THE EFFECT OF ATMOSPHERE COMPOSITION ON E-GLASS FOAMING

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ABSTRACT

The behavior of foams generated in a crucible was investigated to study the effect of furnace atmosphere on E-glass foaming. The study specifically focused on the atmosphere water content in order to understand the effect of oxy-firing. A quartz-crucible furnace equipped with video recording was used to observe the behavior and to evaluate stability of foams generated from the PPG E-glass under various atmospheres. Preliminary results indicate 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 (known as "dilution effect"), not by the effect of humidity on foam lamella stability. The possible explanation for the difference between soda-lime glass and E-glass in the end result of the dilution effect on glass refining and foaming is discussed.

INTRODUCTION

Glass foams generated in glass-melting furnaces reduce energy efficiency and can lead to poor glass quality [1,2]. Foaming of E-glass refined with sulfate is especially severe when processed with oxy-fuel firing [1]. The objective of this study is to assess the effects of the furnace atmosphere, mainly its water content, on E-glass foaming. The ultimate goal is to identify conditions for foam reduction during E-glass processing.

Most of the studies of foaming in silicate melts focused on soda-silicate or soda-lime-silicate melts, or on metallurgical slags. Pilon *et al.* [3] provides thorough reviews of the literature; they also collected data on foaming and correlated the extent of foaming of different high-viscosity liquids with their properties. Unfortunately, little data exist on foaming in E-glass.

Cable *et al.* [4], who studied the foaming of binary silicate melts, observed that foaming temperature was higher in wet atmospheres; also, foam was more stable in pure oxygen, whereas glass did not foam in a pure nitrogen atmosphere. Kappel *et al.* [5] observed that increasing the partial pressure of SO_2 destabilized foam. It has also been observed that foaming increases with the pull rate, the use of recycled, and contaminated cullet of mixed colors [1]. The type of gaseous fuel used to heat the melt and also the luminosity of the flame it produces were reported to affect the foam of iron slags [6].

It is generally believed that severe foaming in oxy-fuel-fired furnaces is caused by a higher partial pressure of water in the furnace atmosphere [1]. However, even for soda-lime glasses and metallurgical slags, the effect of water on foaming is not clearly understood and reported experimental data appear to be contradictory. For example, Cable *et al.* [4] and Laimböck [1] reported that wet atmosphere increased foaming, whereas Kappel *et al.* [5] showed that humidity in the atmosphere destabilized the foam. Water reduces viscosity, thus reducing foam stability by enhancing foam drainage. Water also reduces surface tension [7].[1] However, the effect of surface tension on foam stability is not straightforward depending more on its change with time or its gradient across the foam film thickness.

Laimböck [1] studied the effect of water content in air atmospheres on the foaming of soda-lime glass batch and found that the foam formation started at a lower temperature and the maximum foam volume (and total foam volume) increased as the water content in air increased form 0 to 55%. Laimböck [1] measured the sulfate content in glass before and after foaming and found that the sulfate loss during foaming increased as the water content increased. This increased sulfate loss (lower sulfate retention) at higher water content was responsible for higher foaming. As dissolved water content in glass increases, the partial pressure of H_2O in bubbles also increases, thus diluting the fining gas concentration in bubbles and promoting the transfer of fining gases from the melt into bubbles. In other words, water vapor in bubbles decreases the partial pressure of fining gases, thus increasing the driving force for their transfer from melt and shifting the equilibrium towards a more extensive decomposition of the fining agents. As a result, sulfate begins to decompose at a lower temperature and its decomposition continues to a lower sulfate level retained. This mechanism was mathematically formulated as the “dilution model” [1]. Water in the atmosphere helps the refining action of the sulfate, making it possible to lower the addition of sulfate to obtain an equal refining efficiency compared to dry atmosphere.

Numerous laboratory studies used one of the two methods for foam generation in molten glass: (i) refining gases are generated by increasing temperature or reducing pressure; this creates transient foam that grows and collapses [8,9] and (ii) gas is bubbled into a glass melt at a constant temperature; this produces steady-state foam of constant height [1].

