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MELT RATE IMPROVEMENT FOR DWPF MB3: *Sugar Addition Test* (U)

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APPROVALS

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INTRODUCTION

In order to meet certain production goals, the Defense Waste Processing Facility (DWPF) has focused on implementing a more temporally efficient method of waste vitrification [1,2]. Changes in frit composition and alterations in the feed preparation process were investigated to determine if melt rate could be improved. The addition of sugar as an alternative reductant to formic acid was investigated for Macrobatch 3 (MB3).

In the past, experimental data from tests using Macrobatch 2 (MB2) simulant, Frit 200, and varied amounts of sugar (sucrose) showed positive results: a significant decrease in glass expansion and an increase in melt rate. The required amount of sugar needed per sample for nitrate reduction was calculated using the following equation:

$$4N^{+5} + 5C^{0} \rightarrow 2N_2 + 5C^{+4}$$

The ratio of carbon to nitrate from the equation is 1.25 moles of carbon per mole of nitrate. This method for determination of the sugar addition resulted in improved melt rates, but led to glass that was more reducing than allowed by DWPF process limits [6].

SUMMARY

Tests were conducted to determine if the addition of sugar to the melter feed for MB3 would improve melt rate and to determine the relationship between the amount of sugar added and the measured redox state of the glass produced. Redox, a measure of how reducing or oxidizing the glass is, is defined as the ratio of reduced iron (Fe^{+2}) to the total iron present in the glass. The redox target in DWPF is 0.20 $Fe^{+2}/\Sigma Fe$. The importance of the redox state of the glass is that an oxidizing glass will reduce as the temperature increases and release oxygen ($2MnO_2 \rightarrow 2MnO + O_2$). This oxygen release can lead to foaming in the melt pool and limit melt rate.

The FY01 melt rate tests with MB3 indicated that sugar addition caused a significant increase in the foam generation and a decrease in melt rate, conflicting with results of tests during the MB2 melt rate tests which showed dramatic reductions in the amount of foam generation and significant improvement in melt rate. Changes made to the feed preparation for melt rate testing may have caused the change in behavior; additional tests would be required to verify the cause.

The crucible tests conducted to determine the relationship between the amount of sugar added to the melter feed and the redox state of the glass indicated that the relationship is probably not linear and that small changes in the amount of sugar can significantly increase the redox of the glass. The redox of the glass produced when sufficient sugar is added to reduce the nitrate in the melter feed to nitrogen is above the upper redox limit for DWPF processing.

DISCUSSION

Crucible Redox Tests

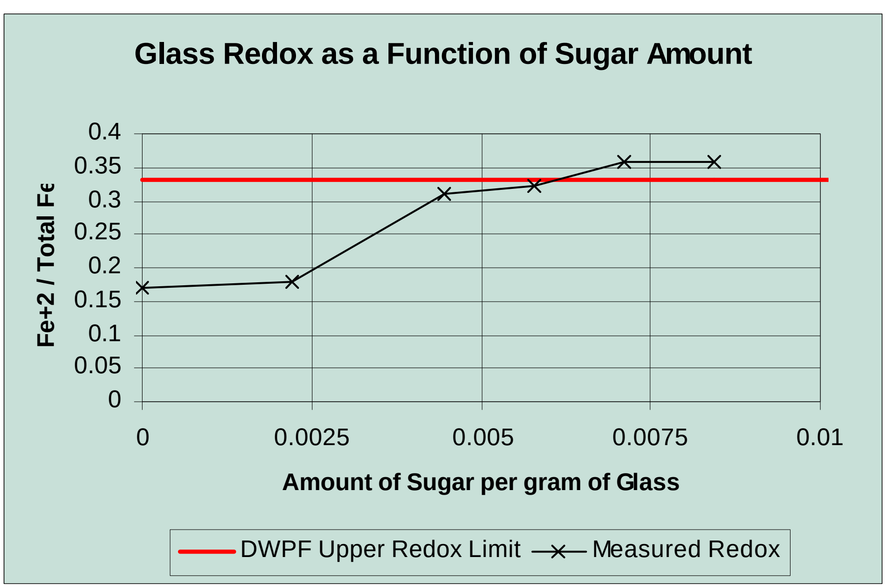
Crucible tests were conducted with Macrobatch 3 SRAT product and Frit 200 with varying amounts of sugar to determine the impact of sugar on the measured redox of the glass product. SRAT product 15-2 [10], with a nitrate concentration of 10,100 ppm, was utilized for the crucible study. The required amount of sugar per 45 grams of glass was calculated to be 0.38 grams based on a ratio of 1.25 moles of carbon per mole of nitrate as determined during MB2 tests. Thirteen samples were tested with varying amounts of sugar per the redox measurement procedure GTOP-3-046, Revision 4. Each crucible was sealed with nepheline gel and fired for one hour at 1150° C [9].

