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MELT RATE IMPROVEMENT FOR DWPF MB3:

Crucible Studies (U)

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GLOSSARY

DOE	U.S. Department of Energy
DWPF	Defense Waste Processing Facility
ITS	Immobilization Technology Section
MB2	Macrobatch 2
MB3	Macrobatch 3
PNNL	Pacific Northwest National Laboratory
QA	Quality Assurance
SRAT	Sludge Receipt Adjustment Tank
SRTC	Savannah River Technology Center
TFA	Tanks Focus Area
TIM	Task Integration Manager

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Contents

GLOSSARY……v

ACKNOWLEDGEMENTS……vii

LIST OF FIGURES……..ix

LIST OF TABLES……x

1.0 SUMMARY……1

2.0 INTRODUCTION……1

3.0 EXPERIMENTAL PROCEDURES……2

3.1 SRAT Product Preparation…….2
3.2 Frit……..2
3.3 Dried Melter-Feed Preparation……..4

4.0 RESULTS AND DISCUSSION……...5

4.1 Baseline Frit 200 and Frit 165……7
4.2 Frit 165 Minus Zirconium…….10
4.3 Batch Chemicals……....11
4.4 Silica Deficient Frits – 165 and 200……..13
4.4.1 Silica Deficient Frit 165……..13
4.4.2 Silica Deficient Frit 200…….16
4.5 Frit 202……..20
4.6 Alternative Frits…….21
4.6.1 Frit 303……21
4.6.2 Frit 304……22
4.6.3 Frit 307……23
4.6.4 Frit 313……24
4.6.5 Frit 314……25
4.6.6 Frit 315……26
4.6.7 Frit 320……27
4.6.8 Frit 322……28
4.6.9 Frit 323……29
4.6.10 Frit 324……30
4.6.11 Frit 325……31
4.6.12 Frit 326……32

5.0 CONCLUSIONS……..33

6.0 REFERENCES……34

APPENDIX……...35

LIST OF FIGURES

Figure 1. Representative samples of a) sintered mass, b) small bubbles, c) medium bubbles, d) large bubbles, and e) complete glass with no bubbles. ……6
Figure 2. Sectioned crucibles of Frit 200 with MB3 ……8
Figure 3. Sectioned crucibles of Frit 165 with MB3 ……9
Figure 4. Frit 165 (minus Zr) with MB3 ……10
Figure 5. Frit 165 (Batch chemicals) with MB3 ……11
Figure 6. Frit 200 (Batch chemicals) with MB3 ……12
Figure 7. Frit 165 (25% silica deficiency) with MB3 ……14
Figure 8. Frit 165 (50% silica deficiency) with MB3 ……15
Figure 9. Frit 165 (75% silica deficiency) with MB3 ……16
Figure 10. Frit 200 (25% silica deficiency) with MB3 ……17
Figure 11. Frit 200 (50% silica deficiency) with MB3 ……18
Figure 12. Frit 200 (75% silica deficiency) with MB3 ……19
Figure 13. Frit 202 with MB3 ……20
Figure 14. Frit 303 with MB3 ……21
Figure 15. Frit 304 with MB3 ……22
Figure 16. Frit 307 with MB3 ……23
Figure 17. Frit 313 with MB3 ……24
Figure 18. Frit 314 with MB3 ……25
Figure 19. Frit 315 with MB3 ……26
Figure 20. Frit 320 with MB3 ……27
Figure 21. Frit 322 with MB3 ……28
Figure 22. Frit 323 with MB3 ……29
Figure 23. Frit 324 with MB3 ……30
Figure 24. Frit 325 with MB3 ……31
Figure 25. Frit 326 with MB3 ……32

LIST OF TABLES

Table I. Frit compositions (in mass percent) of baseline frits……3

Table II. Frit compositions (in mass percent) of alternative frits developed by……..3
SRTC and PNNL.

Table III. Summarization of Crucible Tests of Frits 165, 200, and 303-326 with MB3…..36

Table IV. Foam Summarization of Frits 165, 200, and 303-326 with MB3……38

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1.0 Summary

The objective of this research is to evaluate the melting behavior of Macrobatch 3 (MB3) for the Defense Waste Processing Facility (DWPF). This study focuses on the manipulation of the frit composition in order to enhance the melting rate of MB3, without sacrificing the quality of the final glass form. Formation of a foam layer prevents incoming feed material from converting into a homogeneous liquid melt efficiently (i.e., lowering melt rate or throughput), thus resulting in slower canister production by DWPF over a given time period. The goal is to find the proper frit composition so the development of this insulating layer is averted. Peeler et al. (2001) outline further incentives of this research.

Because of the multiple phenomena occurring at the same time during the melting process, several analytical techniques should be utilized in order to comprehend the mechanisms leading to a low melt rate. This study was performed on a "small scale" by using 100 mL alumina crucibles to evaluate the batch-to-glass conversion process and melt rate of MB3 with existing and alternative frits. The basic understanding of the reaction pathways and melting behavior at this level will then be applied to such larger scale processes as the melt-rate furnace, slurry-fed mini-melter, and the melter in DWPF. Most of the technical issues behind this understanding are discussed by Peeler et al. (2001).

2.0 Introduction

The definition of melt rate in this case is the rate of the batch-to-glass process (i.e., how quickly feed materials are converted to a liquid melt). In an attempt to increase DWPF's rate of production during the MB3 campaign (~50/50 blend of Tank 8 and Tank 40), tests were conducted to determine the potential for increasing melt rate by changing the glass former and/or feed preparation process. Control over the composition of the incoming batch (specifically the composition of the glass former) may adjust reaction pathways within the cold cap in such a way that enhances melt rate and increases melter efficiency. If successful, higher production goals may be met without sacrificing the quality of the final waste (glass) form.

3.0 Experimental Procedures

A series of crucible tests was conducted by mixing 24 different frits separately with a Macrobatch 3 sludge simulant. The approach for the testing design was reported by Stone and Lambert (2000). Subsections 3.1 through 3.3 highlight the sludge fabrication and receipt, production of frit, and mixing and drying techniques.

During the performance of this task, all equipment was controlled in accordance with the Quality Assurance (QA) program identified in the Immobilization Technology Section (ITS) QA Program Description, SRT-PTD-98-0003, Rev. 3, dated 3/5/01. This program implements and complies with the requirements of the WSRC QA Manual, 1Q, QAP 12-1, Control of Measuring and Test Equipment requirements. The QA requirements of RW-0333P do not apply to this task, but any mini-melter runs would have to meet those requirements (HLW/DWPF/TTR-00-0044).

3.1 SRAT Product Preparation

Instructions for the preparation of MB3 Sludge Receipt Adjustment Tank (SRAT) product for melt rate tests was outlined by Stone (SRT-PTD-2000-00082). Preparation of all SRAT product was conducted at TNX and then delivered to the Savannah River Technology Center (SRTC) for crucible testing (see Stone et al. (2001) for more details). However, every SRAT batch was somewhat different due to variances in water content, thereby causing each batch to have different “calcine factors.” This factor dictates how much SRAT product is added to a specified amount of frit for each crucible test. The “calcine factor” of the SRAT product is determined by heating the SRAT product slurry to 900°C and then determining the percentage of SRAT solids remaining. Calcine factors of the different sludge batches received are documented in the appropriate notebook (WSRC-NB-2000-00144).

3.2 Frit

Of the 24 frits tested, three were prefabricated offsite, while the rest were made at SRTC (see WSRC-TR-2001-00152 for more details). The prefabricated frits were Frit 165, 200, and 202 (Lot #’s AX667974 canisters 3 & 4, CS, and CN, respectively). Stone and Lambert (2000) discuss the use of these frits for an evaluation of MB2 melt rate. These frits were also used to evaluate melt behavior/rate for MB3. The compositions of these frits are listed in Table I, and the alternative frit compositions (see Peeler et al. 2001) are shown in Table II.

Table I. Frit compositions of baseline 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

* See Section 4.2 for explanation.

Table II. Frit compositions (in mass percent) of alternative frits[a] 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[b]	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

[a] See Section 4.6 for more details.
[b] Testing with 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.

To fabricate frits at SRTC, the chemicals were batched to target a specified composition and amount of frit, inserted in the furnace set at 1150°C, held at temperature for approximately one hour, and then poured onto a stainless-steel plate and quenched in air (WSRC-TR-2001-00152)[1].

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 make 500g of glass to acquire ~250g of the desired size fraction). It was this -80, +200 mesh-sized frit that was then mixed with the sludge simulant for each crucible test.

3.3 Dried Melter-Feed Preparation

Batching for the crucible tests was based on producing approximately 45 grams of glass and a 23.2% waste loading on an oxide basis. The required amounts of frit and sludge were combined in a 125 mL polyethylene bottle, shaken to ensure complete mixing, and then poured into a 100 mL alumina crucible. Approximately 5 mL of water was used to rinse the polyethylene bottle in order to transfer as much product as possible into each crucible. Each crucible was then covered with an alumina lid and the total, pre-drying weight was recorded.

The crucibles were then inserted without lids into a vacuum oven for drying. The vacuum oven had a setpoint of 70°C (according to GTOP-3-046, Rev.4) with a vacuum of approximately 24 in. Hg pulled on the system, in order to remove as much water as possible from each crucible. Each crucible remained in the vacuum oven under these conditions for at least 18 hours, and sometimes longer, the basis of which was determined by the consistency of the contents. If the sample contained too much liquid, then it was inserted back into the vacuum oven for further drying. If the contents were dry enough (tackiness of peanut butter or drier), then they were removed from the oven and were ready for firing. The original protocol (as defined by SRT-PTD-2000-00088, Rev. 1) called for the sample to be dried to a net weight of 72 grams or less. No water was added back to any crucible after drying. Once drying was complete, the weight of the crucible with the lid was recorded again before insertion into the furnace.

Due to a problem that occurred when placing crucibles that still contained too much water in the furnace at temperature, drying at a temperature higher than 70°C was investigated. It was suggested to dry at 150°C, but there was an issue of whether or not too many formates would be volatilized from the sample at that temperature, thereby altering the redox. Also, it was found that at approximately 80°C, the contents of the crucible began to boil when under a vacuum. This caused splatter in the oven, thus invalidating the runs. Therefore, it was decided to continue drying at 70°C, but for longer time periods, in order to remove as much water as possible.

