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Foaming of E-Glass II (Report for G Plus Project for PPG)

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September 2005

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Summary

In a previous study, the effect of the furnace atmosphere on E-glass foaming was investigated with the specific goal to understand the impact of increased water content on foaming in oxy-fired furnaces. The present study extended the previous study and focused on the effect of glass batch chemical composition on E-glass foaming. The present study also included reruns of foam tests performed in a previous study, which resulted in the same trend: the foaming extent increased nearly linearly with the heating rate and no foam was produced when $\text{CO}_2 + 55\% \text{H}_2\text{O}$ atmosphere was introduced at 300°C . It was shown that the lack of foaming in the test with $\text{CO}_2 + 55\% \text{H}_2\text{O}$ atmosphere introduced at 300°C was caused by a loss of sulfate at $T < 1250^\circ\text{C}$ because of higher water content at the early stages of melting. The tests with new batches in the present study showed that replacing quicklime with limestone tend to decrease foaming, possibly caused by increased sulfate loss during early stages of melting in the batch with limestone. The batches where Na_2SO_4 was replaced with NaNO_3 , $\text{NaNO}_3 + \text{CeO}_2$, or CeO_2 , produced only very limited foaming regardless of the replacing components. As expected, the foaming extent increased as the sulfate content in the batch increased. The results of the present study suggest that foaming can be reduced by using limestone over quicklime and by decreasing the sulfate addition to a minimum required for refining.

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1.0 Introduction

Glass foams generated in glass-melting furnaces reduce energy efficiency and can lead to poor glass quality (Hrma and Kim 1994; Kappel et al. 1987; Kim and Hrma 1991 and 1992; Laimböck 1998; Fedorov and Pilon, 2002). Foaming of E-glass refined with sulfate is especially severe when processed with oxy-fuel firing (Laimböck 1998). In a previous study (Kim et al. 2004) performed in FY 2003, the effect of the furnace atmosphere on E-glass foaming was investigated with the specific goal to understand the impact of increased water content on foaming in oxy-fired furnaces. It was shown that humidity in the furnace atmosphere destabilizes foam, while other gases have little effect on foam stability. It was suggested that the higher foaming in oxy-fired furnace compared to air-fired is caused by the effect of water on early sulfate decomposition, promoting more efficient refining gas generation from sulfate, which is known as “dilution effect.”

The present FY05^(a) study extends the previous study and focuses on the effect of glass batch chemical composition on E-glass foaming. It includes foam tests with previous (FY03) batch to investigate the effect of heating rate on foaming and to verify the previously observed effect of atmospheric humidity at early stages of melting on foaming. Different batch compositions were tested in the present study in order to (1) investigate the effect of changing the source of CaO, one of the main E-glass components, and (2) to examine the effect of decreasing the refining agent addition (Na_2SO_4) and replacing it by NaNO_3 used as an oxidation agent to adjust the redox of glass and/or CeO_2 used as an alternative refining agent.

(a) This project was funded at the end of FY 2004, and the work was performed during FY 2005. The batches tested in this study will be designated as FY05 batches to distinguish them from those used in a previous study (Kim et al. 2004) performed in FY 2003.

2.0 Experimental

This section describes the experimental procedures and glass batches used for studying E-glass foaming.

2.1 Foaming Experiments

The experimental set-up and methods used were described in the previous study (Kim et al. 2004). Briefly, a sample of glass batch placed in a silica-glass cylindrical crucible was heat-treated in the box furnace, shown in Figure 2.1, which was equipped with a silica-glass window in the front door. The sample height-to-width ratio was recorded by a video camera with a long-focus lens. The sample height was determined from the known diameter of the cylindrical crucible. The furnace had a rear recess to provide a darker background for a better contrast at high temperatures.

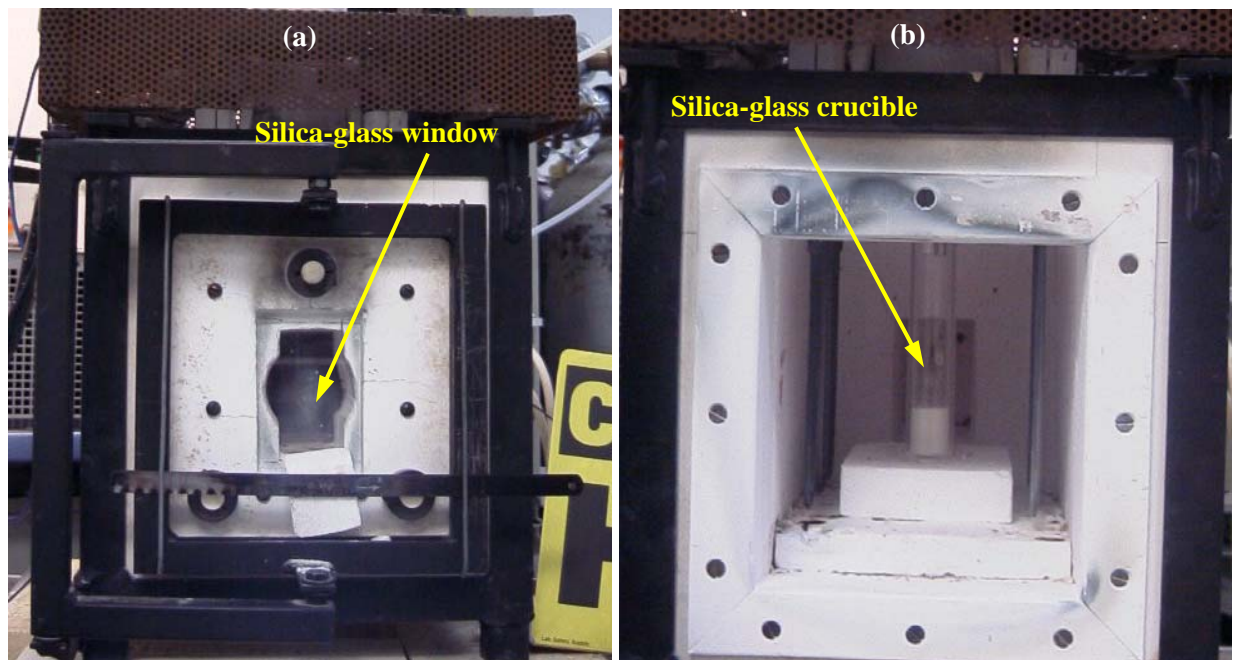


Figure 2.1. The Door (a) and the Interior (b) of the Test Furnace with a Silica-Glass Crucible

For experiments conducted under ambient atmosphere, batches were placed in cylindrical crucibles of 2 cm inner diameter and 10 cm high, heated at 5, 10 and 15°C/min from 300°C to 1500°C, and kept at 1500°C until the foam collapsed. On the other hand, experiments performed under controlled atmosphere were conducted using cylindrical silica-glass crucibles of 2.0 cm inner diameter and 30 cm high. Samples were ramp-heated from 300°C to 1500°C at 5 °C/min.

Figure 2.2 shows a schematic of the experimental set-up used to control the atmosphere above the sample surface. The batch was initially heated under ambient atmosphere, and gas, such as air or carbon dioxide, was introduced into the crucible when the temperature reached 300 or 1250°C. The atmosphere gases were introduced at 1250°C to minimize the effect of atmosphere on glass melting reactions and thus on foaming so that the effect of atmosphere on foam stability can be investigated (Kim et al. 2004). Humidity was controlled by bubbling compressed gas through water held in a flask kept at a constant

temperature in a thermostat water bath. The path of the gas from the flask to the crucible was heated via insulated resistive heating coil wrapped around the gas tube to prevent condensation of water in the gas inlet system. The tip of the gas inlet tube was positioned well above the melt surface to minimize its effect on the temperature inside the crucible. For the same reason, the heating coil was turned on in all tests regardless of humidity in the gas mix.

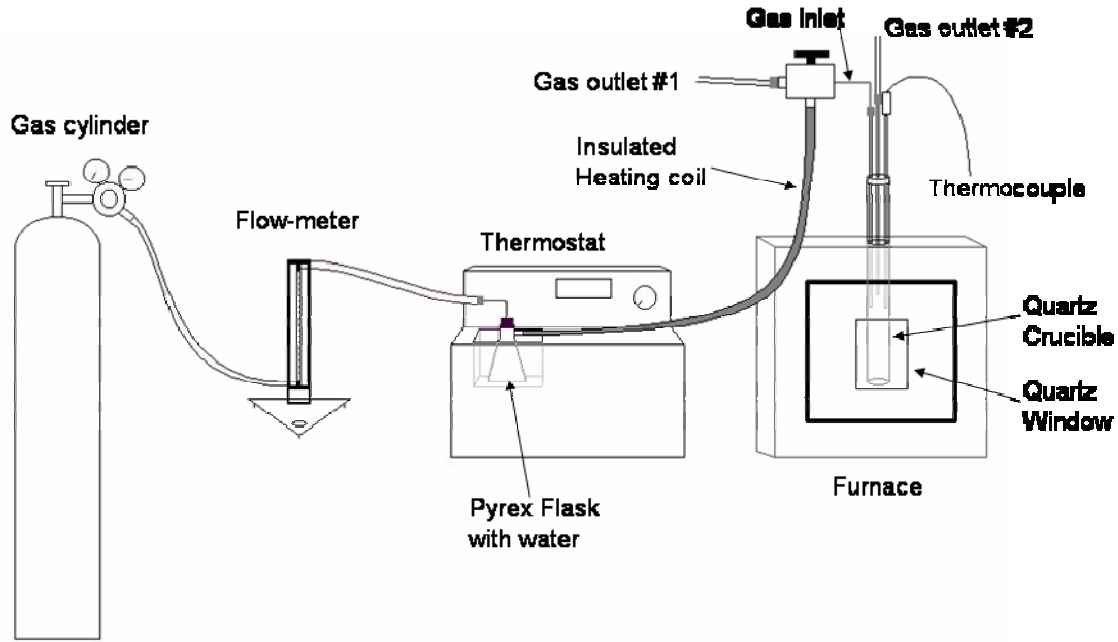


Figure 2.2. Schematic of Experimental Set-up for Transient Foam Study Using Controlled Atmosphere

The gas flow rate was set to $40 \text{ cm}^3/\text{min}$ for most tests. This rate was deemed low enough to avoid mechanical agitation of the foam and a decrease of the temperature above the melt while maintaining a constant atmosphere composition. At this flow rate, the gas content in the crucible would be renewed roughly every 2 min. The volumetric flow rate of gas was measured before the gases were humidified; thus, the actual flow rate was higher for atmospheres containing H_2O .

2.2 E-Glass Batches

To test the effect of the rate of heating on E-glass foaming and to confirm the effect of humidity introduced at early stages of melting, several experiments performed in the previous study (Kim et al. 2004) were repeated in the present study using the same E-glass batch (FY03 batch) that was received from PPG and contained all the raw materials in prescribed proportions except for Na_2SO_4 . Batches were mixed with 0.14 wt% Na_2SO_4 , which results in 0.17 wt% SO_3 in glass, including the sulfate introduced as impurity from other raw materials (roughly half of the total sulfate came from Na_2SO_4). All the tests with FY03 batches were done with 4 g of batch.

Table 2.1 summarizes the current FY05 batches that were also supplied from PPG premixed. The FY05 batches were formulated aimed at (1) investigating the effect of changing the source of CaO (GPlus05B

and C) and (2) examining the effect of decreasing the refining agent (Na_2SO_4) replaced by NaNO_3 and/or CeO_2 (GPlus05D, E, and F). The NaNO_3 is added to adjust the redox of glass and CeO_2 is used as an alternative refining agent. The sulfate addition was higher in FY05 baseline batch, corresponding to 0.25 wt% SO_3 in glass, of which 0.22 wt% SO_3 came from Na_2SO_4 and the rest was introduced as impurity from other raw materials (accordingly, the batches without sulfate addition, GPlus05D, E, and F, had a target SO_3 concentration of 0.03 wt%). The FY03 batch did not contain NaNO_3 or CeO_2 although the sulfate addition was lower than FY05 baseline batch.

