target	Measured	Target	Measured	Target	Measured	Target	Measured
Al_2O_3	2.29	2.27	2.29	1.91	0.00	0.261	0.00	ND*	0.00	0.234	0.00	0.085
B_2O_3	20.13	19.0	6.71	4.70	12.08	11.0	6.71	ND*	20.13	19.0	20.13	19.2
Cr_2O_3	--	0.012	--	<0.010	--	<0.010	--	ND*	--	0.010	--	0.014
Fe_2O_3	--	0.316	--	0.172	--	0.257	--	ND*	--	0.115	--	0.153
Li_2O	10.12	9.52	5.80	4.45	10.74	10.1	10.74	ND*	5.94	5.76	10.03	9.85
MgO	0.00	<0.010	0.00	<0.010	0.00	<0.010	0.00	ND*	0.00	<0.010	0.00	<0.010
Na_2O	0.00	0.239	18.07	14.4	4.67	4.70	8.75	ND*	6.12	6.10	0.00	0.070
NiO	--	0.017	--	0.014	--	0.012	--	ND*	--	<0.010	--	<0.010
SiO_2	67.46	69.8	67.13	74.3	72.51	74.9	73.8	ND*	65.79	67.8	69.84	68.3
ZrO_2	0.00	0.018	0.00	<0.010	0.00	0.011	0.00	ND*	2.01	1.85	0.00	0.012
Total	**100**	**101**	**100**	**99.9**	**100**	**101**	**100**	ND*	**100**	**101**	**100**	**97.7**

* No data available.

(Table III Cont'd)

	Frit 320		Frit 322		Frit 323		Frit 324		Frit 325		Frit 326	
	Target	Measured	Target	Measured	Target	Measured	Target	Measured	Target	Measured	Target	Measured
Al_2O_3	0.00	0.202	0.00	0.272	0.00	0.229	0.00	0.202	0.00	0.346	0.00	0.170
B_2O_3	8.00	7.08	8.00	6.89	15.00	13.4	15.00	13.4	8.55	8.02	8.00	6.54
Cr_2O_3	--	<0.010	--	0.014	--	<0.010	--	0.010	--	0.010	--	<0.010
Fe_2O_3	--	0.091	--	0.215	--	0.159	--	0.246	--	0.123	--	0.122
Li_2O	8.00	7.72	5.00	4.84	5.19	4.84	8.28	7.61	7.55	7.72	8.00	7.40
MgO	0.00	<0.010	0.00	<0.010	0.00	<0.010	0.00	<0.010	1.50	1.11	1.00	0.770
Na_2O	12.00	11.4	10.00	9.87	8.28	8.11	5.19	5.12	9.10	12.1	11.00	8.13
NiO	--	<0.010	--	0.010	--	0.010	--	0.011	--	<0.010	--	<0.010
SiO_2	72.00	76.2	77.00	83.5	71.53	71.5	71.53	76.6	72.8	68.9	72.00	76.6
ZrO_2	0.00	<0.010	0.00	0.013	0.00	0.014	0.00	<0.010	0.50	1.02	0.00	0.012
Total	**100**	**103**	**100**	**105**	**100**	**98.3**	**100**	**103**	**100**	**99.3**	**100**	**97.7**

Table IV. Actual compositions (mass percent) of frits ground at SRTC (analysis by the SRTC-ML).

	Frit 303		Frit 304		Frit 307		Frit 313		Frit 314		Frit 315	
	Target	Measured	Target	Measured	Target	Measured	Target	Measured	Target	Measured	Target	Measured
Al_2O_3	2.29	2.17	2.29	2.36	0.00	0.244	0.00	0.219	0.00	0.217	0.00	0.062
B_2O_3	20.13	20.5	6.71	7.41	12.08	13.0	6.71	7.08	20.13	20.7	20.13	21.4
Cr_2O_3	--	<0.010	--	<0.010	--	<0.010	--	<0.010	--	<0.010	--	<0.010
Fe_2O_3	--	0.080	--	0.045	--	0.057	--	0.066	--	0.037	--	0.048
Li_2O	10.12	9.85	5.80	6.19	10.74	11.0	10.74	11.2	5.94	6.11	10.03	10.4
MgO	0.00	<0.010	0.00	<0.010	0.00	<0.010	0.00	<0.010	0.00	<0.010	0.00	<0.010
Na_2O	0.00	0.121	18.07	14.3	4.67	4.52	8.75	7.82	6.12	5.84	0.00	0.070
NiO	--	<0.010	--	<0.010	--	<0.010	--	<0.010	--	<0.010	--	<0.010
SiO_2	67.46	68.4	67.13	70.0	72.51	72.1	73.8	74.9	65.79	67.4	69.84	72.5
ZrO_2	0.00	<0.010	0.00	<0.010	0.00	0.011	0.00	<0.010	2.01	1.89	0.00	<0.010
Total	**100**	**101**	**100**	**100**	**100**	**101**	**100**	**101**	**100**	**102**	**100**	**104**