Prior to being inserted in the furnace, any material above the top of the batch was scraped from the crucible walls and the original batch height was marked with a high-temperature pen on the outside of each crucible to provide a measure of relative foam height and batch expansion. The

[1] Further documentation of the fabrication of frits at SRTC can be found in WSRC-NB-2000-00144.

ready crucibles were then placed in a secondary (kyanite) crucible and preheated at 70°C for at least 30 minutes to prevent thermal shock (according to GTOP-3-046, Rev. 4). The crucible tests were conducted over a temperature range of 700°C to 900°C in 50° intervals[2]. The charged and covered crucibles were inserted at temperature and held for two hours. After two hours, the crucibles were removed and air-quenched. Once cooled, the weight of the crucible with lid was measured, and then the crucible was cross-sectioned for visual analysis.

4.0 Results and Discussion

More than 175 crucible tests were conducted in the MB3 melt rate study. These small-scale tests were used to provide a basic understanding of the melting processes and behavior of MB3 feed and supplied the basis for interpretation of larger scaled tests. In the following subsections, comparisons of baseline Frit 200 and Frit 165, silica-deficient frits, Frit 202, and alternative frits developed via a joint Pacific Northwest National Laboratory (PNNL) and SRTC effort (Peeler et al. 2001) are made.

It must be noted that all crucible tests performed for this study were done on a single-analysis basis. Due to time and budget constraints, no duplicates for MB3 with any frit were done. However, reproducibility of the results of these tests is assumed. Also, the results of the crucible tests do not give a specific "melt rate," but hopefully will provide insight into the melt behavior of MB3 and be part of the foundation on which a frit selection can be made. The crucible studies are part of a suite of tests discussed by Peeler et al. (2001).

In Figure 1, representative examples of the terminology used in this section to describe the subjective reaction pathways are shown. Figure 1a) depicts a typical sintered mass, where the particles have fused together with no evidence of a liquid phase forming. Figures 1b), 1c), and 1d) represent typical melts containing small, medium, and large-sized bubbles, respectively, and 1e) represents a typical glass with no bubbles.

[2] Initially it was decided to perform the crucible tests over a temperature range of 600°C to 1000°C in 50° intervals. However, it was discovered that the batches were not melted enough at temperatures below 700°C, and nothing new was seen at temperatures greater than 900°C. So, the remainder of the tests was limited to the 700°C to 900°C range, and any other data at different temperatures outside of this range were not mentioned in the results.

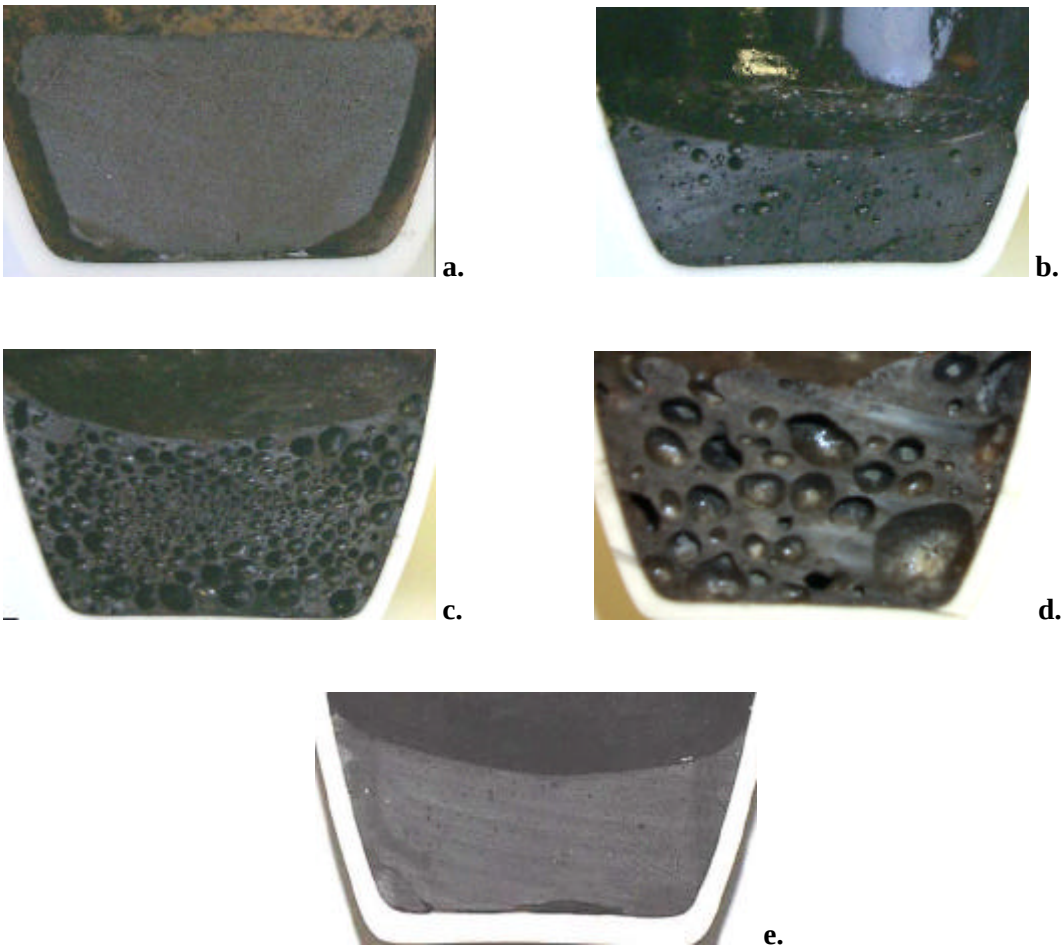


Figure 1. Representative samples of a) sintered mass, b) small bubbles, c) medium bubbles, d) large bubbles, and e) complete glass with no bubbles.

The accumulation of bubbles in the melt could increase foam potential, but does not indicate the level of stability for that foam. Figure 1b) shows how bubbles begin to accumulate in a melt, whereas Figures 1c) and 1d) show foam (larger bubble accumulation with some batch expansion). Batch expansion in these tests does not mean expansion of the melt past the initial batch mark on the outside of the crucible. Upon insertion into the furnace and initial heating, the batch contracted, reached a certain level, and then expanded again with the formation of foam.

4.1 Baseline Frit 200 and Frit 165

Current processing in DWPF of MB2 (Tank 42) utilizes Frit 200. However, Stone and Lambert (2000) concluded that Frit 165 would improve the melt rate of MB2. Given that Frit 200 is the current baseline frit and Frit 165 was shown to improve melt rate for MB2, it seemed logical to begin the assessment of the melting behavior of MB3 with these two frits. Variations of these frits, such as silica deficient Frits 165 and 200[3], Frit 165 minus zirconium, and Frits 165 and 200 using batch chemicals, were also tried and will be discussed in later subsections.

The first baseline frit tested in crucibles with MB3 was Frit 200, and cross-sections are shown in Figure 2. At 700°C, the sample just began to melt and a few tiny bubbles began to form. At 750°C, the batch expanded slightly and the size and quantity of the bubbles began to increase. The temperature at which foaming was the worst was 800°C for Frit 200, where large bubbles formed throughout the melt. As the temperature increased to 850°C though, only small residual bubbles remained mostly close to the top of the melt, while very few, tiny bubbles persisted in the glass at 900°C.

[3] The use of a "silica deficient" Frit 165 or 200 will result in the same targeted glass composition as the existing frits. The only difference is the point at which the SiO_2 is added to the mix. With silica deficient frits, a portion of the SiO_2 was left out of the frit during batching and melting, and then added separately later. See Subsection 4.4 for further explanation.

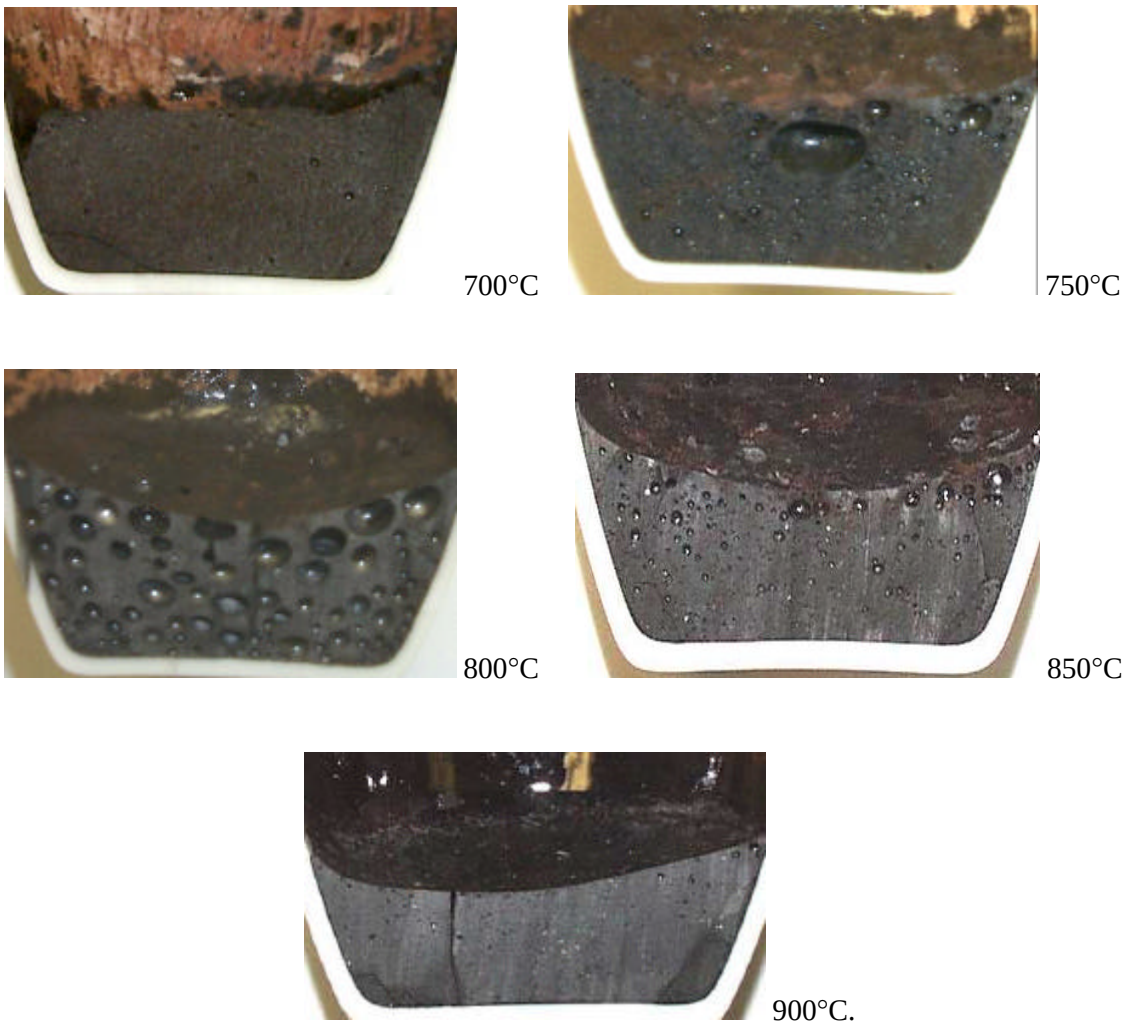


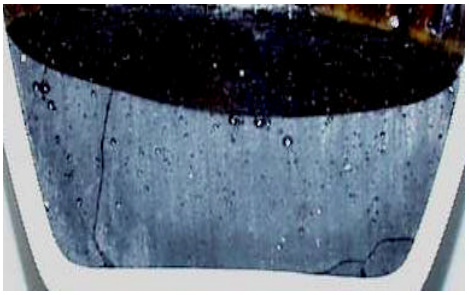
Figure 2. Sectioned crucibles of Frit 200 with MB3.