The initial tests with FY05 batches, except for GPlus05B and C, were conducted initially with 4 g of batch. This amount was later decreased to 3.5 g to keep foaming within the observable range of the experimental setup. The size of GPlus05B and C batches was adjusted to produce the same mass of glass as the baseline; the melt-to-batch mass ratios are given in Table 2.1.

Table 2.1. FY05 Batches

Batch ID	Description	Melt-to-Batch Mass Ratio
GPlus05A	Baseline	0.914
GPlus05B	50% replacement of quicklime by limestone	0.863
GPlus05C	100% replacement of quicklime by limestone	0.801
GPlus05D	100% replacement of Na_2SO_4 by NaNO_3	0.915
GPlus05E	100% replacement of Na_2SO_4 by NaNO_3 with 0.25wt% CeO_2	0.915
GPlus05F	100% replacement of Na_2SO_4 by 0.25wt% CeO_2	0.916

2.3 Sulfate Analyses

To check the hypothesis regarding the reason for the lack of foaming in the test with $\text{CO}_2 + 55\% \text{H}_2\text{O}$ introduced at 300°C and to better understand the dilution effect in E-glass foaming, discussed in our previous study (Kim et al. 2004), selected glasses from foaming experiments were analyzed for sulfate concentration. Two additional experiments were performed with FY03 batch to produce glasses for SO_3 concentration measurement: the batch was heated at $5^\circ\text{C}/\text{min}$ one under ambient atmosphere and the other under $45\% \text{CO}_2 + 55\% \text{H}_2\text{O}$ atmosphere. Both melts were air quenched once the temperature reached 1250°C . Sulfur concentration was determined in the quenched glass samples by inductively coupled plasma-atomic emission spectrometry after digesting the glass with a mixture of concentrated nitric, perchloric, hydrofluoric, and hydrochloric acids.

3.0 Results and Discussion

The foaming test results are given in the form of gas phase-to-liquid phase volume ratio, ψ , defined as

$$\psi = \frac{V_g}{V_m} \quad (3.1)$$

where V_g is the volume of gas in the sample, and V_m is the volume of melt in the sample. Obviously, $V_g = V - V_m$, where V is the total volume of the foam. Since the sample was contained in a vertical cylindrical column of constant cross-sectional area,

$$\psi = \frac{H}{H_m} - 1 \quad (3.2)$$

where H is the sample height, and H_m is the height of the gas free sample. The height H is measured from the video recording whereas H_m is calculated using the formula,

$$H_m = \frac{m_b f_b}{A \rho_m} \quad (3.3)$$

where m_b is the mass of the batch loaded into the crucible, f_b is the melt-to-batch mass ratio, A is the crucible inner cross-section area, and ρ_m is the final melt density.

For the glass in the previous study (Kim et al. 2004), $f_b = 0.899$, $\rho_m = 2.45$ g/mL (estimated at 1350°C), $A = \pi r_c^2$, where $r_c = 10$ mm is the crucible inner radius, and $m_b = 4.00$ g for all experiments. Hence,

$$H_m = 4.67 \text{ mm} \quad (3.4)$$

However, the present study used the batches with various f_b and m_b . In the previous study (Kim et al. 2004) the inner radius r_c was assumed to be a constant at 10 mm for all the crucibles, whereas the r_c was measured for each crucible in the present study. The values of H_m varied between 4.53 and 4.78 mm.

3.1 Tests with FY03 Batches

Six tests were conducted in the present study using the FY03 batch; five of which were the duplicates of the FY03 tests (Kim et al. 2004). The six tests with the FY03 batch aimed at:

- Investigating the effect of heating rate on foaming. Three tests were conducted under ambient atmosphere heated at 5, 10, and 15 °C/min and kept at 1500°C for 30 min (the tests at 5 and 10 °C/min repeated FY03 tests).
- Verifying the previously observed effect of atmospheric humidity at early stages of melting on foaming. Two tests were conducted under controlled atmospheres with the gas introduced at 1250°C, one under dry air and the other under CO₂ + 55% H₂O (re-runs of Tests 1 and 8 reported in

Kim et al. 2004). One test was conducted under CO₂ + 55% H₂O atmosphere with the gas introduced at 300°C (re-run of Test 13 reported in Kim et al. 2004). In all cases, the rate of heating was 5°C/min.

Figure 3.1 compares the FY03 results with the results from the FY05 study. For each plot, “FY03 result” is as reported in Kim et al. 2004, “FY03 Test Re-evaluated in FY05” is the result of the re-evaluation using the video recordings from FY03 study, and the “FY05 result” is the result of FY05 tests performed with the same FY03 batch. Surprisingly, the extent of foaming was substantially lower in the current experiments than in those reported by Kim et al. (2004). Comparable results were obtained only in the test under CO₂ + 55% H₂O atmosphere with the gas introduced at 300°C that did not produce foam.

Several causes were considered to explain the consistently observed lower level of foaming in repeated experiments. Batching error (addition of Na₂SO₄ to the premixed batch of all other raw material) was deemed unlikely after reviewing the test records. The re-evaluation of Kim et al. (2004) test data to check whether the difference was caused by the difference in the measurement method revealed a noticeable difference in calculating the ψ value caused by the difference in obtaining r_c values. It was assumed in Kim et al. (2004) that $r_c = 10$ mm. Figure 3.1 shows that with corrected data, based on estimated r_c values (not measured in previous tests in FY03), the difference between previous and present results is decreased, but does not disappear. Another possible explanation is the effect of the lab atmosphere humidity. Indeed, the humidity during the early stage of melting below 1250°C has a strong effect on the sulfate decomposition and foaming (see Section 3.2). The previous testing was conducted in July, 2003, the present testing in November, 2004. Figure 3.2 compares the absolute humidity over 30 days in each month. The absolute humidity, ω , was obtained using the equation

$$\omega = \frac{0.622\phi P_g}{P - \phi P_g} \quad (3.5)$$

where P_g is the saturation pressure of water at the average temperature, P is the atmospheric pressure, and ϕ is the relative humidity which was obtained from internet^(a). Although there were a few spikes when the humidity during November was higher than that of July, the overall difference was only 0.002 kg H₂O/kg air in monthly averages. Thus, it is unlikely that the difference in foaming was caused by the difference in air humidity. There is a possibility that the change of batch humidity with time during storage has an effect, which was not verified in the present study. Because of this difference between FY03 and FY05 data with the same batch, it was not attempted to consolidate the results of FY03 and FY05 tests for general discussion.

Though the consistent difference between the previous and present data remains unclear, both studies show the same trend that glass foaming increases with increasing rate of heating, as discussed below, and agree that no foam is produced when CO₂ + 55% H₂O atmosphere is introduced at 300°C (Figure 3.1e).

^(a) <http://www.wunderground.com/>.