EXPERIMENTS

Four grams of E-glass batch with 0.14 wt% Na_2SO_4 (corresponding to 0.17 wt% SO_3 in glass including the sulfate introduced from other raw materials) was placed in a cylindrical silica-glass crucible with 2 cm inner diameter and 30 cm height. The system was ramp-heated in a high temperature furnace from 300°C to 1500°C at 5 °C/min. These conditions produced an adequate maximum foam height for our experimental setup and 5 °C/min is believed to be close to the typical heating rate of the batch in the glass furnace [10]. The sample height-to-width ratio was recorded by a video camera with a long-focus lens. The sample height was determined from the diameter of the cylindrical crucible. The furnace had a rear recess that was kept at a lower temperature than the crucible area to provide a darker background for a better contrast at high temperatures.

Figure 1 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 gases, such as air or carbon dioxide, were introduced into the crucible when the temperature reached 1250°C. Humidity was controlled by bubbling compressed gas through water held in a flask at a constant temperature. The tube conducting 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

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[1] According to Parikh [7], polar gases such as sulfur dioxide (SO_2), ammonia (NH_3), hydrogen chloride (HCl), and water vapor (H_2O) lower the surface tension, whereas nonpolar gases such as dry air, dry nitrogen, helium and hydrogen have no effect on it. Among the polar gases cited, water has the largest dipole moment and therefore has the strongest effect on the surface tension. Parikh [7] showed that the surface tension decreases with the square root of the partial pressure of water.

the gas inlet system. The tip of the gas inlet tube was placed 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 mixture.

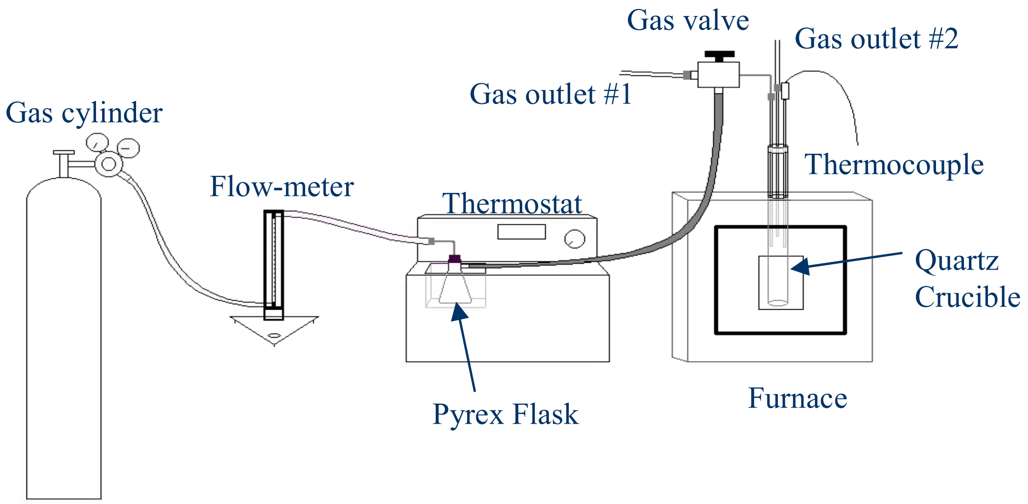


Figure 1. Schematic of experimental setup for transient foam study using controlled atmosphere

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

Table I summarizes the test conditions used in the present study. It is assumed that dry air was composed of 80% N_2 and 20% O_2 and the gases introduced in the flask reached equilibrium H_2O concentration. Although the amount of H_2O in each condition was not measured, it is assumed that the actual water content does not significantly deviate from the calculated value given the slow gas flow rate.