Frit 165 is represented in Figure 3. A basic sintered mass with a few bubbles just beginning to form at the initial melt occurs for Frit 165 at 700°C. The foam problem was the worst (greatest batch expansion) at 750°C though, with many medium-to-large sized bubbles present throughout the melt. At 800°C, most of the foam dissipated to where only small residual bubbles remained. By 850°C, and especially 900°C, the melt was completely glass with few or no bubbles remaining.

700°C

750°C

800°C


850°C

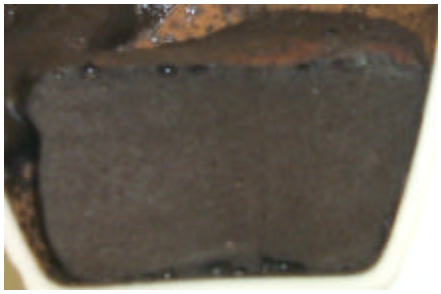
900°C.

Figure 3. Sectioned crucibles of Frit 165 with MB3.

As evidenced by Figures 2 and 3, the main difference between these two existing frits is the temperature at which foaming was the worst. For Frit 200, the most and largest bubbles arise at 800°C, while it is 750°C for Frit 165. Only subtle contrasts were seen at other temperatures, so it is deemed that the melting behavior of MB3 is virtually the same when mixed with either Frit 200 or Frit 165, based on the crucible tests. A summary of what occurred for Frits 165 and 200 is shown in Appendix A.

4.2 Frit 165 minus Zirconium

Frit 165 contains 1 mass% ZrO_2 for the stated purposes of increased durability. Based on a request from DWPF however, Frit 165 was "redesigned" without ZrO_2 (all other components renormalized (see Table I)) to distinguish if any variations in melt behavior or melt rate could be detected . Frit 165 without ZrO_2 may relieve burdensome documentation given that the current reporting documents do not include ZrO_2. Figure 4 shows the results of the Frit 165 without ZrO_2 crucible tests.



700°C

750°C

800°C

850°C

900°C

Figure 4. Frit 165 (minus Zr) with MB3.

Clearly the temperature at which foam is the worst for this frit is 750°C. Based on this single analysis, the potential for foam is higher than that of Frits 165 or 200. However, once 800°C is reached in this case, very few bubbles remain and a complete glass is formed, based on the series of isothermal tests. It appears that removing the zirconium from Frit 165 does not impact the melting behavior of MB3 versus the original Frit 165.

4.3 Batch chemicals

In Section 4.2, the melting behaviors of pre-fabricated Frit 165 and Frit 200 coupled with MB3 were assessed via the isothermal crucible tests. It was decided though to assess the potential impact of using batch chemicals (compositionally the same as the prefabricated frits) – combine all individual components (listed in Table I) of the frit separately. The results of Frit 165 (batch chemicals) and Frit 200 (batch chemicals) are shown in Figures 5 and 6, respectively.

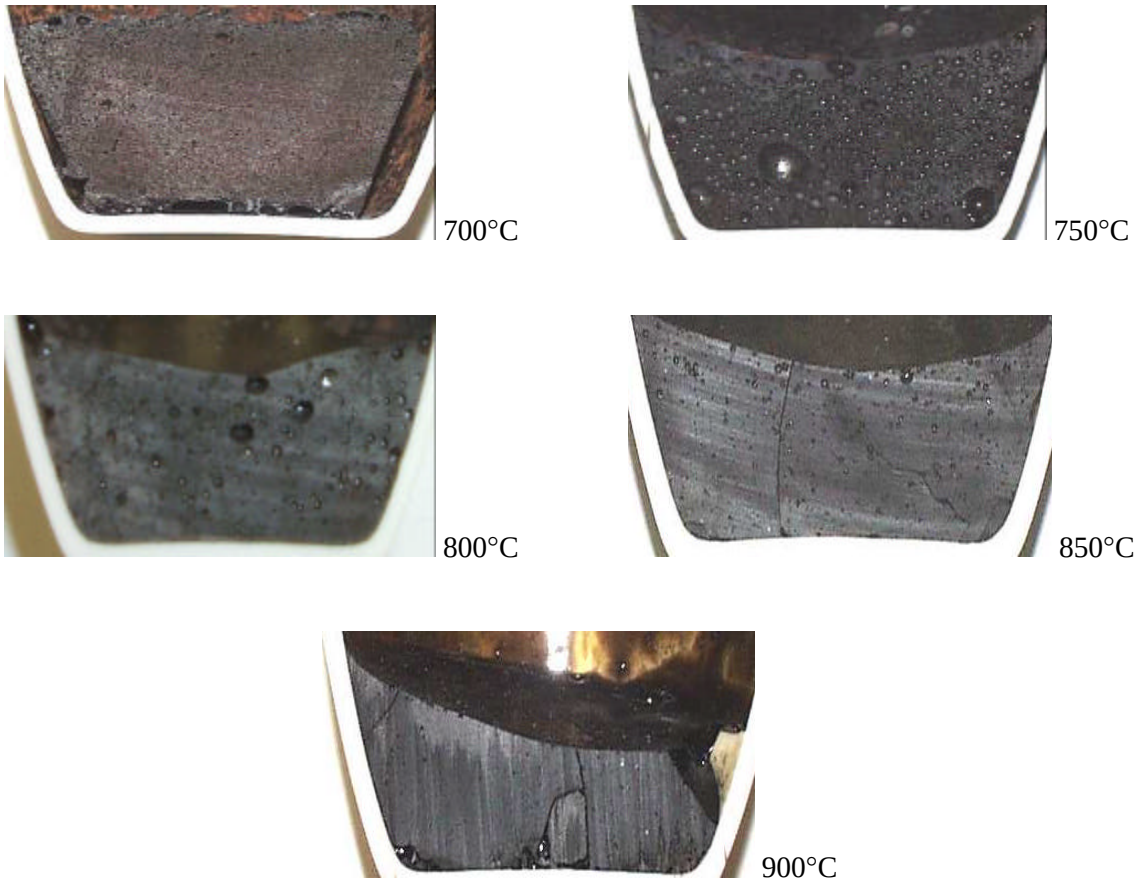


Figure 5. Frit 165 (Batch chemicals) with MB3.

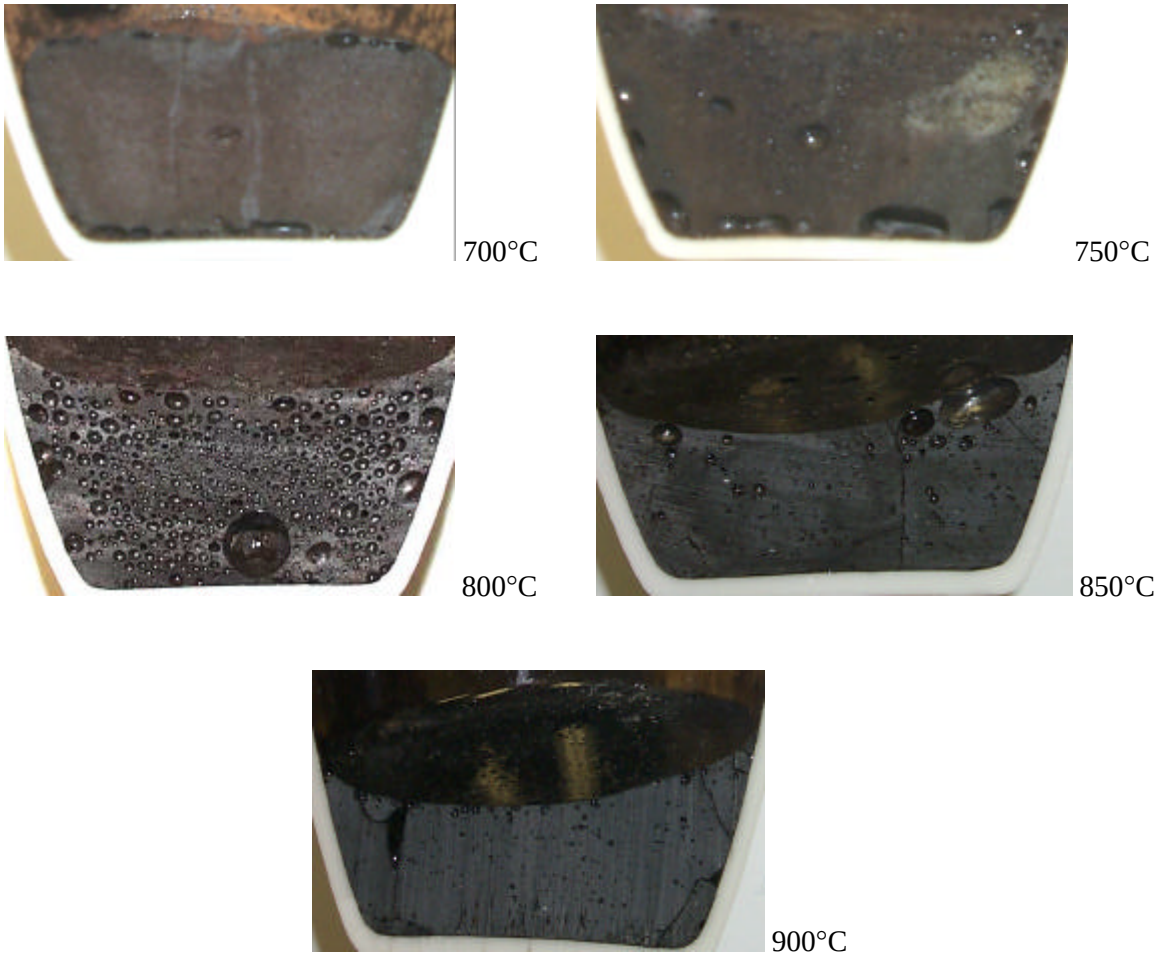


Figure 6. Frit 200 (Batch chemicals) with MB3.