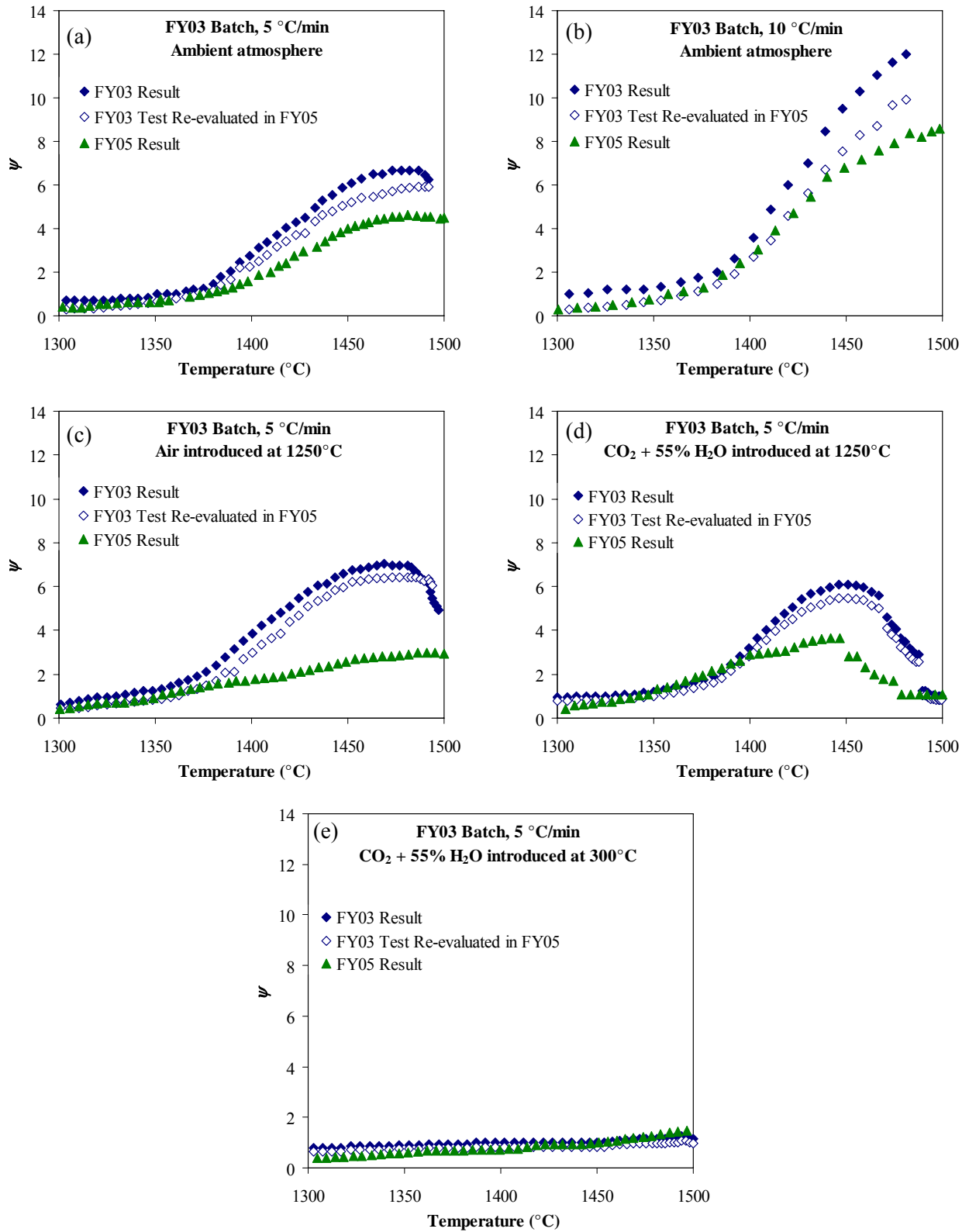


Figure 3.1. Comparison of FY03 Results with FY05 Results Repeated in This Study

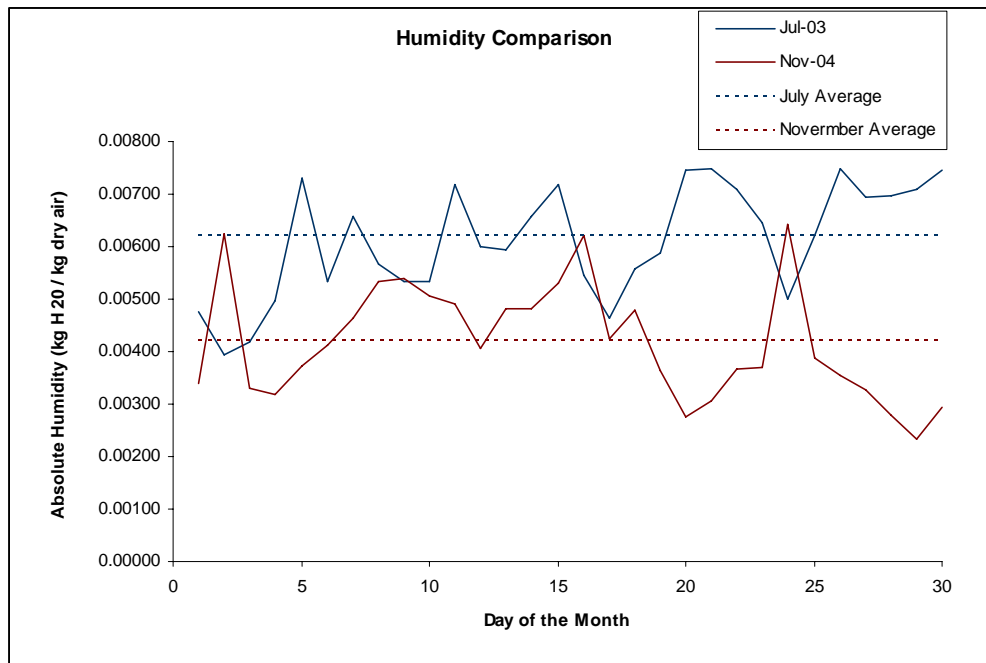


Figure 3.2. Humidity during July 2003 and November 2004

Figure 3.3 shows the ψ as a function of temperature for the FY03 batch tested in FY05 at three different heating rates. Figure 3.4 shows the maximum ψ as a function of heating rate. Figure 3.5 shows the data points on the linear portion of the foaming curve used to obtain the $d\psi/dT$ and Figure 3.6 shows the $d\psi/dT$ as a function of heating rate. Both the maximum ψ and $d\psi/dT$ increased nearly linearly with the heating rate.

Figure 3.7 shows the ψ as a function of temperature for the FY03 batch tested in FY03 and FY05 at three different atmospheres: ambient, air introduced at 1250°C, and CO₂ + 55% H₂O introduced at 1250°C. The FY05 results confirm the trend found previously, namely, that the atmosphere had no noticeable effect on the maximum ψ within the experimental uncertainty and CO₂ + 55% H₂O atmosphere introduced at 1250°C caused the foam to collapse earlier. For the tests under ambient and under air introduced at 1250°C, the FY03 results showed distinct peaks at about 1470°C whereas FY05 results did not. The reason for this difference is not clear.

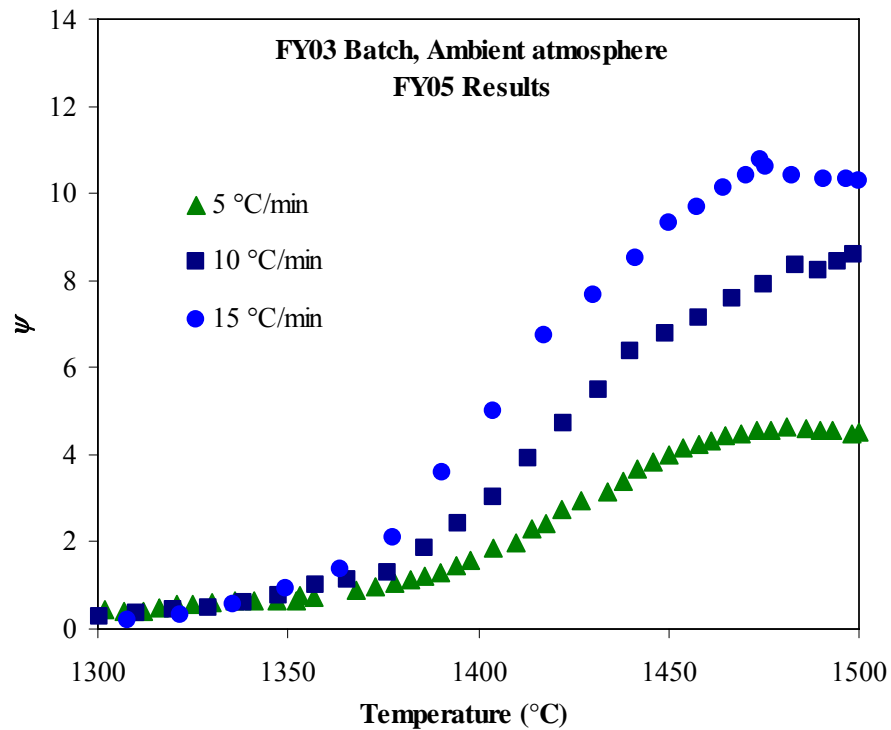


Figure 3.3. ψ Versus Temperature Showing the Effect of Heating Rate on Foaming

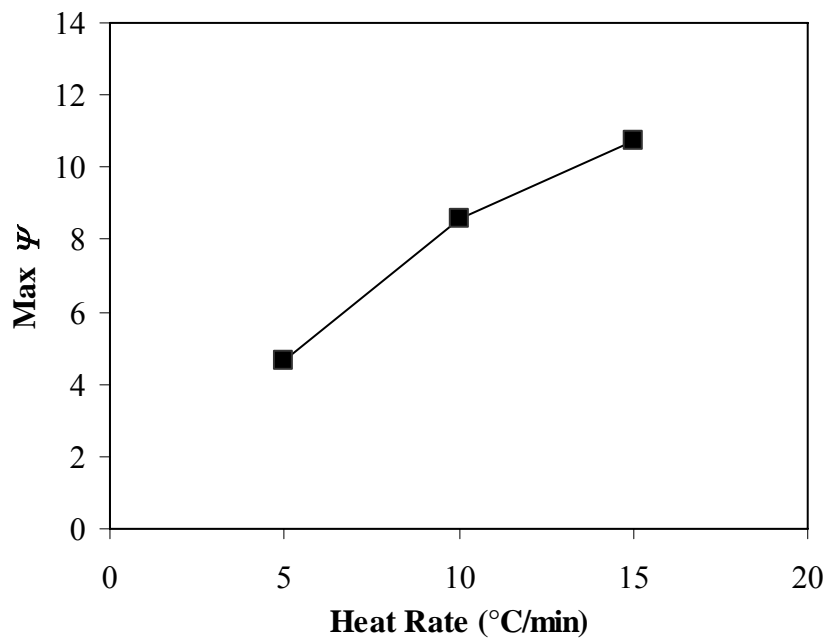


Figure 3.4. Effect of Heating Rate on the Maximum ψ

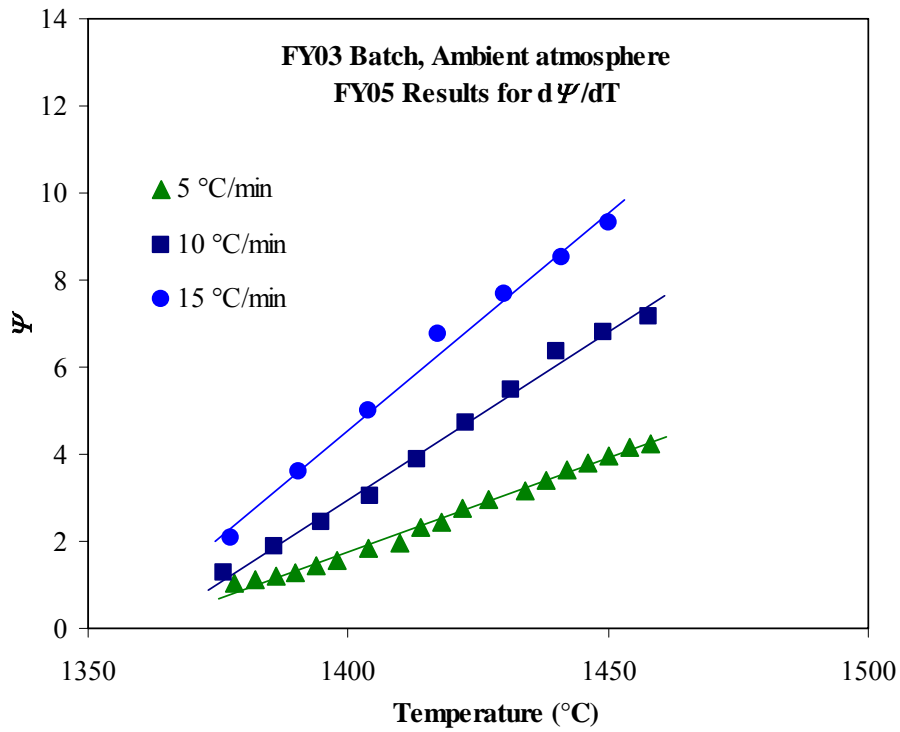


Figure 3.5. ψ Versus Temperature Showing the Data Points Used to Obtain $d\psi/dT$