RESULTS

The results are shown in the form of gas phase-to-liquid phase volume ratio, ψ, defined as $\psi = V_g / V_m$ where V_g and V_m are the volume of gas and of melt in the sample, respectively. Obviously, $V_g = V - V_m$, where V is the total sample volume. Hence, if the sample shape is a vertical cylindrical column of a constant cross-section area,

$$\psi = \frac{H}{H_m} - 1 \tag{1}$$

where H is the sample height and H_m is the height of a gas phase-free sample. The height H is measured from the video record while H_m is calculated using the formula

$$H_m = \frac{m_b f_b}{A\rho_m} \tag{2}$$

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 melt density. For the E-glass provided by PPG, Inc., $f_b = 0.899$, $\rho_m = 2.45$ g/cm^3 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 leading to $H_m = 4.67\text{ mm}$.

Table I. Description of tests and calculated gas compositions

Test #	Description	Gas Volume % N_2	O_2	CO_2	H_2O
1	Air	80	20		
2	Air, repeat of #1	80	20		
3	Air, higher flow rate[(a)]	80	20		
4	Air + 20% H_2O	64	16		20
5	Air + 55% H_2O	36	9		55
6	CO_2			100	
7	CO_2 + 20% H_2O			80	20
8	CO_2 + 55% H_2O			45	55
9	90% (CO_2 + 55% H_2O) + 10% O_2		10	40.5	49.5
10	CO_2 + 20% O_2		20	80	
11	CO_2 + 20% N_2	20		80	
12	CO_2 + 80% N_2	80		20	
13	CO_2 + 55% H_2O[(b)]			45	55

(a) The flow rate of 90 cm^3/min instead of 40 cm^3/min used for all other tests.

(b) Gas was introduced from 300°C instead of 1250°C used as for all other tests.

To avoid the time shift between experiments, the time was set to zero when the furnace temperature reached 1300°C. Figure 2 displays ψ and T as functions of time. The target temperature history (ramping at 5°C/min to 1500°C) is also shown. Typically, ψ reaches maximum at a temperature below 1500°C. As Figure 2 shows, the actual temperature history somewhat differs from the targeted one (the rate of heating slows down before reaching the final temperature) and the final temperature slightly differs from experiment to experiment, but the time-temperature curves up to the final temperature are almost identical. The inability to keep the final temperature the same in each experiment is inherent to the current experimental setup. Consequently, the foam starting temperature, maximum foam height, and foam generation rate occurred under well-controlled experimental conditions, whereas the foam collapse occurred at temperatures that were not exactly identical, not to mention the poor visibility of the collapsing sample caused by bursting of bubbles that obscured the crucible wall.

For the three tests with air flow, for which ψ versus time is displayed in Figure 2, the average maximum ψ was $\psi_{max} = 7.00$ with a standard deviation of 0.46, corresponding to the reproducibility conservatively estimated at 13%. Figure 3 through 5 show ψ versus time for experiments conducted under different atmospheres: (i) dry and humid air (Figure 4), (ii) dry and humid CO_2 (Figure 5), and (iii) various dry atmospheres (Figure 5).