In comparing Figure 5 with Figure 3 and Figure 6 with Figure 2, there are virtually no differences. For example, in comparing the pre-fabricated Frit 165 (Lot #AX667974 canisters 3 & 4) versus 165 from batch chemicals, the temperature with the worst foaming was 750°C. It is apparent that the size and quantity of the bubbles for each option at this temperature are practically the same. Once at 800°C, both frits are at the same stage again, where foam still remains, but the amount of bubbles is less. Strong similarities can be seen between Frit 200 (Lot #CS) and 200 from batch chemicals as well, based on the isothermal crucible tests. Therefore, there appears to be no advantage of utilizing the batch chemical versions of Frits 165 and 200 over using the prefabricated frits.

4.4 Silica deficient frits – 165 and 200

Another option explored for Frits 165 and 200 was leaving out a certain percentage of the silica present in the original frit and adding it back at a later stage (for more details, see WSRC-TR-2001-00152). Compositionally the frits are the same, but instead of adding one component to the sludge (frit only), two components are added (a silica deficient frit plus SiO_2)[4]. Frits 165 and 200 were tested at 25%, 50%, and 75% silica deficiencies and the results are shown in Figures 7-12.

4.4.1 Silica deficient Frit 165

In analyzing these three separate, silica deficiencies of Frit 165, foaming problems occur for each – it is just a matter of when and how much. For the 25% and 50% silica deficiencies, the greatest amount of foam and volume expansion occurred at 750°C. For the 75% deficiency it appears to begin to happen at 700°C and is probably worst somewhere between 700°C and 750°C. The 75% silica deficiency foaming at a lower temperature than the 25% and 50% deficiencies can probably be attributed to the greater amount of SiO_2 that was added separately from the silica deficient frit (see Lorier (2001) for more details). For all three, most of the foam is decreasing by 800°C, and no bubbles appear any more once 900°C is reached.

[4] The required amount of "total" frit needed for one crucible test is 34.56 grams, and assume the frit is Frit 165 at 25% silica deficiency. Instead of adding 34.56 grams of pure Frit 165, 28.68 grams of 25% silica deficient Frit 165 plus 5.88 grams of SiO_2 are added.

700°C

750°C

800°C

850°C

900°C

Figure 7. Frit 165 (25% silica deficiency) with MB3.

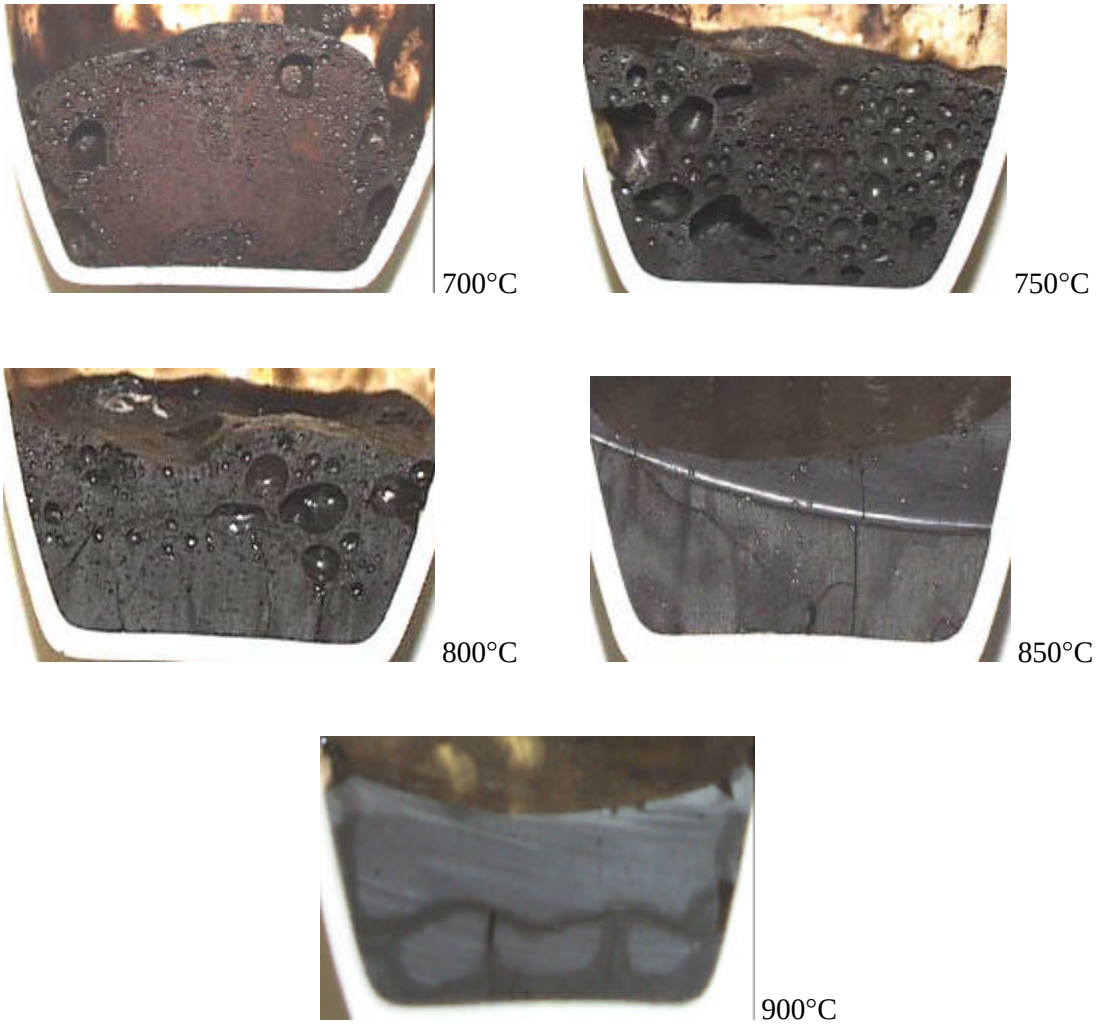
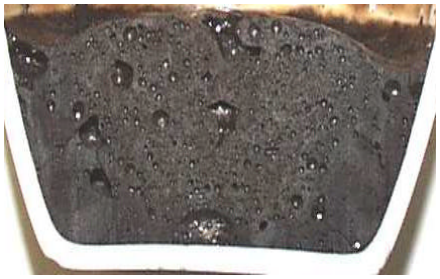


Figure 8. Frit 165 (50% silica deficiency) with MB3.

700°C

750°C


800°C

850°C

900°C

Figure 9. Frit 165 (75% silica deficiency) with MB3.

4.4.2 Silica deficient Frit 200

Trends similar to those of silica deficient Frit 165 were observed for the silica deficient 200 frits For the 25% and 50% deficiencies of Frit 200, severe foam (batch expansion) appeared at 700°C with the most severe foaming and batch expansion at 750°C. However, the foam seemed to endure to higher temperatures than those of 165. Once at 900°C though, virtually all bubbles were gone. For the 75% silica deficient 200 frit, not much foam appeared until 900°C though, but most of the bubbles resided at the top of the glass melt.

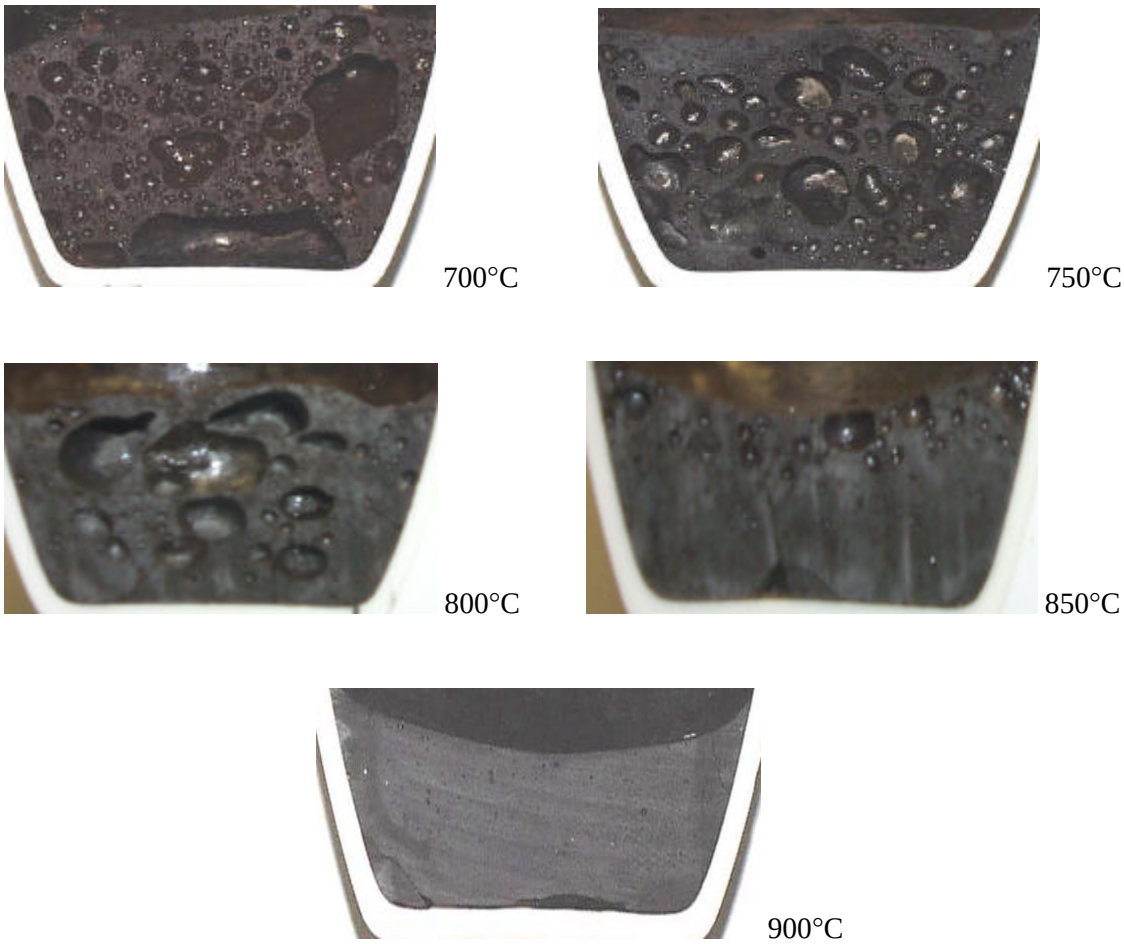


Figure 10. Frit 200 (25% silica deficiency) with MB3.