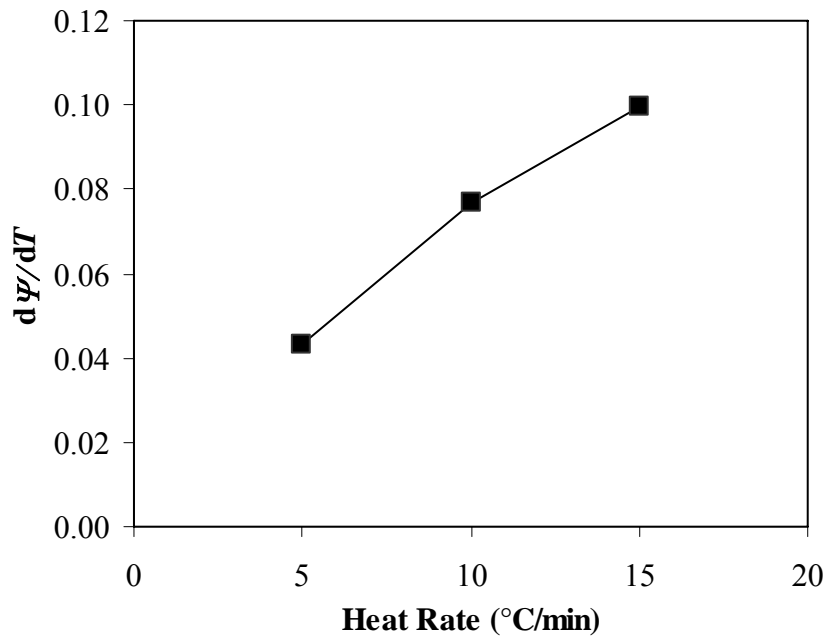


Figure 3.6. $d\psi/dT$ Versus Heating Rate

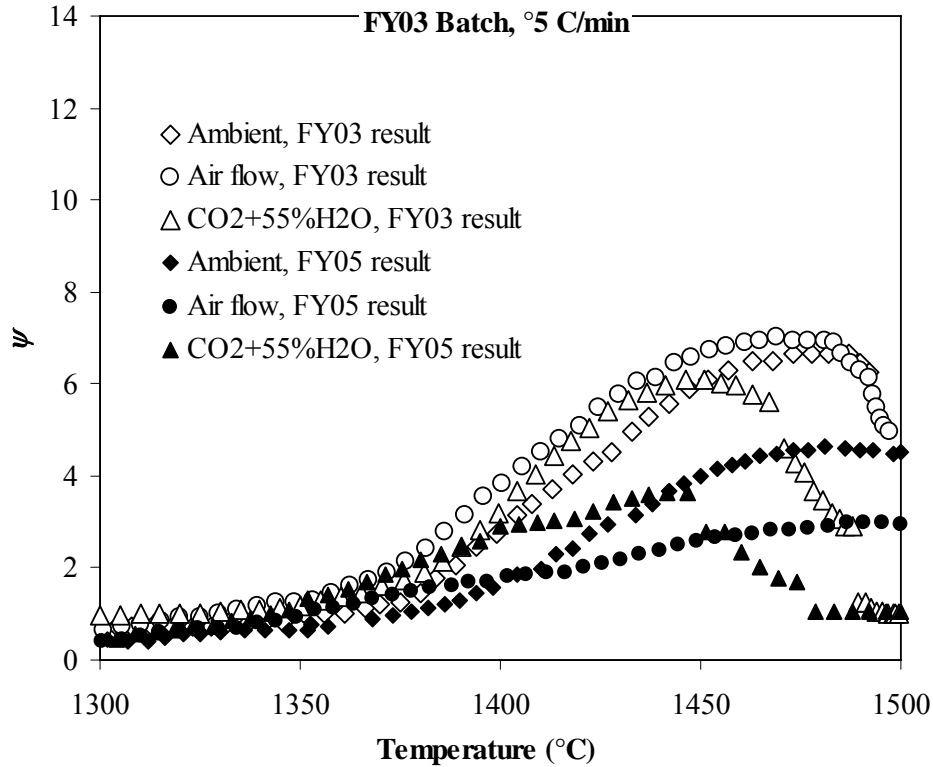


Figure 3.7. ψ Versus Temperature Showing the Effect of Atmosphere on Foaming

3.2 Sulfur Analyses on FY03 Test Glasses

The results of sulfate analyses are summarized in Table 3.1. Figure 3.8 shows a plot of wt% SO_3 versus temperature for three sets of atmospheric conditions. Error bars represent an estimated analytical uncertainty of $\pm 15\%$. During heating from 300°C to 1250°C , the batch heated under $45\% \text{CO}_2 + 55\% \text{H}_2\text{O}$ atmosphere lost $\sim 80\%$ of the sulfate whereas the batch heated under ambient atmosphere had no measurable sulfate loss within analytical uncertainty. This result confirms our reasoning that the lack of foaming in Test 13 (the test under $\text{CO}_2 + 55\% \text{H}_2\text{O}$ atmosphere with the gas introduced at 300°C , see Figure 3.1e) is caused by a loss of sulfate at $T < 1250^\circ\text{C}$ because of higher water content at the early stages of melting (Kim et al. 2004). During heating from 1250 to 1500°C , the batch heated under $45\% \text{CO}_2 + 55\% \text{H}_2\text{O}$ atmosphere had a somewhat larger sulfate loss than the batch heated under air flow. This suggests that introducing the humid gas flow when the temperature reached 1250°C also produced the dilution effect to some extent. However, reduced foaming under humid atmospheres observed in the present study under crucible melting conditions suggests that the effect of reduced surface viscosity caused by dissolved water which decreases foaming outweighed the dilution effect which increases foaming (Kim et al. 2004).

Table 3.1. SO₃ wt% Measured in Glasses after Heating to 1250 or 1500°C under Various Atmospheres

FY03 Test Number	300 - 1250 °C	1250 - 1500 °C	SO ₃ wt%
1	Ambient	Air flow	0.083
8	Ambient	CO ₂ + 55% H ₂ O	0.050
13	CO ₂ + 55% H ₂ O	CO ₂ + 55% H ₂ O	0.032
1 (or 8) modified	Ambient	N/A	0.187
13 modified	CO ₂ + 55% H ₂ O	N/A	0.035

Test # refers to the FY03 test matrix in Kim et al. 2004.
N/A: not applicable; heating was stopped at 1250°C.

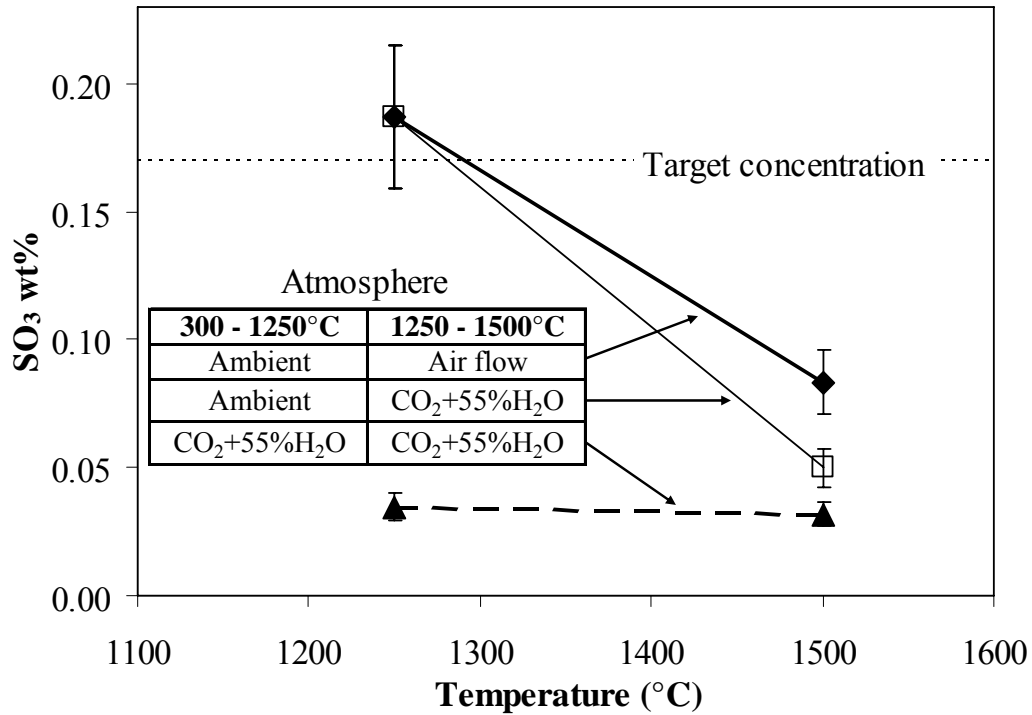


Figure 3.8. SO₃ wt% in Final Glass Versus Temperature (The trend lines are for visual guidance only)

3.3 Tests with FY05 Batches

Table 3.2 shows the test matrix for the foaming tests with FY05 batches. Tests number 13, 15, and 17 to be conducted at a heating rate of 5 °C/min in ambient or controlled atmosphere with GPlus05E and GPlus05F batches were not performed because the corresponding tests at 10 °C/min did not produce foam (in general foam increases as heating rate increases). These are not included in Table 3.2.

Table 3.2. Test Matrix for FY05 Foaming Tests

Test #	Batch ID	Mass of batch (g)	Atmosphere	Heating rate (°C/min)
FY05-1a	Gplus05A	4.000	Ambient	5
FY05-2a	Gplus05A	4.000	Ambient	10
FY05-3a	Gplus05A	4.000	Air flow introduced at 1250°C	5
FY05-1	Gplus05A	3.500	Ambient	5
FY05-2	Gplus05A	3.500	Ambient	10
FY05-3	Gplus05A	3.500	Air flow introduced at 1250°C	5
FY05-4	Gplus05A	3.500	CO ₂ + 55% H ₂ O introduced at 1250°C	5
FY05-5	Gplus05B	3.706	Ambient	5
FY05-6	Gplus05B	3.500	Ambient	10
FY05-7	Gplus05C	3.994	Ambient	5
FY05-8	Gplus05C	3.500	Ambient	10
FY05-9	Gplus05B	3.706	CO ₂ + 55% H ₂ O introduced at 1250°C	5
FY05-10	Gplus05D	3.500	Ambient	5
FY05-11	Gplus05D	3.500	Ambient	10
FY05-12	Gplus05D	3.500	CO ₂ + 55% H ₂ O introduced at 1250°C	5
FY05-14	Gplus05E	3.500	Ambient	10
FY05-16	Gplus05F	3.500	Ambient	10
FY05-20	75% GPlus05A and 25% GPlus05D	3.500	Ambient	5
FY05-21	75% GPlus05A and 25% GPlus05D	3.500	Ambient	10
FY05-22	50% GPlus05A and 50% GPlus05D	3.500	Ambient	5
FY05-23	50% GPlus05A and 50% GPlus05D	3.500	Ambient	10
FY05-24	25% GPlus05A and 75% GPlus05D	3.500	Ambient	5
FY05-25	25% GPlus05A and 75% GPlus05D	3.500	Ambient	10

Test IDs #18 and 19 were omitted accidentally.

3.3.1 Foaming of Baseline Batch

Figure 3.9 shows ψ as a function of temperature for tests conducted with the FY05 baseline batch (GPlus05A) and Figure 3.10 shows the ψ as a function of temperature for tests conducted in this study with FY03 batch. Separate plots were used to evaluate the effect of different batches (FY03 or FY05 batch), batch size, heating rate, and atmosphere on foaming. Figure 3.11 shows that the FY05 batch containing more sulfate produces a substantially higher foam than the FY03 batch. Plots in Figure 3.11, (a) to (c), show that batch size had no noticeable effect on foaming within estimated experimental

uncertainty. Therefore, further FY05 tests were conducted with the 3.5 g batch to keep the maximum foam height within the observable range. Figure 3.12 shows that the increase of heating rate from 5 to 10 °C/min did not produce a difference in foaming of FY05 bathes up to 1450°C with only a small increase within the temperature range from 1450°C up to 1500°C. It is likely that the difference in foaming between 5 and 10 °C/min will continue to increase further if the batches are heated beyond 1500°C. Unlike FY05 batch, the increase of heating rate from 5 to 10 °C/min increased foaming of FY03 batch nearly twice within the temperature range tested up to 1500°C. Figure 3.13 confirms the previous observation (Kim et al. 2004) that there is no noticeable difference in foaming between air flow and CO₂ + 55% H₂O atmosphere, considering the test reproducibility to be within 13% as roughly estimated by Kim et al. (2004). Interestingly, when the FY03 batches were tested in FY05 under the CO₂ + 55% H₂O atmosphere, foam collapsed much earlier than under air flow. The same effect was observed previously in Kim et al. (2004) for the same batch. This early foam collapse under the CO₂ + 55% H₂O atmosphere was not observed in the FY05 batches.