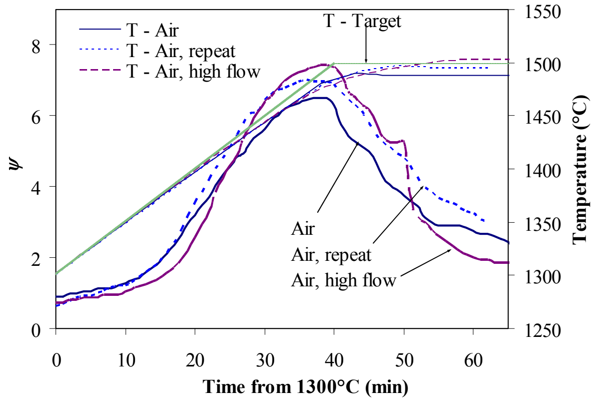


Figure 2. ψ and furnace temperature versus time for the tests with air flow

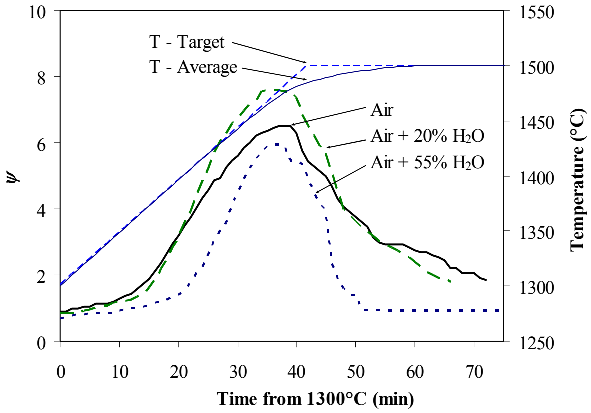


Figure 3. ψ and furnace temperature versus time for tests in air-based atmospheres

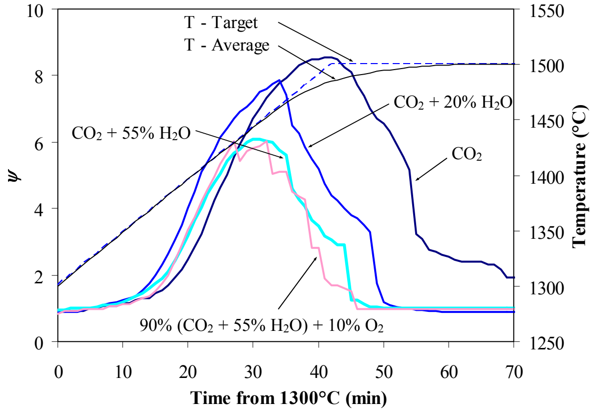


Figure 4. ψ and Furnace temperature versus time for tests in CO_2-based atmospheres

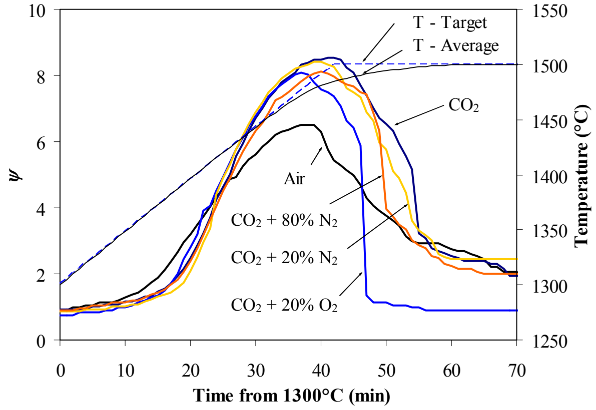


Figure 5. ψ and furnace temperature versus time for tests in dry atmospheres

Another way of analyzing the transient foam results is to examine the melt expansion rate, defined as $r_\psi = \mathrm{d}\psi/\mathrm{d}t$. There are two intervals on the foaming curve, on which r_ψ is of a nearly constant value. The first is the "primary" interval where pre-existing bubbles expand with increasing temperature. During the second interval, "fining" interval, the bubbles grow as a result of fining reactions. The corresponding two r_ψ values were obtained from data points on these nearly linear portions of the foaming curve. The low-temperature r_ψ values are virtually identical for all tests. Similarly, the $\mathrm{d}\psi/\mathrm{d}T$ values are obtained from the plot of ψ versus temperature. Table II summarizes r_ψ and $\mathrm{d}\psi/\mathrm{d}T$ values for the "fining" interval.

The foam decay is the least reproducible process under the present test conditions. It is governed by the rate of bursting of bubbles, which is a random process. In addition, the temperature at the maximum foam height slightly varied from experiment to experiment. Nevertheless, the duration of foam collapse was measured and the results are shown in Table II. The symbols $t_{0.5}$ and $t_{0.25}$ denotes the times for the foam to collapse to $1/2\psi_{\max}$ and $1/4\psi_{\max}$, respectively. Note that some samples did not reach $1/4\psi_{\max}$ before the test was terminated.