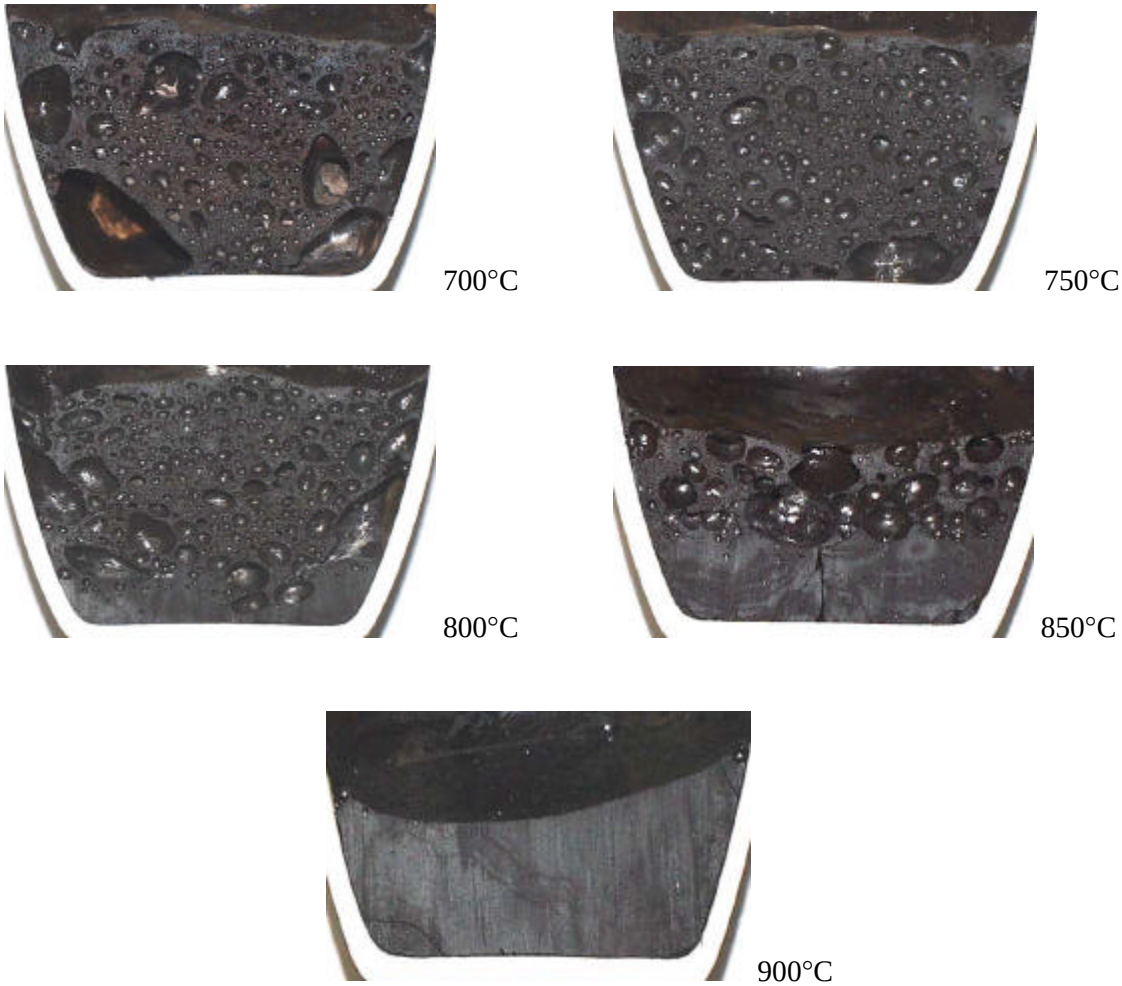


Figure 11. Frit 200 (50% silica deficiency) with MB3.

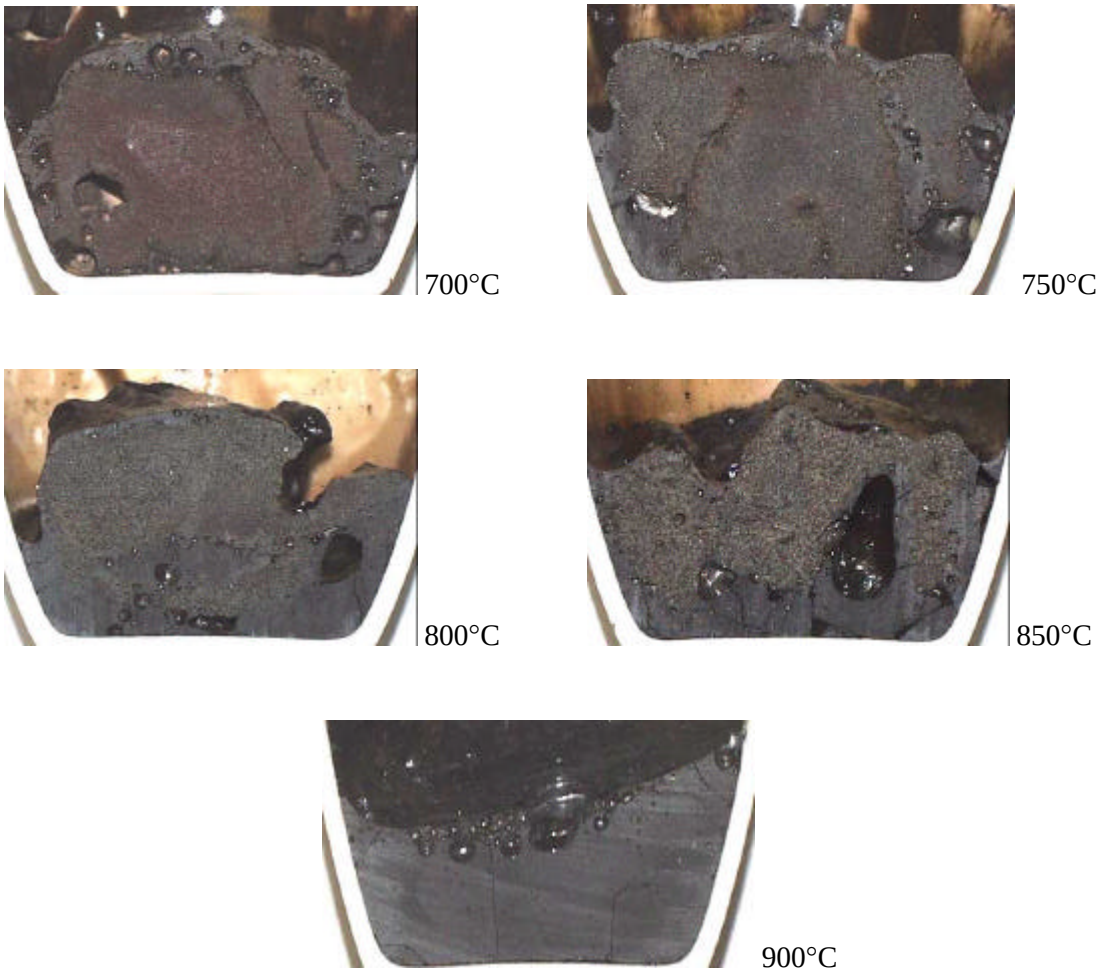


Figure 12. Frit 200 (75% silica deficiency) with MB3.

Analysis of these silica deficiency tests shows several advantages of not utilizing silica deficient frits versus Frit 165 or 200. The amounts and duration of the foam in the cases of silica deficient 165 and 200 are greater than the pure frits. Another issue is that the combination of a silica deficient frit plus SiO_2 might melt too slowly because the rate-limiting step may be the dissolution of the SiO_2 into the glass. This is especially evidenced by the 75% silica deficient frits. Other problems include density differences, sampling issues in the SME if implemented in DWPF, and qualification concerns. Finally, having a “two-component” frit by adding a silica deficient frit and SiO_2 separately complicates the process over only adding a pure frit (single component).

4.5 Frit 202

Frit 202 contains the same components as Frit 200, but is more refractory due to the increased amount of SiO_2 and lesser alkali and boron contents. Testing was conducted with this frit to determine whether or not creating a more viscous melt affects the melt rate of MB3. The results are shown in Figure 13.

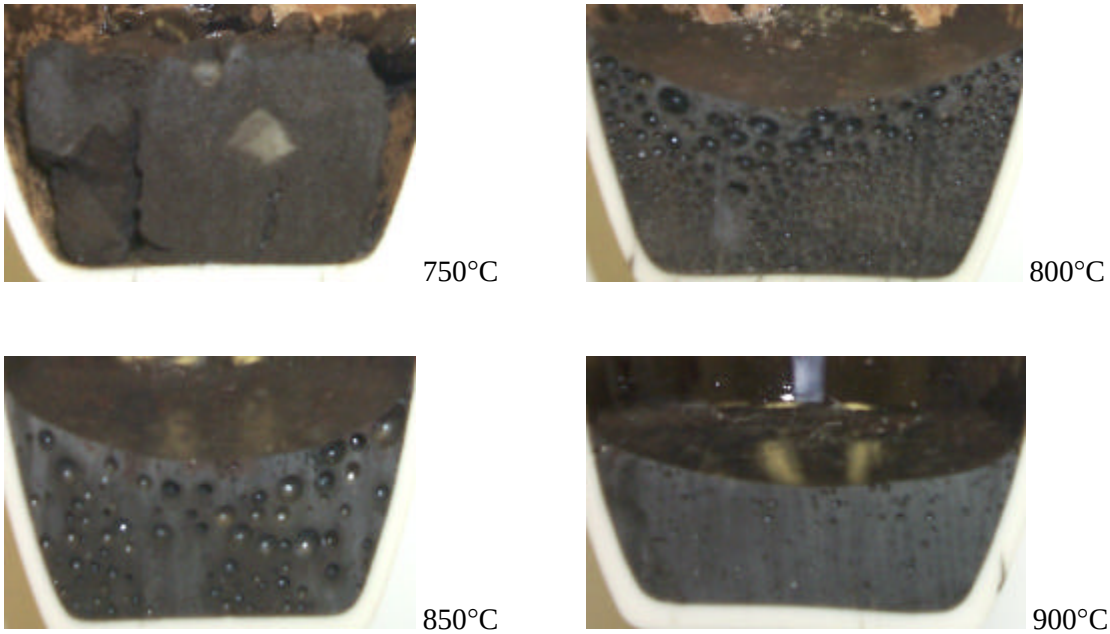


Figure 13. Frit 202 with MB3.