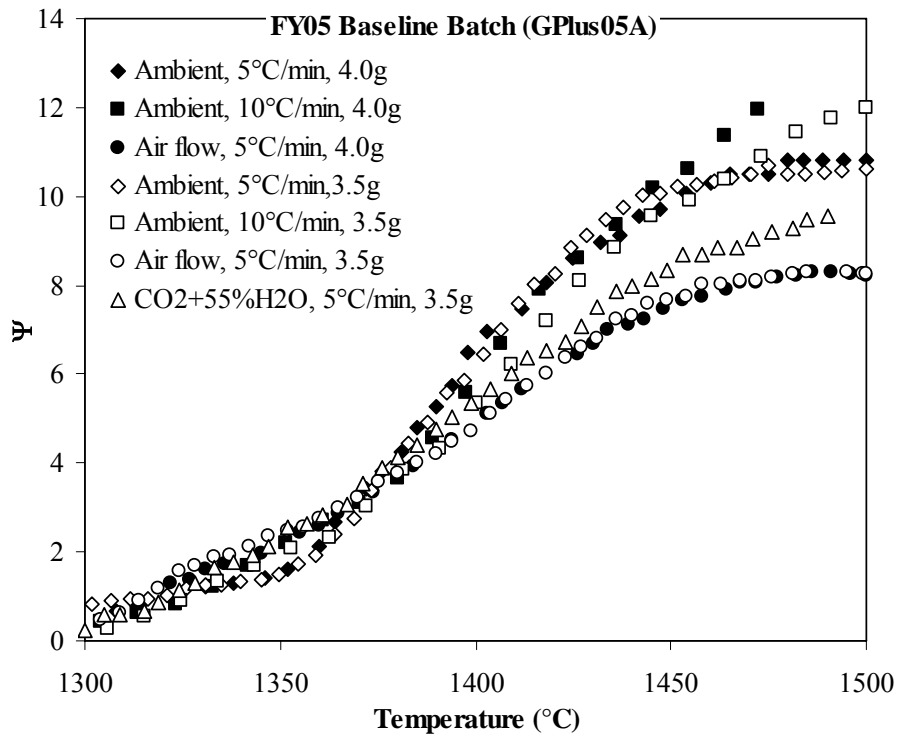


Figure 3.9. ψ Versus Temperature for Tests with Baseline FY05 Batch (GPlus05AS)

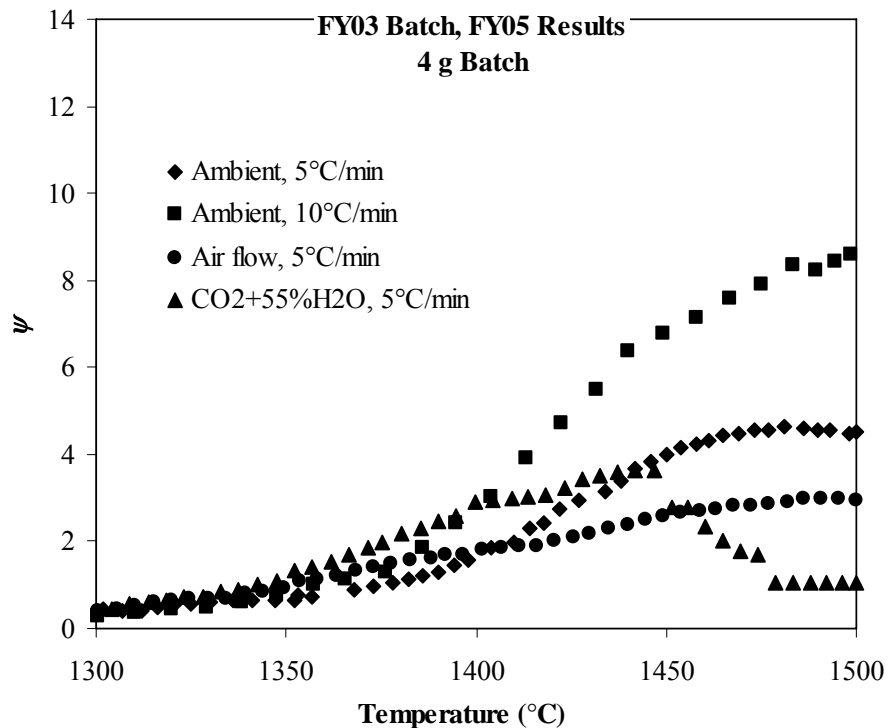
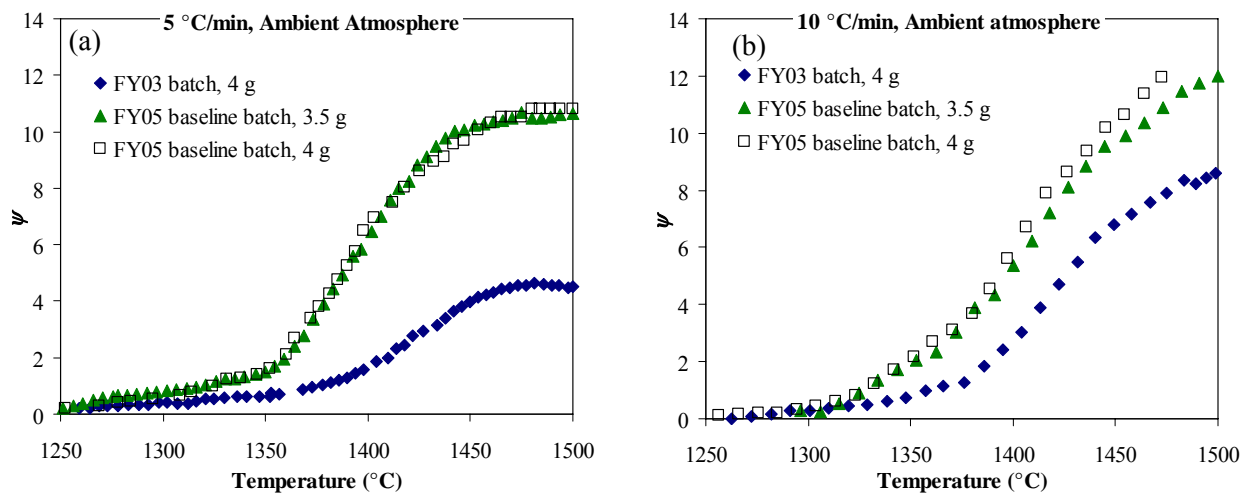


Figure 3.10. ψ Versus Temperature for Tests with the FY03 Batch (Performed in FY05)



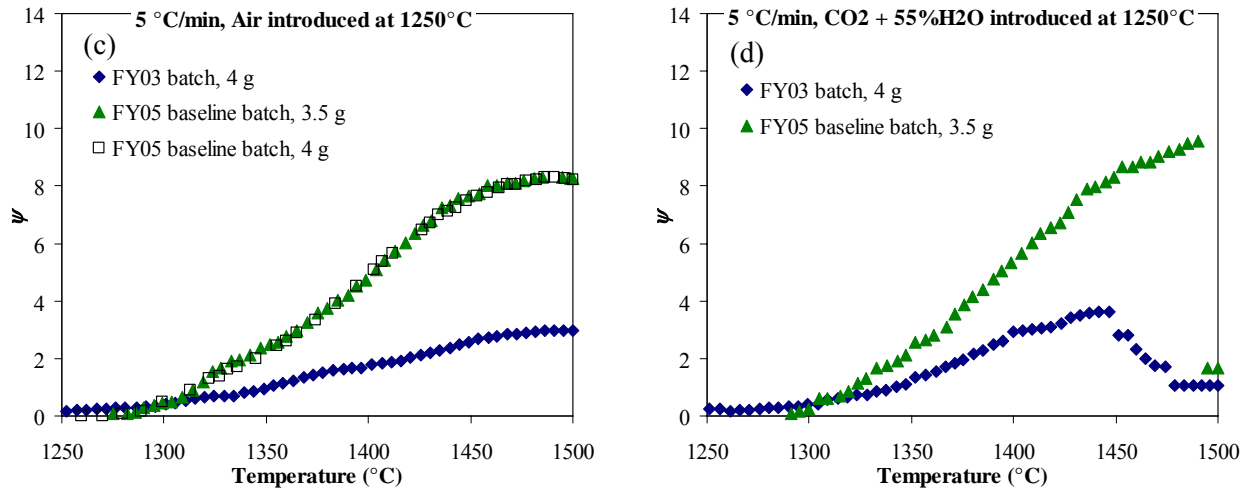


Figure 3.11. Foaming Plots to Compare Foaming in FY03 and FY05 Batches under Various Conditions. (a) Ambient, 5 °C/min; (b) Ambient, 10 °C/min; (c) Air flow introduced at 1250°C, 5 °C/min; and (d) CO₂ + 55% H₂O introduced at 1250°C, 5 °C/min

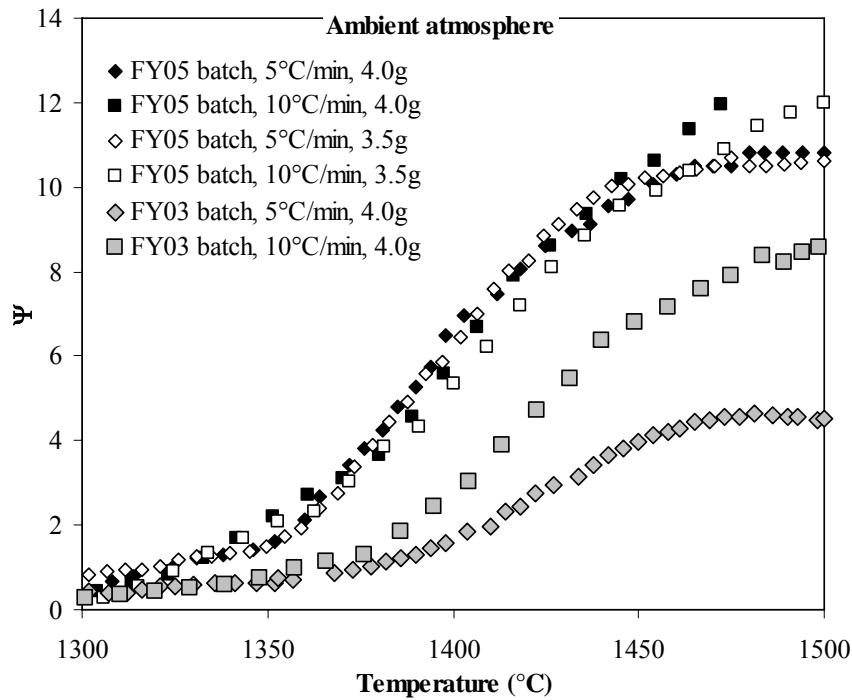


Figure 3.12. ψ Versus Temperature for Tests under Ambient Atmosphere Showing the Different Effect of Heating Rate in FY03 and FY05 Batches

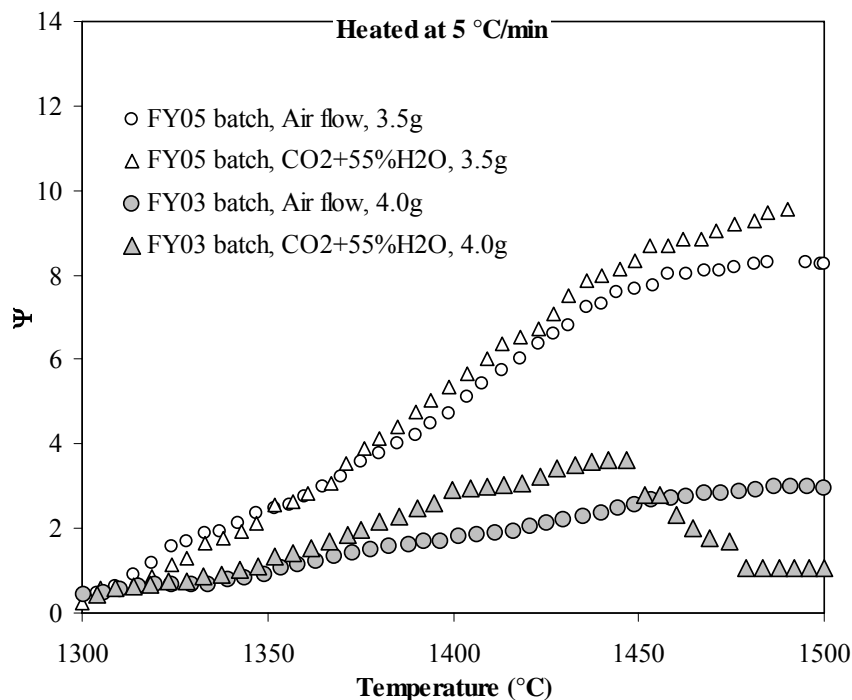


Figure 3.13. ψ Versus Temperature for Tests at 5 °C/min Showing the Effect of Atmosphere in FY03 and FY05 Batches

3.3.2 Replacing Quicklime with Limestone

Figure 3.14 and Figure 3.15 show the effect of replacing quicklime with limestone in the baseline batch. Replacing 50% quicklime with limestone did not have any effect on foaming at both 5 and 10 °C/min heating rates. Replacing 100% quicklime with limestone decreased foaming only at 5 °C/min heating rate, and had no effect at 10 °C/min heating rate until 1500°C, when the test was terminated. Replacing quicklime with limestone shows a tendency to decrease foaming and this effect would probably be manifest even at the 10 °C/min heating rate if the test continued beyond 1500°C. However, more tests would be needed to confirm the effect of replacing quicklime with limestone.