Table II. Maximum ψ, ψ_{max} increase rates, and foam collapse times for all foaming tests

Test #	Description	Max ψ	ψ increase rate		Foam collapse time (min)[a]	
			$d\psi/dt$	$d\psi/dT$	$t_{0.5}$	$t_{0.25}$
1	Air	6.52	0.27	0.058	16	-
2	Air, repeat of #1	7.03	0.33	0.070	22	-
3	Air, higher flow rate	7.44	0.40	0.089	14	-
4	Air + 20% H_2O	7.59	0.40	0.090	15	31
5	Air + 55% H_2O	5.93	0.37	0.079	10	13
6	CO_2	8.55	0.44	0.108	14	28
7	CO_2 + 20% H_2O	7.86	0.45	0.095	11	15
8	CO_2 + 55% H_2O	6.08	0.40	0.086	12	14
9	(CO_2 + 55% H_2O) + 10% O_2	6.04	0.42	0.088	12	19
10	CO_2 + 20% O_2	8.09	0.41	0.090	10	10
11	CO_2 + 20% N_2	8.41	0.42	0.087	15	-
12	CO_2 + 80% N_2	8.13	0.42	0.090	14	25
13	CO_2 + 55% H_2O, introduced at 300°C	Did not foam				

(a) Time to reach the specified fraction of the maximum porosity.

Figures 6 and 7 show $\psi_{\max}$ and $d\psi/dT = (d\psi/dt)/(dT/dt)$, as a function of H_2O vol.% while Figure 8 and 9 show $t_{0.5}$ and $t_{0.25}$ as a function of H_2O vol.%. Based on these plots, the major observations can be summarized as follows:

1. The foaming extent decreased as the gas humidity increased, except for 0 to 20 vol.% H_2O in air. Changing air for CO_2 had little effect on foaming when humidity was 20 to 55 vol.% H_2O.
2. The foaming extent was lower in dry air than in other gases tested (pure CO_2, CO_2 + 20% O_2, CO_2 + 20% N_2, and CO_2 + 80% N_2). There was no other noticeable effect of dry gas composition on foaming.
3. The 10% O_2 addition to CO_2 with 55% H_2O had no noticeable effect on foaming.
4. No noticeable trend was observed in foam starting temperature between tests (1370 to 1380°C) except in air with 55% H_2O, where the foam starting temperature was noticeably higher (>1400°C).

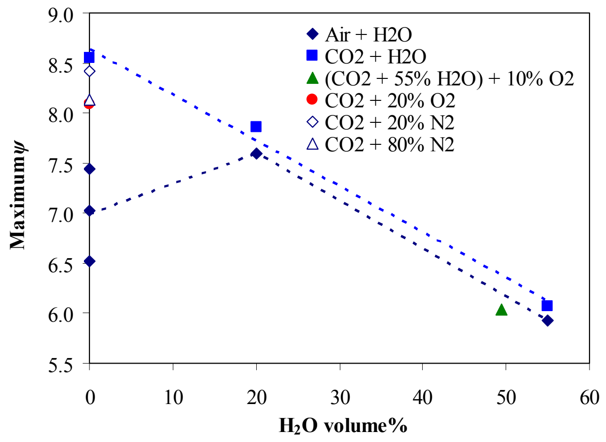
DISCUSSION

Foam stability

Foam stability can be measured using $d\psi/dT$, $\psi_{\max}$, or $t_{0.5}$. Experimental results indicate that stability of E-glass foam decreases with increasing humidity level. This is most likely due to the decrease in surface viscosity of the melt film. Therefore, enhanced foaming observed in oxy-fired E-glass melting furnaces may not be attributed to the effect of water vapor dissolved in the melt on the foam stability.

Moreover, except for dry air and water vapor, the atmosphere composition had no noticeable effect on the foam stability. This is particularly true in simulated oxy-fired environment with excess of O_2. These observations indicate that changing the furnace atmosphere, if such a change was technologically and economically feasible, is not expected to reduce the current level of foaming.