The SRTC Mobile Laboratory determined the redox. The average results are shown in Table 1 and plotted in Figure 1. Based on previous redox studies, a sealed crucible should give a conservative (most reduced) value for the glass redox versus an open crucible [11]. The DWPF melter and the melt rate furnace are not sealed, therefore the redox under true melter conditions would be less. The redox of DWPF glass is not measured, so the amount of conservatism in the sealed crucible test is not known.

Table 1. Glass Redox Results

Amount of Sugar (grams)	Amount of Sugar (grams / gram of glass)	Total Number of Batched Crucibles	Redox Results $Fe^{+2}/\Sigma Fe$
0.00	0.00	3	0.17
0.10	0.0022	3	0.18
0.20	0.0044	3	0.31
0.26	0.0058	2	0.32
0.32	0.0071	1	0.36
0.38	0.0084	1	0.36

Figure 1. Glass Redox versus Sugar Addition



The tests indicate that very small changes in the amount of sugar are capable of significantly changing the redox of the glass product and that the required amount of sugar based on the ratio to nitrate is above the redox limit in DWPF. The number of runs is not sufficient to develop a correlation for redox based on the amount of sugar present, but a non-linear function is suggested by the limited data.

Melt Rate Tests

Test Methods

The baseline Macrobatch 3 SRAT product (Batch 15-3/4) [10], with a nitrate concentration of 12,800 ppm, was combined with 5.83 grams of sugar during the melt rate furnace test to produce 500 grams of glass [8]. The SRAT product, Frit 200, and sugar were combined as a slurry then dried to a batch weight of 551 grams. The melt rate test was conducted in the melt rate furnace in the same manner as the alternative frit tests [5] and was assigned run number 200-MB3-SUGAR-MRF.

Results

The addition of sugar to the Macrobatch 3 baseline SRAT product did not improve melt rate, as shown in Table 2. In addition, a severe volume expansion was noted during the run with the batch height rising to within 1 inch of the top of the beaker, as shown in Figure 2 and indicated by the rapid rise in temperature of the 2” thermocouple, as shown in Figure 3. The results are in direct contrast with the results obtained during tests with Macrobatch 2. The differences between the feed preparation process used during this test and the MB2 test may explain the difference in the impact of the sugar addition. Melt rate was determined by the linear and volumetric methods utilized during alternative frit tests, as calculated in Table 3, based on the sectioned beaker shown in Figure 4.

Table 2. Melt Rate Comparison

	Sugar Amount (gram/gram glass)	Melt Rate (in/hr)	Melt Rate (in^3/hr)
Baseline Process	0	0.75	11.0
Baseline Process with Sugar	0.012	0.70	9.2

During the MB2 melt rate test with sugar, oxidizing SRAT product (mostly nitric acid added during SRAT cycle) was utilized. The SRAT products were dried and size-reduced prior to addition of frit. This method produced a batch with frit as the continuous phase with very large particles of SRAT product. Severe volume expansions were noted during the MB2 melt rate tests with the oxidizing SRAT product when sugar was not added. The sugar was never dissolved in a slurry and did not undergo a drying process prior to the melt rate furnace test since the 42 grams of sugar (0.084 grams sugar per gram of glass) were added to dried SRAT product. The sugar eliminated the volume expansion and dramatically increased the observed melt rate [6].

Baseline SRAT product was prepared during MB3 by processing the sludge simulant in a SRAT cycle with nitric acid and formic acid addition to target a redox of 0.2 $Fe^{+2}/\Sigma Fe$. The sugar and frit were added to the SRAT product slurry instead of dried SRAT product. The prepared feed was then dried and size-reduced prior to testing in the melt rate furnace. Less than 6 grams of sugar was required to reduce the nitrate in the baseline feed. The dissolution of sugar in the melter feed slurry may have affected the rheology of the feed and/or the dissolution and drying processes may have affected the sugar, causing the volume expansion noted during the test.

Volume expansions were not observed during Macrobatch 3 tests, except for the run with sugar. A run was conducted with the MB2 feed (oxidizing and reducing slurry blended to target a 0.2 $Fe^{+2}/\Sigma Fe$ redox) prepared in the same manner as the MB3 tests with no observed volume expansion [5]. The volume expansion is mitigated by the feed preparation method used during MB3, which is closer to the process that will occur in DWPF than the method used during MB2 tests.