We can reason that the effect of replacing the quicklime with limestone on batch melting reaction will in turn affect the sulfate decomposition. One possible explanation would be that the generation of CO₂ from limestone may increase sulfate loss during early stages of melting. Figure 3.16 compares the baseline batch with and without 50% quicklime replaced with limestone under ambient condition and under CO₂ + 55% H₂O atmosphere. The observed decrease in foaming under CO₂ + 55% H₂O atmosphere compared to under ambient condition, both in the baseline and the batch with 50% quicklime replaced with limestone, is as expected from the previous study on the effect of humidity on foaming.

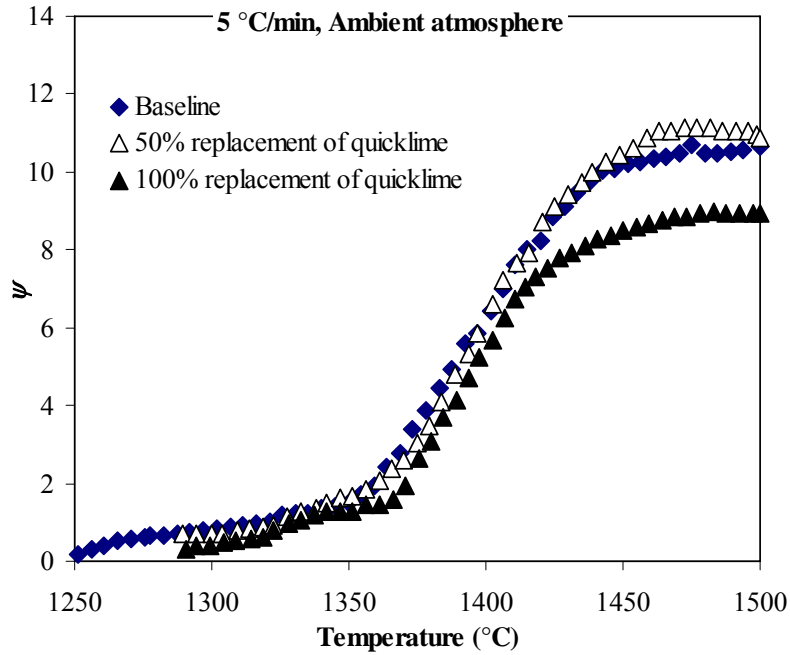


Figure 3.14. ψ Versus Temperature for Tests at 5 °C/min under Ambient Atmosphere Showing the Effect of Replacing Quicklime with Limestone

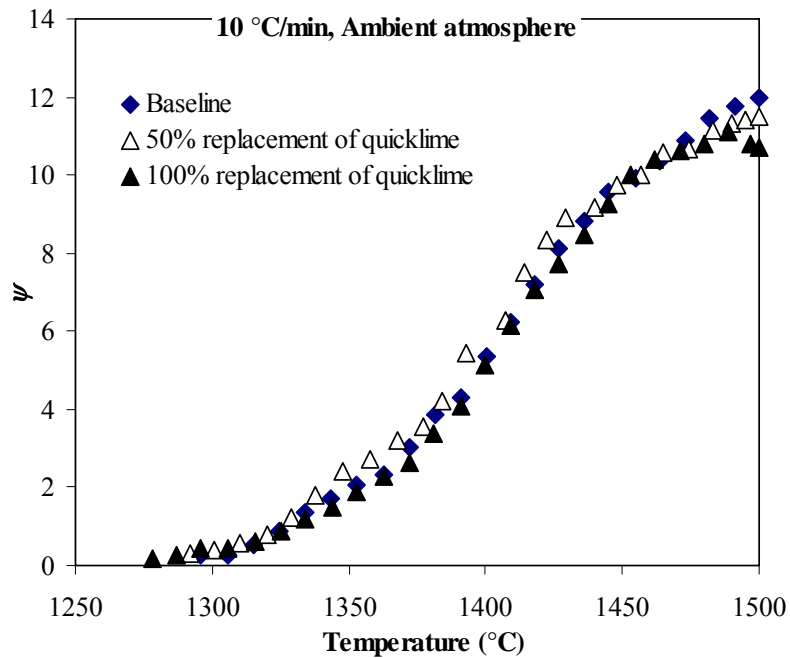


Figure 3.15. ψ Versus Temperature for Tests at 10 °C/min under Ambient Atmosphere Showing the Effect of Replacing Quicklime with Limestone

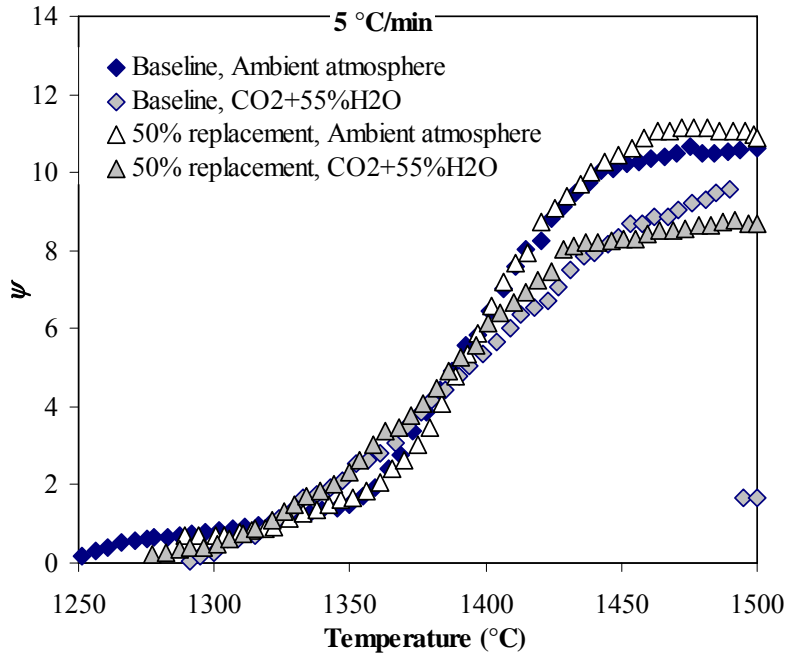


Figure 3.16. ψ Versus Temperature for Baseline and 50% Limestone Batch Heated at 5 °C/min under ambient and CO₂+ 55% H₂O Atmosphere

3.3.3 100% Replacement of Na₂SO₄ with NaNO₃ and/or CeO₂

Figure 3.17 shows that the replacement of 100% Na₂SO₄ with NaNO₃ almost eliminated foaming under both ambient and CO₂ + 55% H₂O atmospheres; ψ increased only very slightly at 5°C/min up to 1500°C, though somewhat more at 10 °C/min, probably due to the sulfate present as impurity in raw materials. It is likely that further increase of temperature beyond 1500°C may show clear increase of foaming at 10 °C/min. Figure 3.18 shows that only very limited foaming occurs in the batches when Na₂SO₄ is fully replaced with NaNO₃, NaNO₃ + CeO₂, and CeO₂ regardless of the replacing components.

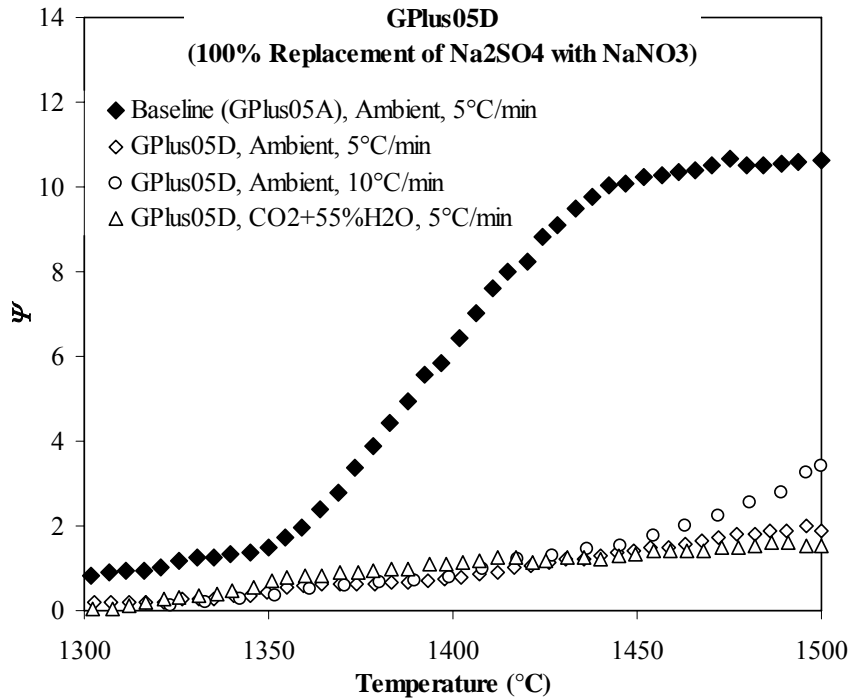


Figure 3.17. ψ Versus Temperature in the Batches with 100% Na_2SO_4 Replaced with NaNO_3 Compared with the Baseline Batch

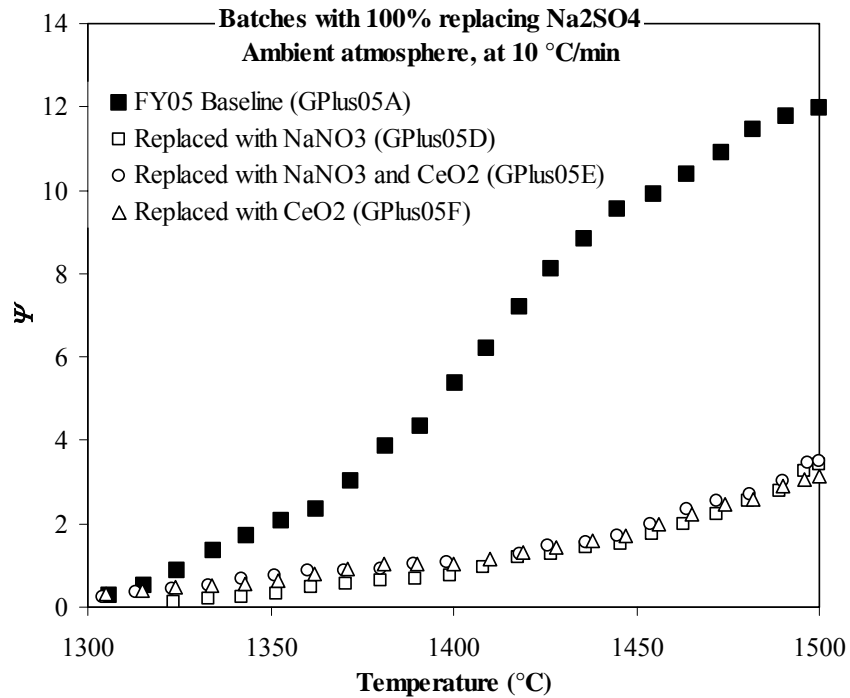


Figure 3.18. ψ Versus Temperature in the Batches with 100% Na_2SO_4 Replaced with NaNO_3 , NaNO_3 and CeO_2 , and CeO_2 Compared with the Baseline Batch

3.3.4 Gradual Replacement of Na₂SO₄ with NaNO₃

To investigate the effect of gradually replacing Na₂SO₄ with NaNO₃, new batches were made up using GPlus05A and GPlus05D batches: 25% replacement (75% GPlus05A and 25% GPlus05D), 50% replacement (50% GPlus05A and 50% GPlus05D), and 75% replacement (25% GPlus05A and 75% GPlus05D). Each of these variations was made in 16-g batches by mixing in an agate mill for 4 minutes. These batches were tested under ambient atmosphere at 5 and 10 °C/min.