Finally, the foam-destabilizing effect of dry air as compared to other dry gases is not understood at present. However, additional experiments that would verify and elucidate this observation do not appear relevant to the main objective of the current research, which is foam reduction in oxy-fired furnaces.



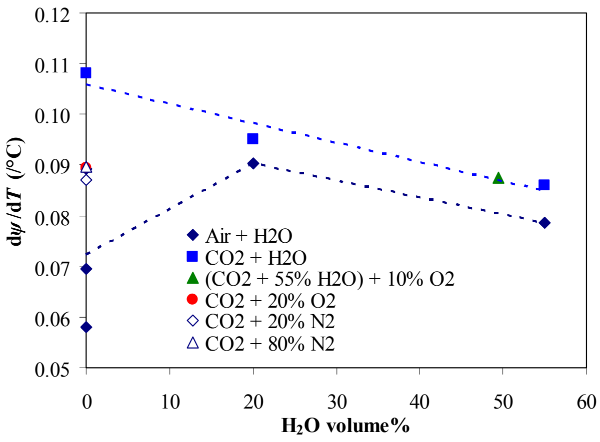
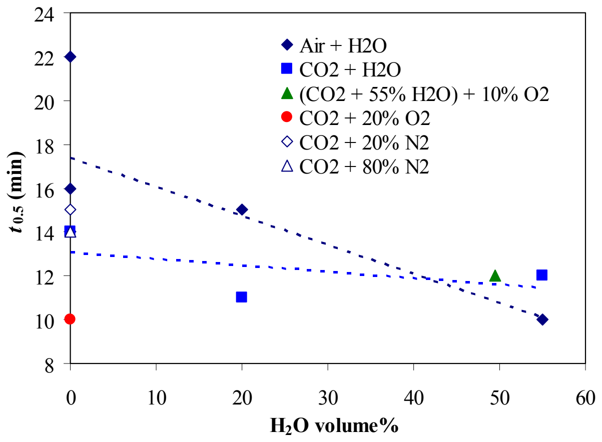


Figure 6. Maximum volume fraction vs H_2O content

Figure 7. Volume fraction increase rate ($\mathrm{d}\psi/\mathrm{d}T$) vs. H_2O content

Effect of water on refining reactions

According to Laimböck [4] and Beerkens *et al.* [11], the increased foaming that occurs in oxy-fired furnaces is caused by the increased humidity of the furnace atmosphere. Water dissolves in glass and tends to establish the same partial pressure of H_2O in the gas bubbles as in the atmosphere above the melt. As a result, the fining gases, such as SO_2 and O_2, are diluted in the bubbles. The decreased partial pressure of the fining gases in bubbles results in an increase of the driving force for the fining reactions. Thus, a substantially larger volume of gaseous phase is released under humid atmosphere, leading to enhanced foaming. This dilution model is well developed mathematically and is supported by strong experimental evidence from foaming studies conducted on soda-lime glasses. The decrease in viscosity due to increased humidity seems insignificant for soda-lime glass, where the dilution effect dominates.