(Table IV Cont'd)

	Frit 320		Frit 322		Frit 323		Frit 324		Frit 325		Frit 326	
	Target	Measured	Target	Measured	Target	Measured	Target	Measured	Target	Measured	Target	Measured
Al_2O_3	0.00	0.223	0.00	0.535	0.00	0.212	0.00	0.213	0.00	0.214	0.00	0.229
B_2O_3	8.00	9.18	8.00	8.57	15.00	16.0	15.00	14.9	8.55	9.82	8.00	8.24
Cr_2O_3	--	<0.010	--	<0.010	--	<0.010	--	<0.010	--	<0.010	--	<0.010
Fe_2O_3	--	0.071	--	0.043	--	0.036	--	0.064	--	0.081	--	0.056
Li_2O	8.00	8.45	5.00	5.20	5.19	5.48	8.28	8.77	7.55	8.51	8.00	8.28
MgO	0.00	<0.010	0.00	<0.010	0.00	<0.010	0.00	<0.010	1.50	0.941	1.00	1.00
Na_2O	12.00	10.4	10.00	8.90	8.28	7.72	5.19	5.40	9.10	10.2	11.00	9.84
NiO	--	<0.010	--	0.024	--	<0.010	--	<0.010	--	<0.010	--	<0.010
SiO_2	72.00	73.8	77.00	78.7	71.53	74.9	71.53	74.4	72.8	68.9	72.00	75.5
ZrO_2	0.00	<0.010	0.00	0.028	0.00	<0.010	0.00	<0.010	0.50	0.914	0.00	<0.010
Total	**100**	**102**	**100**	**102**	**100**	**104**	**100**	**103**	**100**	**99.6**	**100**	**103**

Even though some of the values of Fe_2O_3, NiO, and Cr_2O_3 are higher in Table III than they are in Table IV, it was determined that the increases were not significant enough to impact the assessment of melt rate in the crucible and melt-rate furnace tests.

Once the number of frits was narrowed down to six, it was decided to make enough additional frit to complete two more melt-rate furnace runs for each of these six frits. The grinding of frit for these tests was also done at CETL, but because of the contamination concerns raised earlier, the plates on the disc-mill grinder were changed from the carbon-steel plates to ceramic plates that were more abrasion-resistant. Some of Frit 307 was ground first to see if the ceramic withstood the grinding. It was noticed that many ceramic shavings ended up in the ground frit and the plates showed wear, just after the initial trial run with those plates. Given the ceramic contamination could not be removed through the use of a magnet, the plates were changed again, this time to hardened-steel plates. The remainder of Frit 307 and all of the rest of the frits were ground with these plates. These plates showed some abrasion as well, but it was not nearly as much as the ceramic plates. Once the grinding and sieving were completed, magnetic separation was used to remove the iron from the frit before the melt-rate furnace runs commenced. The six frits were also sent to the SRTC-ML for chemical composition analysis, and the measured and target compositions are shown in Table V.

Table V. Actual compositions* of six remaining frits ground at CETL (analysis by SRTC-ML).

	Frit 304	Frit 307	Frit 313	Frit 320	Frit 323	Frit 326
Al_2O_3	1.84	0.215	0.221	0.206	0.210	0.212
B_2O_3	6.96	12.4	6.79	8.02	14.9	8.28
Cr_2O_3	0.014	0.012	<0.010	0.010	0.014	0.010
Fe_2O_3	0.063	0.063	0.055	0.074	0.057	0.116
Li_2O	5.65	10.5	10.4	7.63	4.88	7.80
MgO	<0.010	<0.010	<0.010	<0.010	<0.010	0.865
Na_2O	17.2	4.84	8.68	11.8	8.29	10.2
NiO	0.016	0.015	<0.010	<0.010	0.014	0.016
SiO_2	66.6	72.8	72.8	70.8	70.8	72.8
ZrO_2	<0.010	<0.010	<0.010	<0.010	<0.010	0.011
Total	**98.4**	**101**	**99**	**98.6**	**99**	**100**

* Target compositions listed in Tables III and IV.

Again, the melt rate team decided that the levels of Fe_2O_3, NiO, and Cr_2O_3 were not high enough to negatively impact the assessment of melt rate.

4.0 Conclusions

Small amounts of contamination that appear during the frit production process are very difficult to avoid. This could come from a number of sources: the grinder, the sieves, etc. During the production of all frits used for the melt rate study, every precaution was taken to keep these levels of contamination to a minimum. For those frits produced, all of the targeted compositions were met.

5.0 References

Lorier, T.H., 2001. "Melt Rate Improvement for DWPF MB3: Crucible Studies (U)," WSRC-TR-2001-00151, Westinghouse Savannah River Company, Savannah River Technology Center, Aiken, SC.

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