Figure 3.19 and Figure 3.20 show the decreasing trend of foaming with progressing replacement of Na₂SO₄ by NaNO₃ over the temperature range explored. Figure 3.21 shows five sets of plots showing the effect of the heating rate in each batch with varied fractions of Na₂NO₃ replacement. Interestingly, the difference in maximum ψ between 5 and 10 °C/min heating rate increases from the baseline to 50% replacement and then decreases as the replacement reaches 100%.

Figure 3.22 summarizes the effect of percent replacement of Na₂SO₄ with NaNO₃ on the maximum ψ that is used as key measure of foaming extent. The maximum ψ decreased as the replacement of Na₂SO₄ with NaNO₃ increased. The two horizontal lines included in Figure 3.22 represent the maximum ψ for the FY03 batches tested in the present study. Another measure of foaming extent is the melt expansion rate, $d\psi/dT$. Figure 3.23 shows the data points on the linear portion of the foaming curve used to obtain the slope $d\psi/dT$ and Figure 3.24 summarizes the effect of percent replacement of Na₂SO₄ with NaNO₃ on $d\psi/dT$. The two horizontal lines also represent the maximum $d\psi/dT$ for the FY03 batches tested in the present study. The $d\psi/dT$ for the tests at 5 °C/min decreased almost linearly with the percent replacement of Na₂SO₄, similar to maximum ψ , whereas the slope $d\psi/dT$ for the tests at 10 °C/min did not change up to 50% replacement and then decreased.

For the tests at 10 °C/min, the change of $d\psi/dT$ with percent replacement of Na₂SO₄ clearly shows that there is a slope transition at a 50% replacement (Figure 3.24) although it is not so obvious for the change of maximum ψ (Figure 3.22). It is also acceptable for the maximum ψ versus percent replacement of Na₂SO₄ to just draw a straight line with larger scatter. More tests would be needed to confirm the actual trend. It was assumed in Figure 3.22 that there was a slope transition at a 50% replacement similar to the $d\psi/dT$ data. The results in Figure 3.24 suggest that there is a foam destabilizing effect in a batch with high sulfate content. The similar effect of high sulfate content on the maximum foam height (equivalent to ψ of this study) was observed in previous foam studies with a soda-lime glass (Kim and Hrma 1992; Kokubu et al. 1977). When sulfate content exceeds a certain level, some sulfate may remain undissolved at a temperature of foam generation and form a separated salt phase that may suppress foam. This foam suppressing effect is likely more pronounced for the tests with higher heating rate, which provides a less time for sulfate to dissolve.

The two tests with FY03 batch resulted in the maximum ψ and $d\psi/dT$ in the range that would result from FY05 batches with roughly 50% to 70% replacement of Na₂SO₄ with NaNO₃ (see Figure 3.22 and Figure 3.24). Table 3.3 summarizes the target SO₃ concentrations in the FY03 batch and FY05 batches with gradual replacement of Na₂SO₄ with NaNO₃. The FY05 batches that resulted in the similar foaming extent to the FY03 batch had a target SO₃ concentration of 0.15 to 0.10 wt%, which is lower than that in the FY03 batch, 0.17 wt%. However, it is noted that the SO₃ from Na₂SO₄ was similar, i.e., FY03 batch

had 0.085 wt% SO₃ from Na₂SO₄ while FY05 batches that resulted in the similar foaming extent to the FY03 batch had 0.12 to 0.07 wt%. Considering that there are some differences between FY03 and FY05 batches in the glass composition and batch formula^a and source of SO₃ (from Na₂SO₄ or impurity), the results from thy FY03 batch matches reasonably well with those from FY05 batches.

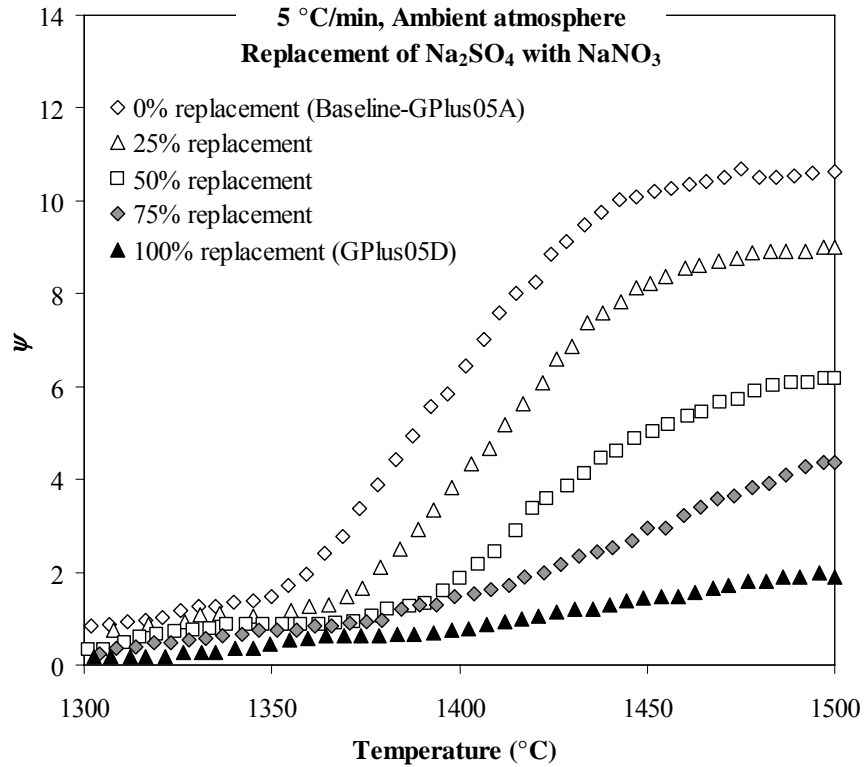


Figure 3.19. ψ Versus Temperature in the Batches with 0 to 100% Na₂SO₄ Replaced with NaNO₃, Tested Under Ambient Atmosphere at 5 °C/min

^a Not reported because it is confidential information.

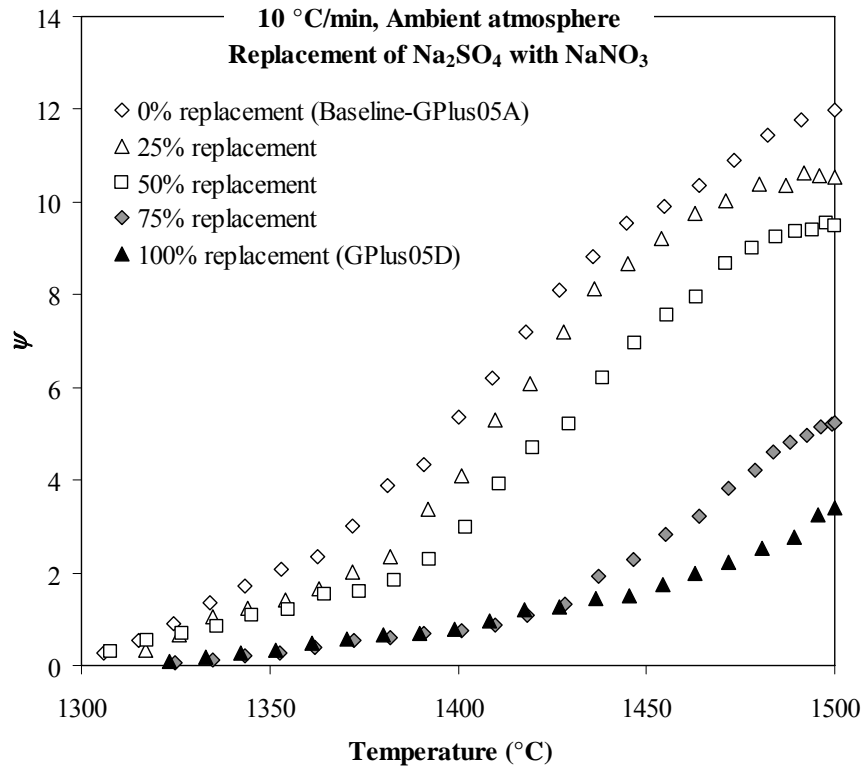
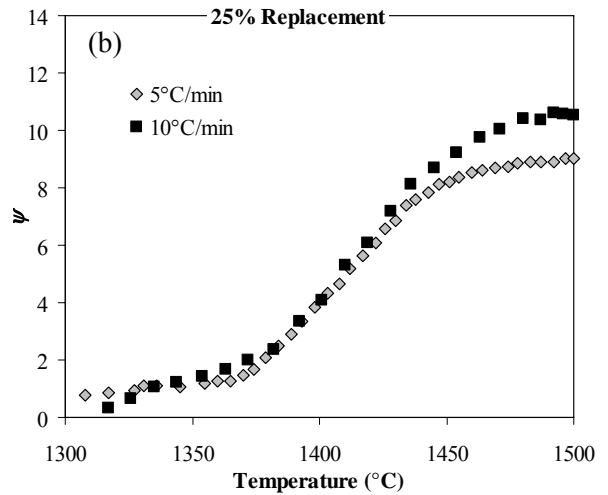
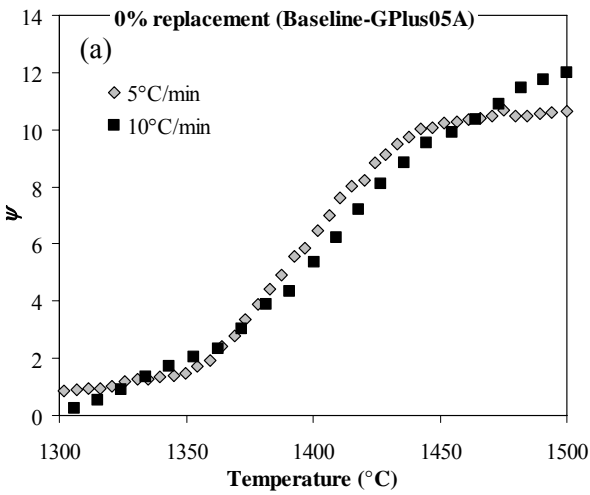


Figure 3.20. ψ Versus Temperature in the Batches with 0 to 100% Na_2SO_4 Replaced with NaNO_3 , Tested under Ambient Atmosphere at $10^\circ\text{C}/\text{min}$