Being more refractory causes Frit 202 to not melt as quickly as other frits that have a lesser silica content. That is why no figure appears for Frit 202 at 700°C – sintering of the raw material had not occurred to the point that the sample could be cross-sectioned. At 750°C, the sample is just forming a sintered mass. At 800°C, the temperature of worst foam in this case, there was some slight volume expansion up the sides of the crucible and many small to medium bubbles materialized throughout the melt. Several larger bubbles remained at 850°C, but there were fewer of them relative to those at 800°C, and by 900°C all foam/batch expansion had subsided and only tiny residual bubbles remained in the complete glass melt.

4.6 Alternative frits

Twelve alternative frits, developed through a joint SRTC/PNNL effort, were recommended by the melt rate team for further testing in order to evaluate melt rate of MB3. The criteria for how these twelve frits were chosen are: 1) boron in glass ranges 5% < B ≤ 11%, 2) no non-lithium frits (minimum 3.5 mass%), 3) total alkali ≤ 20%, 4) no ZrO_2, 5) no Al_2O_3, and 6) need to push Li_2O limits (Peeler et al. 2001; WSRC-NB-2000-00144). The frits and their compositions (mass percent) are listed in Table II in subsection 3.2, and a summary of the major observations in the crucible tests for each frit is given in Tables III and IV of the Appendix.

4.6.1 Frit 303

At 700°C, the sample was not sintered sufficiently to enable cross-sectioning of the crucible, so no figure appears. At 750°C, small bubbles began to form throughout the melt, but a majority of the batch was still "unreacted." The greatest batch expansion and foam occurred at 800°C, where many large bubbles had formed. Significant volume reduction occurred by 850°C, with residual bubbles remaining at the top of the melt, and at 900°C a complete glass had formed.

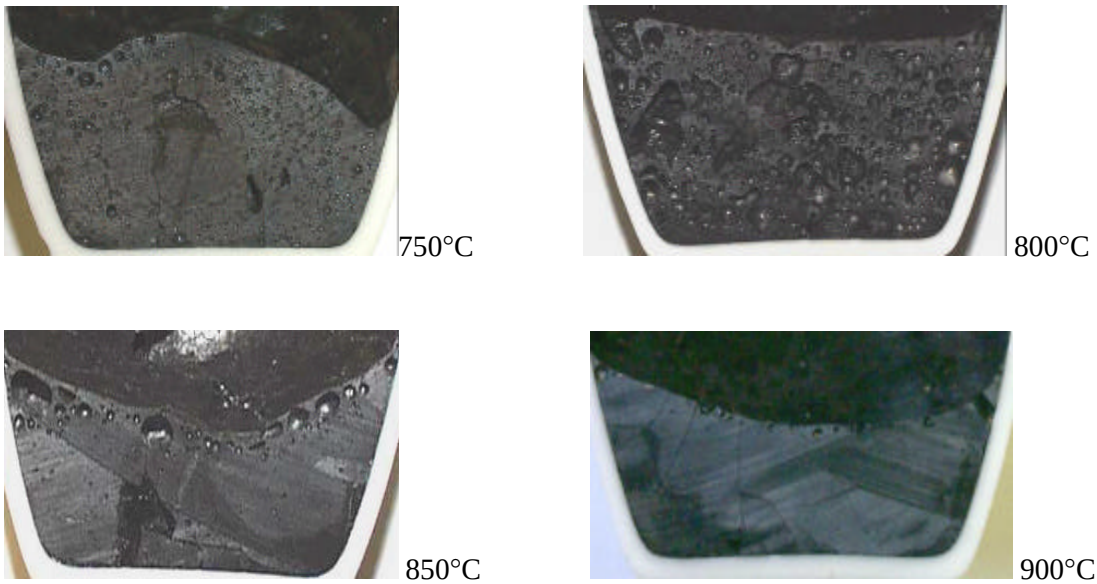
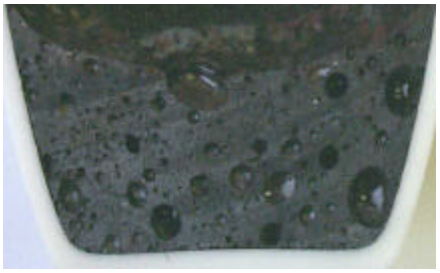


Figure 14. Frit 303 with MB3.

4.6.2 Frit 304

The greatest foaming problems/batch expansion for Frit 304 occurred at a lower temperature than those of any other frits tested. Large bubbles throughout and batch expansion were evident at 700°C, but the batch volume was reduced greatly by 750°C[5]. At 800°C, only small residual bubbles remained; and at temperatures of 850°C and above a complete glass sample had formed. By this isothermal analysis it appears that Frit 304 melts quite rapidly.

700°C


750°C

800°C

850°C

900°C

Figure 15. Frit 304 with MB3.

[5] The figures of all crucibles are not on the same exact scale, so small differences may be difficult to see.

4.6.3 Frit 307

For Frit 307, the sample was a sintered mass at 750°C and below, with no expansion or glass phase observed. By 800°C though, the batch had expanded with many medium and large bubbles present throughout the melt. At 850°C, only small bubbles were trapped at the melt surface. The sample was glass at 900°C, with no bubbles remaining (the dark, triangular portion of the picture is where a small piece of glass broke off during sectioning).

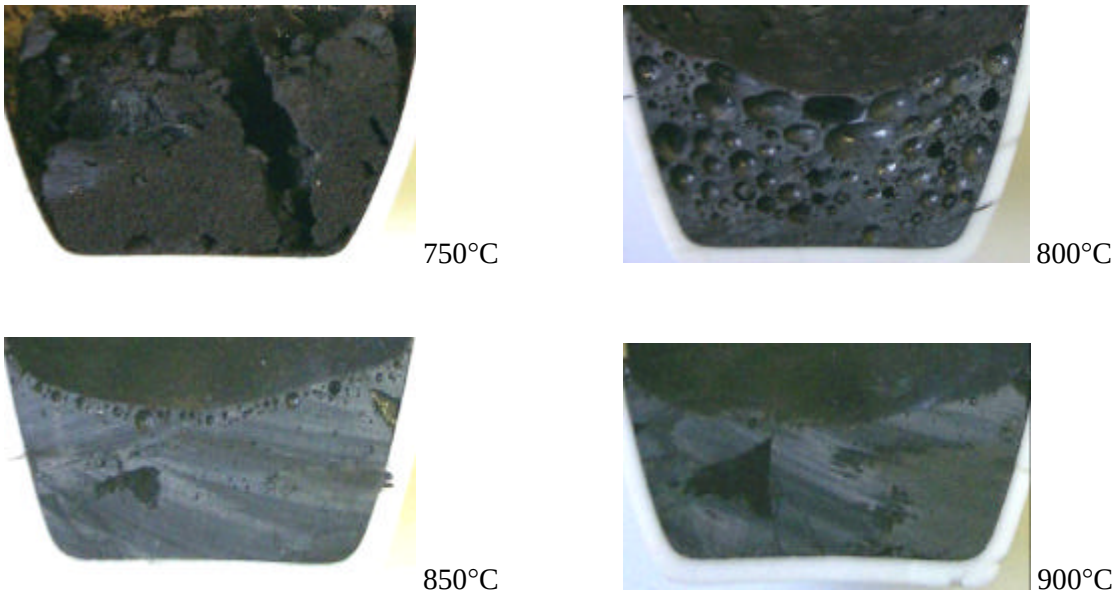


Figure 16. Frit 307 with MB3.

4.6.4 Frit 313

The batch with Frit 313 was basically a sintered mass at both 750°C and 800°C, with only slightly more reaction and volume reduction at 800°C. Volume reduction continued at 850°C, with only small bubbles residing at the top of the melt. By 900°C, all bubbles had disappeared and a complete glass had formed. By observation, it does not seem that Frit 313 has a significant foam or batch expansion potential with MB3, based on these crucible tests.

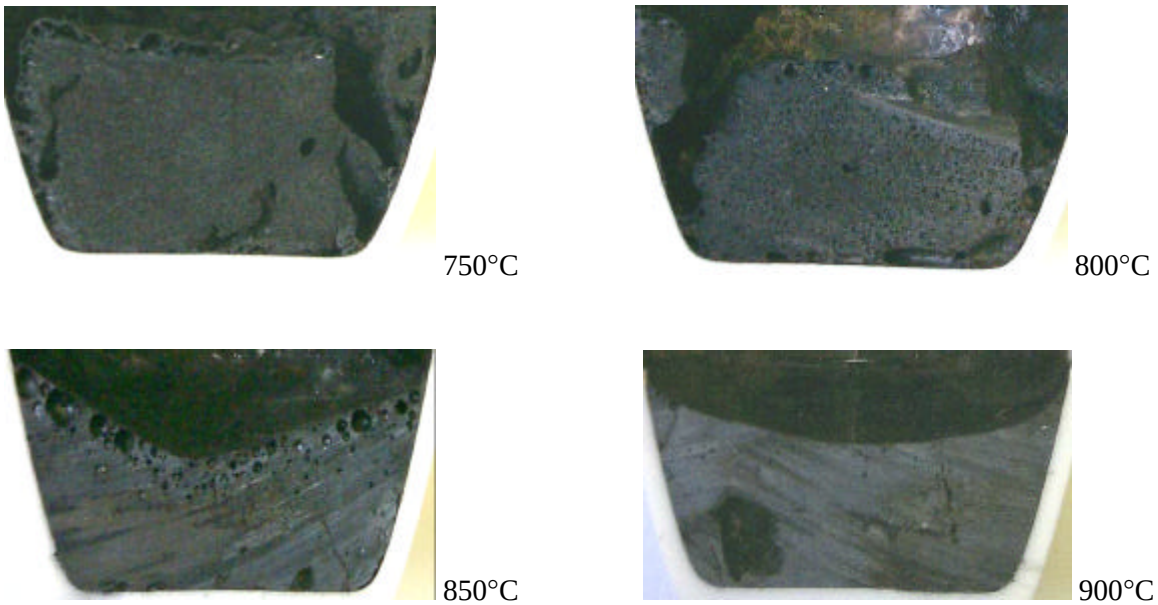


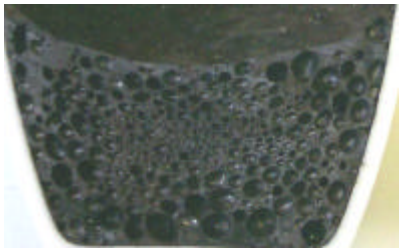
Figure 17. Frit 313 with MB3.