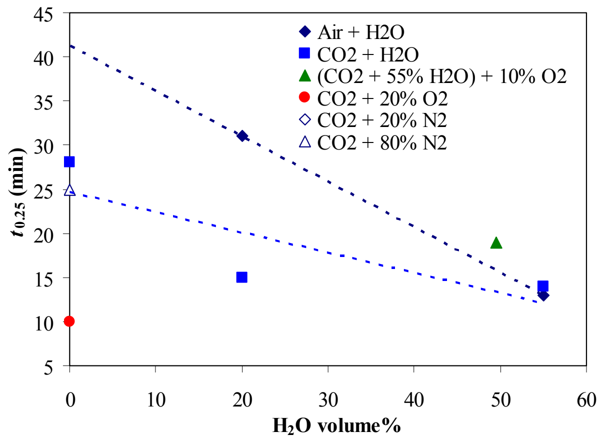


Figure 8. Foam collapse time to 50% of maximum ψ vs. H_2O content

Figure 9. Foam collapse time to 25% of maximum ψ vs. H_2O content

In our current experiments with E-glass except Test 13, the possibility of water dissolution in glass at early stages of melting and thus the dilution effect was minimized by introducing humid gas only after the batch reactions were completed. The Test 13 in which the humid gas (45% CO_2 + 55% H_2O) was introduced at an early stage in the melting process did not produce any foam whereas Test 8 with the same humid atmosphere introduced at 1250°C produced foam. The reason for the lack of foaming in Test 13 is most likely due to the early loss of sulfate caused by higher water content at early stages of melting.

Sulfate loss due to evaporation proceeds at temperatures well below the sulfate decomposition temperature. Moreover, sulfate evaporation is promoted by humidity. If losses due to evaporation are such that the partial pressures of SO_2 and O_2 in glass are too low to cause an appreciable growth of bubbles, no foaming will occur. This may be a possible explanation for the absence of foam in Test 13. The proof of this hypothesis can be obtained if the glass is analyzed for the content of SO_3 for the samples taken at several stages of melting. This was unfortunately beyond the scope of the present work.

Laimböck measured the sulfate loss in soda lime glass at early stages of melting as well as during fining. The initial SO_3 concentration was 0.66 wt.%. The SO_3 concentration before fining was 0.55~0.53 wt.% and 0.32~0.15 wt.% after fining. These numbers are large compared to the as-batched SO_3 concentration in E-glass of the present study, which was 0.17 wt.%; roughly a half of this amount came from Na_2SO_4 and the rest was impurity from other raw materials. Estimating that SO_3 concentration dropped to 0.01 wt.% after fining (typical measured concentration in the product glass), and considering possible evaporation of sulfate before fining, the loss of SO_3 during foaming was less than 0.16 wt.%. Hence, only a low amount of sulfate is available for gas generation in the E-glass as compared to soda-lime glass. Consequently, relatively small losses of sulfate from E-glass may be sufficient to decrease the gas generation rate beyond the critical level needed for foaming.

Accordingly, fining and foaming behaviors of E-glass and soda-lime glass are substantially different. However, the crucible test results may not be directly applicable to plant condition because the critical level of gas generation for foaming in plant will be different, primarily because of the difference in size and geometry of the melt pool, which produces different thermal history of the glass batch. For example, the as-melted materials below the batch pile in the glass furnace is remixed to the already refined melt so that the part of the gases generated by early decomposition of sulfate may also contribute to foaming. The observation that oxy-firing tends to increase the foam in E-glass suggests that the dilution effect on refining and foaming should also be applicable to E-glass melting in the commercial melting furnaces.

In a very simplistic argument, if the sulfate added to the batch is controlled solely by the refining behavior, like in a typical clear soda-lime glass, the dilution effect in oxy-fired condition would require smaller addition of sulfate to achieve the same refining efficiency and would result in the same foaming extent. However, when the sulfate in E-glass serves other purposes, such as redox control, in addition to refining, the sulfate addition may not be decreased to a sufficiently low level, which will result in increased foaming. This may explain why the oxy-fired E-glass furnaces produce more foam than air-fired.

CONCLUSIONS AND RECOMMENDATIONS

The results of foaming experiments with varying gas atmospheres conducted in this study point that the higher foaming in oxy-fired furnace (compared to air-fired) in E-glass production is not caused by water vapor which contradicts the general hypothesis. The higher foaming in oxy-fired E-glass furnace can be attributed to the dilution effect of water on sulfate decomposition, discussed in the literature primarily for the soda-lime glasses. However, the difference is that the sulfate in E-glass has other function in addition to refining, which may prevent the decrease of sulfate to a sufficiently low level to compensate the increased refining gas generation in oxy-fired furnaces.

Finally, the possibility that small changes in the gas atmosphere composition may have a significant effect on foam stability was not confirmed at least within the range of atmosphere compositions tested in this study.

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