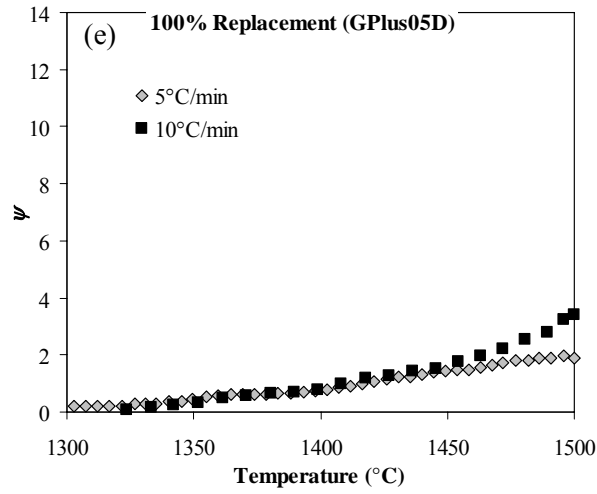
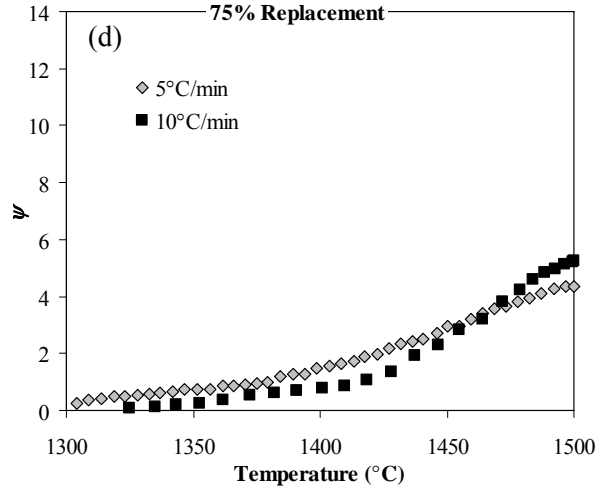
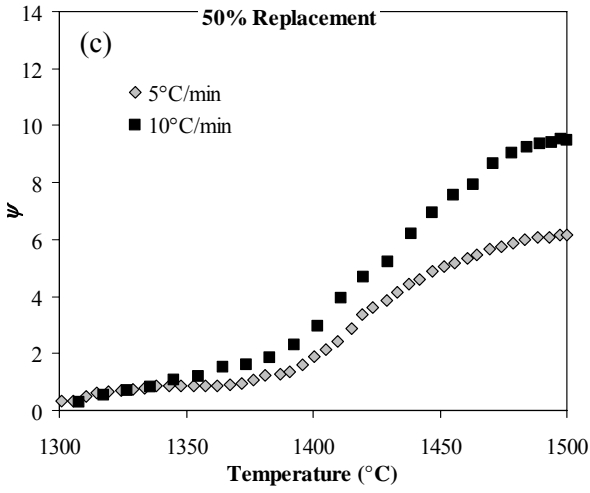


Figure 3.21. ψ Versus Temperature in the Batches with 0 to 100% Na_2SO_4 Replaced with NaNO_3 Showing the Effect of Heating Rate

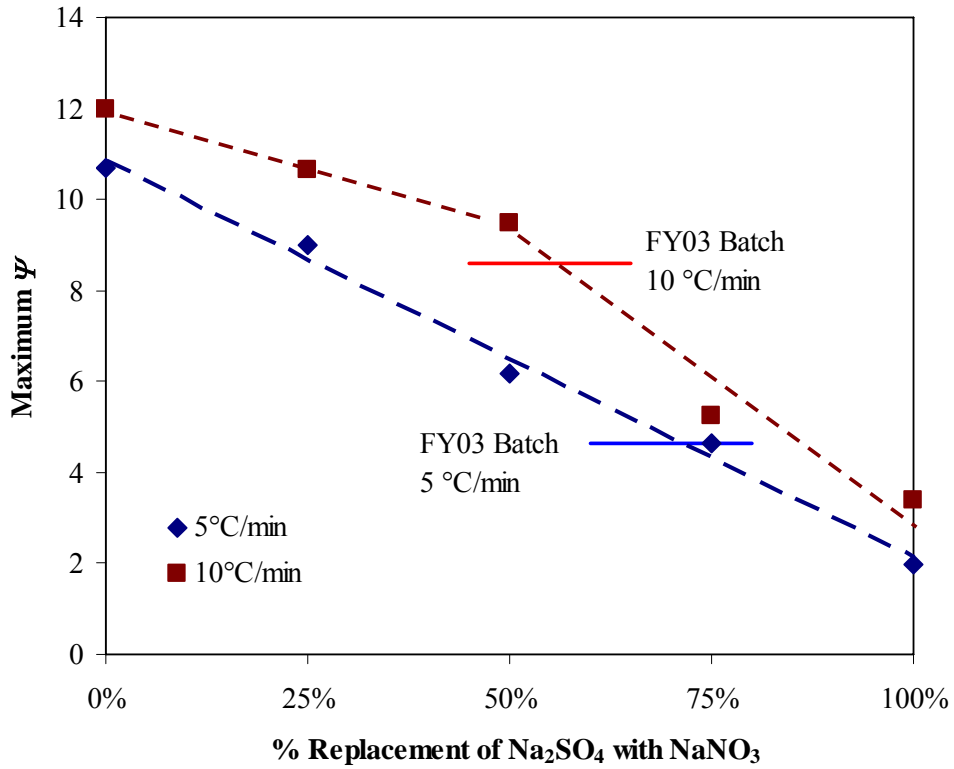


Figure 3.22. Maximum ψ Versus Percent Replacement of Na_2SO_4 with NaNO_3

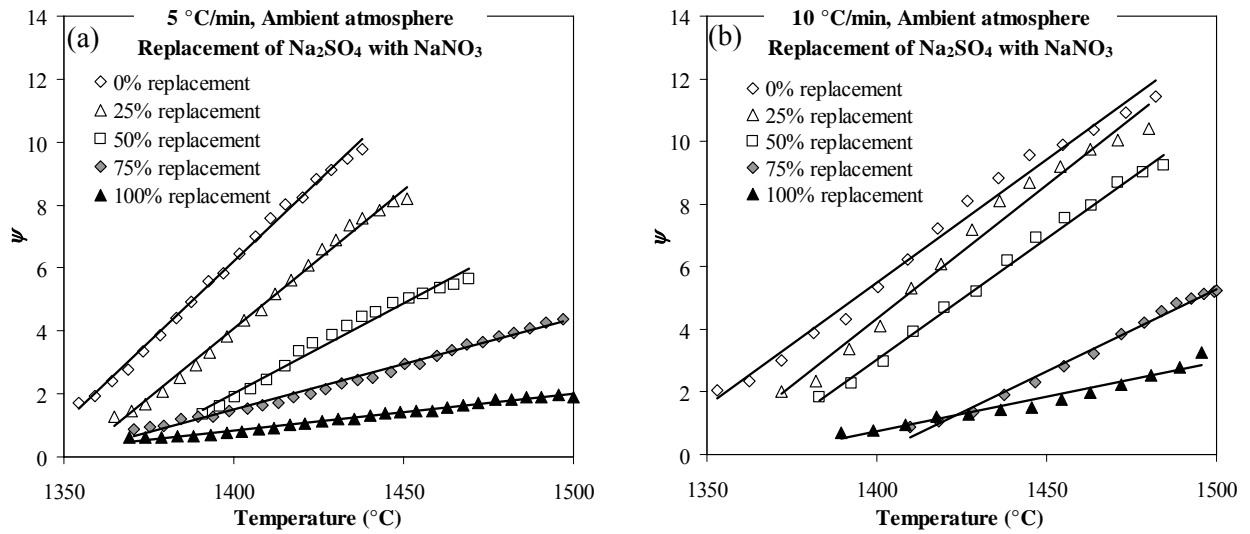


Figure 3.23. ψ Versus Temperature Showing the Data Points Used to Obtain $d\psi/dT$ for the Tests at (a) $5\text{ }^\circ\text{C/min}$ and (b) $10\text{ }^\circ\text{C/min}$

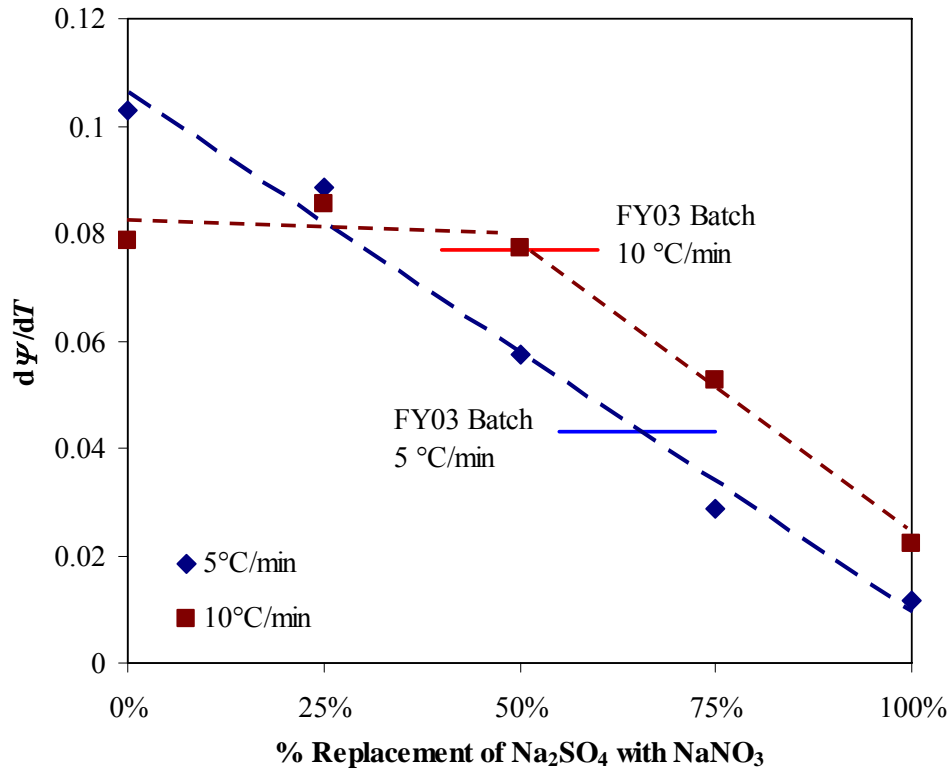


Figure 3.24. $d\psi/dT$ Versus Percent Replacement of Na_2SO_4 with NaNO_3

Table 3.3. Target SO_3 Concentration in FY03 and FY05 Batches

Replacement of Na_2SO_4	FY05 Batch					FY03 Batch
	0%	25%	50%	75%	100%	
Total target SO_3 wt%	0.25	0.22	0.15	0.09	0.03	0.17
SO_3 wt% from Na_2SO_4	0.22	0.19	0.12	0.06	0.00	0.085

4.0 Conclusions

Reruns of foaming tests with the E-glass batch used in a previous study (Kim et al. 2004) and designated as FY03 batch, resulted in the same trend as observed in a previous study: the foaming extent, measured by maximum ψ and $d\psi/dT$, increased nearly linearly with the heating rate and no foam was produced when $\text{CO}_2 + 55\% \text{H}_2\text{O}$ atmosphere was introduced at 300°C . The results of sulfate analyses retained in the glass after foaming tests confirmed that the lack of foaming in the test with $\text{CO}_2 + 55\% \text{H}_2\text{O}$ atmosphere introduced at 300°C was caused by a loss of sulfate at $T < 1250^\circ\text{C}$ because of higher water content at the early stages of melting.

The tests with FY05 baseline batch containing more sulfate than the FY03 batch produced substantially higher foam and did not show noticeable effect of the heating rate on the foaming extent. Replacing quicklime with limestone showed a tendency to decrease foaming, possibly caused by increased sulfate loss during early stages of melting in the batch with limestone. The batches where Na_2SO_4 was replaced with NaNO_3 , $\text{NaNO}_3 + \text{CeO}_2$, or CeO_2 , produced only very limited foaming regardless of the replacing components. As expected, the foaming extent decreased as the replacement of sulfate by NaNO_3 increased and thus the sulfate content in the batch decreased. The results of the present study with FY05 suggest that foaming can be reduced by using limestone over quicklime and by decreasing the sulfate addition to a minimum required for refining.

5.0 References

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