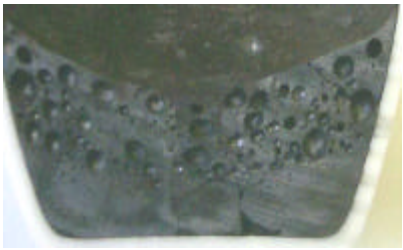
4.6.5 Frit 314

At 700°C, the Frit 314 sample was still a sintered mass with a mostly unreacted batch. More melting occurred at 750°C, where small and medium-sized bubbles formed. The foam was worst at 800°C, where larger bubbles were present throughout the entire melt. At 850°C, the bubbles that persisted were in the top half of the melt with a complete glass beneath. No bubbles remained once at 900°C.

700°C

750°C


800°C


850°C

900°C

Figure 18. Frit 314 with MB3.

4.6.6 Frit 315

Of the frits tested, Frit 315 is the only one that contained only three components – B_2O_3, Li_2O, and SiO_2. All the others contained at least four components. For Frit 315 at 750°C, most of the sample was a sintered mass, with an initial liquid formed at the surface. At 800°C, volume reduction occurred with a few medium bubbles formed towards the center of the melt. Basically the same happened at 850°C, and by 900°C, only tiny bubbles remained in the top half of the melt. So based on these crucible-scale tests, Frit 315 does not seem to have a significant foam or batch expansion problem.

750°C

800°C

850°C

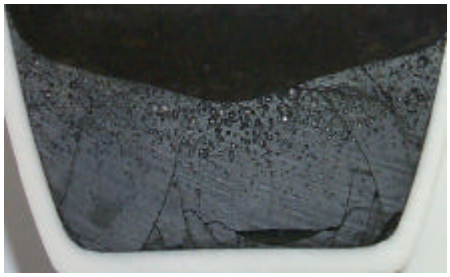
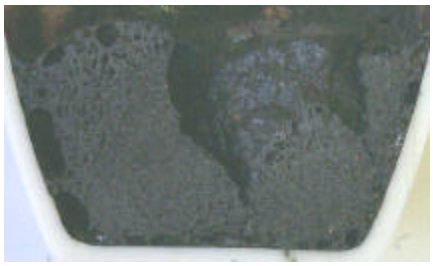

900°C

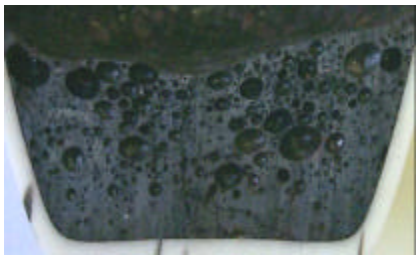
Figure 19. Frit 315 with MB3.

4.6.7 Frit 320

The samples of Frit 320 at 700°C and 750°C were essentially "unreacted", with some initial melting occurring at 750°C. At 750°C, larger bubbles began to form at the surface and along the sides. The temperature of greatest foam was 800°C, where numerous small, medium, and large bubbles formed throughout the melt. Virtually all foam was gone once 850°C was reached, with only few residual bubbles remaining. By 900°C, the melt was in a complete glass form.

700°C


750°C


800°C

850°C

900°C

Figure 20. Frit 320 with MB3.

4.6.8 Frit 322

The worst foam formation and expansion for Frit 322 was observed at 750°C, but only small bubbles were noted throughout the melt. Medium or large bubbles never materialized. At 800°C, the bubbles were even smaller and a slight volume reduction had occurred. Only residual bubbles were present near the tops of the melts at 850°C and 900°C. The samples were complete glasses at these temperatures.

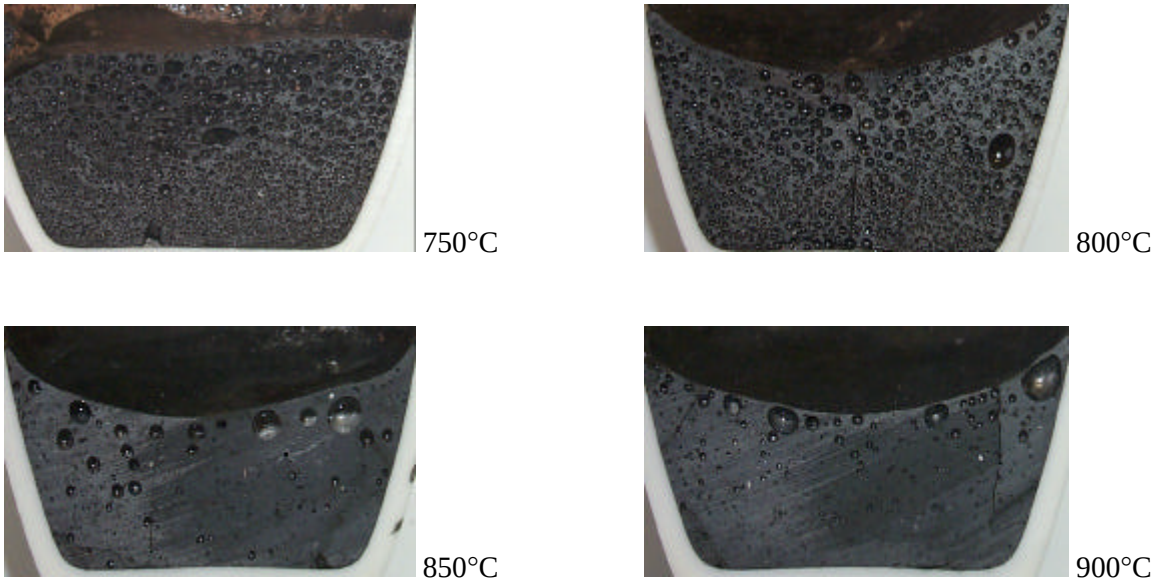


Figure 21. Frit 322 with MB3.

4.6.9 Frit 323

A sintered mass formed for Frit 323 at 700°C. By 750°C, many tiny bubbles formed throughout the melt, along with a few medium-sized bubbles. A slight volume reduction occurred at 800°C as a glass began to form, but small bubbles resided in the entire melt. At 850°C only a few residual bubbles remained in the glass. The same is true for the sample at 900°C, where virtually no bubbles remained.

700°C

750°C

800°C

850°C

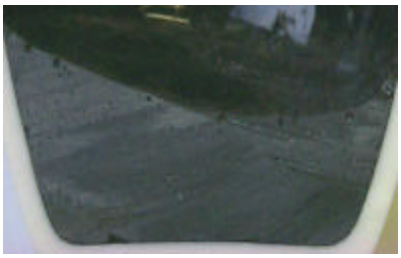

900°C

Figure 22. Frit 323 with MB3.

4.6.10 Frit 324

Frit 324 differed from Frit 323 compositionally by reversing the concentrations of sodium and lithium. Frit 323 had the higher sodium content, while Frit 324 had the higher lithium content. At 750°C, the Frit 324 sample was still a sintered mass where little melting had occurred. At 800°C, tiny bubbles began to form, with one very large bubble in the middle of the melt. The foam resided mostly at the top of the melt at 850°C. All bubbles had subsided by 900°C. Comparison of Frits 323 and 324 indicates that Frit 324 would be a more preferred frit because the foam potential did not seem as dramatic as Frit 323, based on these isothermal crucible tests.

750°C

800°C

850°C

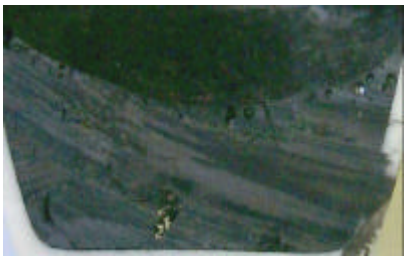

900°C

Figure 23. Frit 324 with MB3.

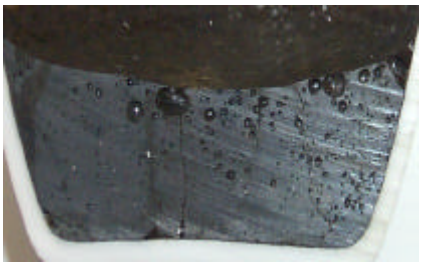
4.6.11 Frit 325

When tested with Macrobatch 3, Frit 325 was combined with Frit 202 in a 1:1 ratio and then mixed with the sludge. At 700°C, the sample was sintered, but by 750°C, melting had begun and foam had formed throughout the entire melt. One very large bubble formed in the middle of the melt at 800°C, along with tiny to medium-sized bubbles throughout. Residual bubbles persisted at 850°C, and the melt was completely glass by 900°C (a piece of glass broke away from the rest of the sample upon sectioning).

700°C

750°C

800°C


850°C

900°C

Figure 24. Frit 325 with MB3.

4.6.12 Frit 326

Frit 326 is compositionally the same as Frit 320, except that 1 mass% MgO has been added at the expense of 1 mass% Na_2O (see Table 2). Since adding MgO to a frit may augment the final glass' performance/durability, it was decided to add it and evaluate how or if it affected melt rate or melt rate behavior as defined by the tests utilized in this study. Adding MgO to Frit 320 was based on the following criteria: 1) the viscosity of Frit 320 is low, 2) ΔG_p (limit for durability) is low, 3) waste loadings are high, and 4) removing 1% Na_2O from Frit 320 to compensate for the 1% addition of MgO causes the ratio of lithium to sodium in the frit to be higher.