Figure 2. Pre-sectioned Beaker for 200-MB3-SUGAR-MRF

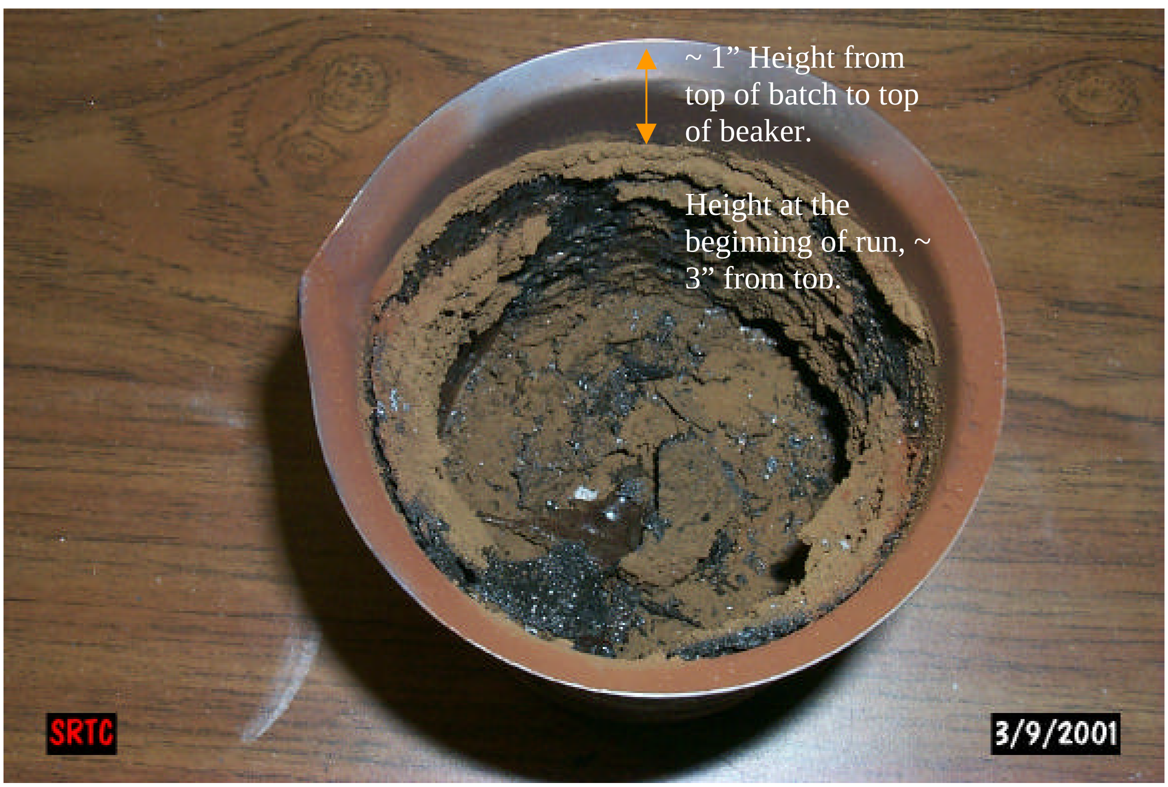


Figure 3. Temperature versus Run Time

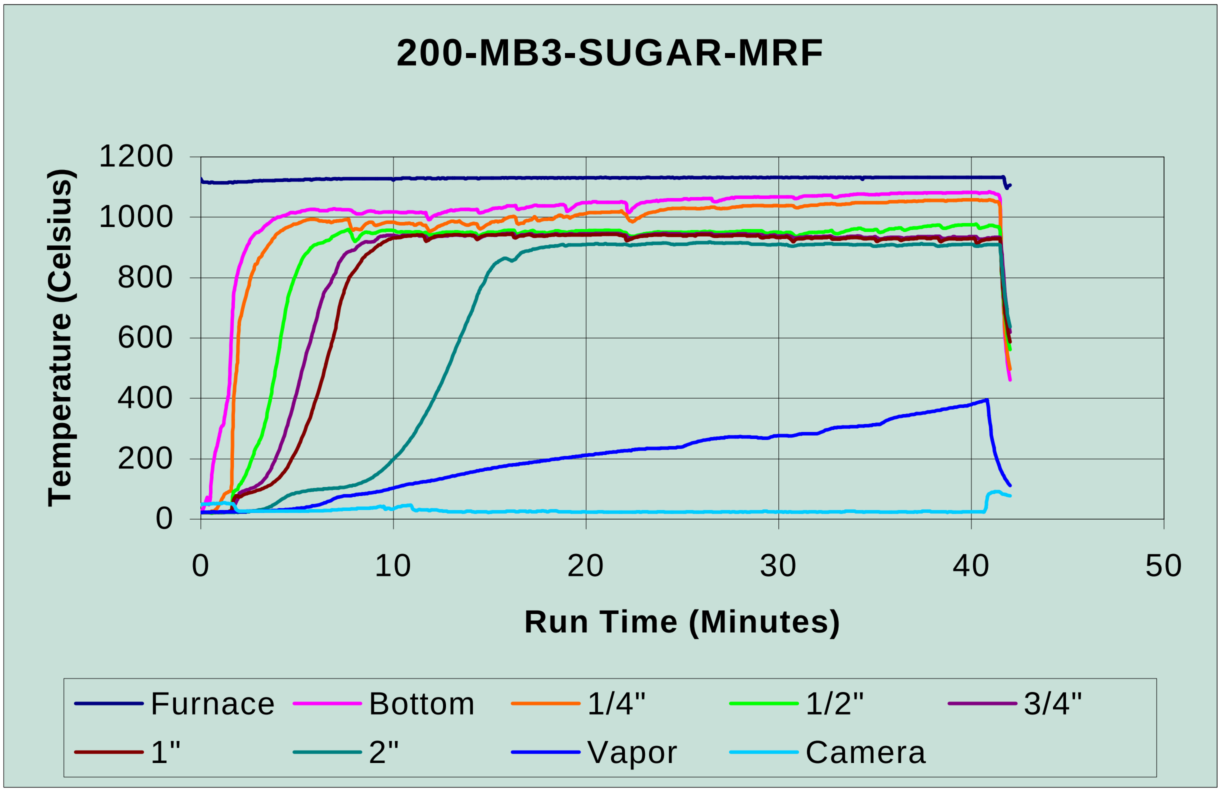


Figure 4. Sectioned Beaker for 200-MB3-SUGAR-MRF

Table 3. Melt Rate Determination

Linear Melt Rate Determination: in/hr				Volumetric Melt Rate Determination: Cubic inches per hour			
Distance from Center	200-8	200-7	Sugar	Distance from Center	200-8	200-7	Sugar
2	0.55	0.7	0.6	2	0.81	1.03	0.88
1.75	0.55	0.7	0.6	1.75	0.70	0.89	0.77
1.5	0.55	0.75	0.65	1.5	0.59	0.81	0.70
1.25	0.55	0.7	0.6	1.25	0.49	0.62	0.53
1	0.55	0.7	0.5	1	0.38	0.48	0.34
0.75	0.55	0.8	0.3	0.75	0.27	0.39	0.15
0.5	0.55	0.3	0.3	0.5	0.16	0.09	0.09
0.25	0.55	0.3	0.35	0.25	0.05	0.03	0.03
0.25	0.55	0.3	0.2	0.25	0.05	0.03	0.02
0.5	0.55	0.25	0.2	0.5	0.16	0.07	0.06
0.75	0.55	0.25	0.2	0.75	0.27	0.12	0.10
1	0.55	0.25	0.7	1	0.38	0.17	0.48
1.25	0.55	0.35	0.7	1.25	0.49	0.31	0.62
1.5	0.55	0.9	0.7	1.5	0.59	0.97	0.76
1.75	0.55	0.9	0.6	1.75	0.70	1.15	0.77
2	0.55	0.9	0.6	2	0.81	1.33	0.88
Average	0.55	0.57	0.49	Sum	6.91	8.50	7.18
Run Time	42	48	42	Run Time	42	42	47
Melt Rate	**0.79**	**0.71**	**0.70**	Melt Rate	**9.9**	**12.1**	**9.2**

CONCLUSIONS

The addition of sugar to MB3 melter feed did not improve melt rate. In addition, glass produced in a sealed crucible has a predicted redox of >0.33 $Fe^{+2}/\Sigma Fe$, which is above the DWPF redox limit.

The impact of the addition of sugar to reduce nitrate to nitrogen during the melting process was dramatically different for the MB3 test than the MB2 test. Changes to the feed preparation method may have caused the difference in behavior, but additional tests would be required to verify the cause.

Glass redox is strongly influenced by the addition of sugar. The amount of sugar calculated to reduce the nitrate available in the SRAT product produces glass that exceeds the DWPF upper limit on redox. Small changes in the amount of sugar can significantly shift the glass redox and the relationship between redox and sugar amount is likely non-linear.

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