For Frit 326 at 750°C, bubbles began to form in the initial liquid phase along the sides and surface, but most of the batch was still unreacted. The greatest amount of foam arose at 800°C, where medium-sized bubbles resided towards the top of the melt and smaller bubbles throughout. As evidenced by the figures, the samples were mostly glass at 850°C and 900°C, with very few bubbles remaining.

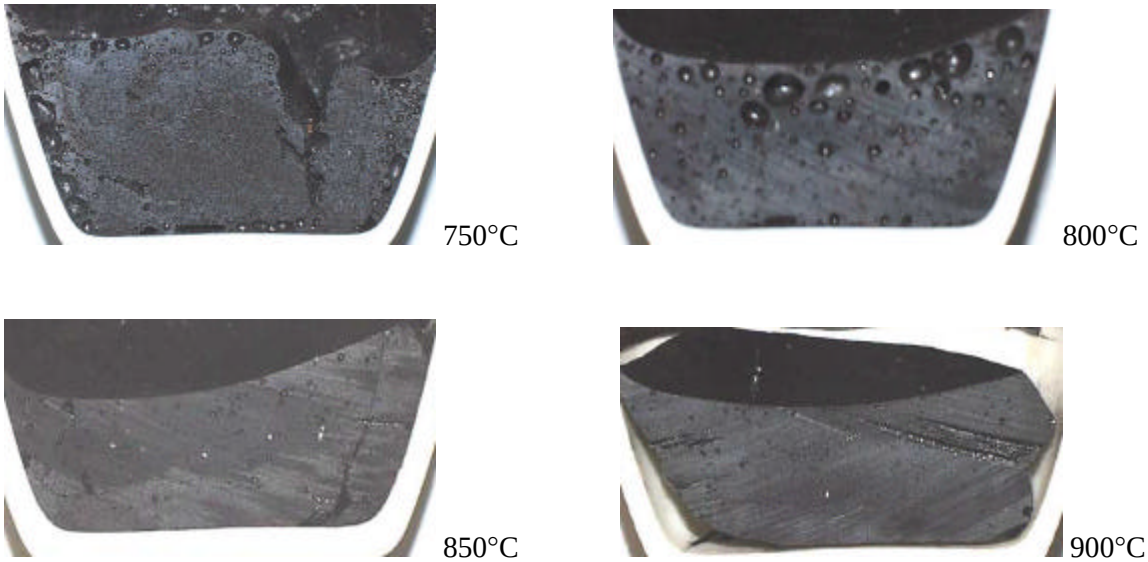


Figure 25. Frit 326 with MB3.

In comparing Frit 326 to 320, the temperature where foam was the biggest problem was 800°C for each. However, it was not as dramatic for Frit 326 as it was for 320. Larger bubbles formed

for Frit 320, and in a larger quantity. By this comparison, the presence of MgO may slightly enhance melt rate based on the crucible tests.

5.0 Conclusions

These crucible tests have been effective in giving a basic understanding of the melting behavior of MB3 over a series of frit compositions. The testing of 24 different frits has shown that there may be potential foaming issues with MB3, some worse than others. The problems can be alleviated though with the proper frit composition. This could minimize any bubbles or foam from being trapped during the melting process and slowing melt rate.

Several conclusions were made from the results of these crucible studies, which indicated the following:

1) The small-scale crucible studies are capable of distinguishing differences in the melting behavior of frits in testing of MB3.
2) Those frits that appeared to have the least foaming potential for MB3 and melted the fastest are Frits 313, 315, 323, 324, and 326.
3) Those frits that seemed to have foaming potential, but not extreme, were Frits 165, 200, 165 (75% silica deficiency), 200 (75% silica deficiency), 165 (batch chemicals), 200 (batch chemicals), 202, 303, 304, 307, 320, and 325.
4) Those frits with the most serious foaming potential appeared to be Frits 165 (25% and 50% silica deficiency), 200 (25% and 50% silica deficiency), 165 without ZrO_2, 314, and 322.
5) Melt rate can be enhanced via alteration of the frit composition, based on the crucible test.
6) Removal of ZrO_2 from Frit 165, does not affect melt rate, based on the crucible tests.
7) The addition of 1 mass% MgO at the expense of Na_2O did not appear to affect melting behavior for Frit 326. If deemed necessary, 1 mass% MgO could be added to meet other performance issues without negatively impacting melt rate, based on these crucible studies.

Again, these conclusions are based solely on results obtained from the crucible-scale tests and are highly subjective. Since there is no one “silver bullet” test that can ultimately produce all of the answers, further testing beyond these studies is required.

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Technical Task Request #HLW/DWPF/TTR-00-0044, DWPF Macrobatch 3 Melt Rate Study.

Laboratory notebook #WSRC-NB-2000-00144.

Appendix

Table III. Summarization of Crucible Tests of Frits 165, 200, and 303-326 with MB3.

Table IV. Foam Summarization of Frits 165, 200, and 303-326 with MB3.

Table III. Summarization of Crucible Tests of Frits 165, 200, and 303-326 with MB3.

Frit	700°C	750°C	800°C	850°C	900°C
165	Little melt	Foam throughout (1-8 mm diameter bubbles)	Smaller residual bubbles throughout (0.25-3 mm diameter)	Glass – dull on top	Glass – shiny on top
200	Little melt; few bubbles beginning to form	Mostly small bubbles throughout (0.25-1 mm diameter); few larger bubbles also (2-10 mm diameter)	Large bubbles throughout (1-5 mm diameter)	Residual bubbles mostly at the top (0.25-2 mm diameter)	Glass – shiny and homogeneous on top
303	Sintered	Small bubbles throughout (0.5-2 mm diameter)	Many large bubbles throughout (1-7 mm diameter)	Few residual bubbles at top (0.5-4 mm diameter)	Glass (bubble free) – dull and homogeneous on top
304	Much foam throughout (1-14 mm diameter bubbles)	Fewer and smaller bubbles throughout (0.5-5 mm diameter)	Small bubbles throughout (0.25-1 mm diameter)	Glass (bubble free)	Glass – shiny on top
307	Sintered	Little to no melt	Much foam throughout (0.25-9 mm diameter)	Few, small residual bubbles at top (0.25-1 mm diameter)	Glass – dull and homogeneous on top
313	Sintered	Little to no melt	Still in initial melting stage; very tiny bubbles throughout (0.25 mm diameter)	Few residual bubbles at top (0.25-4 mm diameter)	Glass – shiny on top
314	Little melt (no bubbles)	Foam throughout (0.25-4 mm diameter bubbles)	Larger bubbles (foam is worse) throughout (2-5 mm diameter bubbles)	Fewer bubbles, but mostly in top half of melt (1-3 mm diameter bubbles)	Glass – dull and homogeneous on top
315	Sintered	Little melt; initial bubbles beginning to form	Very tiny bubbles throughout; few larger bubbles also (2 mm diameter)	Tiny bubbles throughout; one large bubble in middle of melt	Small residual bubbles in top half of glass (0.5 mm diameter); glass is

					dull and homogeneous on top
320	Little melt	Tiny bubbles beginning to form throughout; larger bubbles along the sides	Large bubbles throughout (1-5 mm diameter)	Few residual bubbles (0.5 mm diameter)	Glass – shiny and homogeneous on top
322	Sintered	Many small bubbles throughout (0.25-3 mm diameter)	Small bubbles still throughout, but not as pronounced (0.25-3 mm diameter)	Very few residual bubbles (0.25-3 mm diameter)	Glass – dull and homogeneous on top; few residual bubbles remain at top
323	Little melt (no bubbles)	Very tiny bubbles throughout (0.25-3 mm diameter)	Foam throughout (0.5-3 mm diameter bubbles)	Few residual bubbles at top	Glass – shiny and homogeneous on top
324	Sintered	Little to no melt	Tiny bubbles beginning to form at top (0.25 mm diameter)	Bubbles mostly in top half of melt (0.5-5 mm diameter)	Glass – dull and homogeneous on top
325	Little melt (no bubbles)	Foam throughout (0.25-4 mm diameter bubbles)	Very tiny bubbles throughout (0.25-4 mm diameter); one large bubble in middle (13 mm diam.)	Very few residual bubbles, but mostly at top (1-3 mm diameter)	Glass – shiny and homogeneous on top
326	Sintered	Onset of bubble formation; larger bubbles along sides	Few larger bubbles, but mostly at the top (0.5-4 mm diameter)	Few residual bubbles (0.5 mm diameter)	Glass – shiny on top

Table IV. Foam Summarization of Frits 165, 200, and 303-326 with MB3.

Frit	Temp. of initial bubbles	Temp. of largest bubbles (worst foam)	Temp. when clear (bubble free)
165	750°C	750°C	850°C
200	750°C	800°C	900°C
303	750°C	800°C	900°C
304	700°C	700°C	850°C
307	800°C	800°C	850°C
313	800°C	850°C	900°C
314	750°C	800°C	900°C
315	750°C	850°C	900°C
320	750°C	800°C	900°C
322	750°C	750°C	850°C
323	750°C	800°C	900°C
324	800°C	850°C	900°C
325	750°C	800°C	900°C
326	750°C	800°C	900°C

Distribution

W. D. Kerley, 704-S
J. F. Ortaldo, 704-S
R. E. Edwards, 704-3N
M. R. Norton, 704-27S
J. E. Occhipinti, 704-27S
J. F. Sproull, 704-30S
D. C. Iverson, 704-30S
R. J. O'Driscoll, 704-30S
L. M. Papouchado, 773-A
E. W. Holtzscheiter, 773-A
R. H. Spires, 773-A
D. A. Crowley, 773-43A
S. L. Marra, 704-1T
D. F. Bickford, 773-43A
C. M. Jantzen, 773-A
D. C. Witt, 704-1T
M. E. Stone, 704-1T
D. P. Lambert, 704-1T
M. F. Williams, 704-1T
D. C. Koopman, 704-1T
T. K. Snyder, 773-42A
J. J. Connelly, 773-41A
K. G. Brown, 704-1T
D. R. Best, 773-41A
D.K. Peeler, 773-43A
T.H. Lorier, 773-23A
D. H. Miller, 786-1A
T. B. Edwards, 773-42A
J.C. George, 773-43A
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