The Role of Structural SO_3 of Clay on the Melting and Fining of E-Glass

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Clay is one of the major raw materials used in the production of E-glass, and depending upon the origin, it contains SO_3 to different extents in its structure. In this study, clay samples with different SO_3 contents are used in the batch of E-glass and their effects on foaming and fining of the melts are compared. It is observed that after certain value of SO_3 content of clay, the structure of foam changes. At lower SO_3 levels of clay, the foam layer consists of unmelted batch, whereas at higher amounts, the foam layer consists of only bubbles without any batch particles with a high rate of foam disappearance. The seed free time experiments reveal a similar anomaly at certain value of SO_3 of clay. At this threshold value, the number of bubbles initially formed in the glass is minimum. After this point with increasing SO_3 amount of clay, in spite of the higher number of bubbles formed at the beginning, the fining rate increases due to the fining action of a certain amount of Na_2SO_4 in the batch.

1. INTRODUCTION

When glass batch is melting, at high temperatures from the decomposition of sulfates, which are used as fining agents, a foam layer is produced at the surface of the melt, which is called as secondary foaming. As the high amount of dissolved sulfate containing glass melt enters the hotter parts of the furnace, the partial pressures of SO_2 and O_2 increase up to a level at which the specific gas volume is more than 0,02 ml per gram of glass, causing gas bubbles[(1)]. The formation of these bubbles aids the fining of the glass melt as they ascend to the surface of the melt. When the specific gas volume is greater than 0,1 ml/gram glass, these bubbles start to accumulate at the surface. This process is defined as secondary foaming. The temperatures at which the bubbles and the foam are formed are usually close to each other in the range of 10 to 20 °C. In sulfate fined oxidized glass melts, the sulfate decomposition temperature depends on the amount of the sulfate in the batch and the glass composition, or the basicity of the melt, which affects the sulfate solubility.

Sulfate solubility is known to be low in E-glass due to its acidic nature because of its high alumina, B_2O_3 and very low alkali oxide contents, compared to soda lime silica glasses. Therefore only a small excess amount of sulfate is required in oxidized E-glass after the initial batch melting, and too large an excess should be avoided in order to prevent foaming. An accurate sulfate balance is required for an adequate fining. As Laimbock[(1)] explains in his work, the optimum amount of sulfate is determined by adding up the sulfate loss that takes place during the initial batch melting, the sulfate solubility of E-glass ($[SO_3]_{E\text{-}glass}$) at the hotspot temperature and the amount of sulfate needed for sufficient fining. As the sulfate solubility at the melting temperature is low in E-glass, optimum sulfate level in the batch is less than that of the oxidized soda lime silicate glass, and sulfur impurities of the raw materials become significant on the batch sulfate level. The major raw material as SiO_2 and Al_2O_3 source used in the production of E-glass is clay and it contains differing amounts of

SO_3 depending on its origin. In this study, the effect of structural SO_3 of different clays on foaming and fining behavior of E- glass melts is studied in reference to those, which contain Na_2SO_4 as the main SO_3 source since clays obtained from different sites in Turkey may differ in their SO_3 contents.

Table 1: Amount and the Source of SO_3 in Glasses together with Foam% and the Number of Bubbles

SO_3 % of Clay Sample		**0,34 (C1)**				**0,40 (C2)**	**0,47 (C3)**			**0,72 (C4)**		**1,5 (C5)**
Glass No		G1	G2	G3	G4	G5	G6	G7	G8	G9	G10	G11
Total SO_3 % in Batch		0,230	0,282	0,355	0,512	0,312	0,320	0,372	0,425	0,460	0,512	1,122
SO_3 % from Na_2SO_4		-	0,052	0,105	0,282	0,052	-	0,052	0,105	-	0,052	0,052
SO_3 % from Clay		0,23	0,23	0,23	0,23	0,26	0,32	0,32	0,32	0,46	0,46	1,07
% Surface Area Covered by Foam	10 min.	23	25	33	40	40	30	35	45	70	80	70
	20 min.	18	20	15	30	20	15	12	15	5	5	20
	30 min.	10	15	7	20	15	10	8	10	3	2	15
	40 min.	5	10	5	10	8	7	5	7			5
	50 min.	2	5	3		4	1	2	4			2
Number of Bubbles	50 min.	409	316	345	447		266	212	220	304	355	
	90 min.	177	158	170	226		188	174	186	249	174	

2. EXPERIMENTAL STUDIES

To study the effect of structural SO_3 of clay, 5 clay samples with different SO_3 contents (C1 to C5) are examined. To disregard the possible effect of particle size on melting and fining, the clay samples are brought to a similar particle size distribution by adequate grinding. Batches that yield 100 g of E-glass are prepared by using clays with different SO_3

contents. To distinguish the effect of structural SO_3 from clay and SO_3 contributed by conventional fining agents, batches where Na_2SO_4 is the main SO_3 source are also prepared. The SO_3 amounts contributed separately from clay, Na_2SO_4 and the total SO_3 content of the batches are given in Table 1. The effect of structural SO_3 of clay on melting and fining behavior of E-glass is observed by conducting foam disappearance and seed free time experiments. The % area covered by foam on the surface of glasses that are melted in 95%Pt-5%Au crucibles at 1500^0C in an electric furnace for 10-50 min. at 10 min. intervals is recorded by Abacus evaluation method. For the determination of the fining rate, the number of the bubbles that remained in the 100g of glass samples, after melting the corresponding batches in porcelain crucibles at 1500^0C in an electric furnace for 50-90 min. at 10 min. intervals, are counted, and the logarithms of the number of bubbles are plotted against their corresponding melting times. The slope of the said graphs is defined as the fining rate. All the data points given in the text and shown in Table 1 are the arithmetic average of at least 3–4 experiments.

3. RESULTS and DISCUSSION

3.1. Foaming Behavior

To determine the effect of SO_3 introduced into the batch by Na_2SO_4 on the foaming behavior of E-glass batch, foam disappearance experiments are conducted at increasing percentages of Na_2SO_4 in batches that contain clays with different SO_3 contents (C1, C3, C4). When the SO_3 content of the clay increases, at 10 min. melting time, the % of foam covered area of glasses that do not contain Na_2SO_4 increases (G1, 6, 9) since glasses made from high SO_3 containing clays initially contain more total SO_3. As 0.052 and 0.105 % SO_3 is added to G1, G6 and G9 from Na_2SO_4 the difference between the % of foam covered area of the glasses (G2,3; G7,8; G10) and their no Na_2SO_4 containing counterparts increases as the clays contain more SO_3, i.e. increasing Na_2SO_4 becomes more effective in foam formation when higher SO_3 containing clays are used in the batch. To differentiate between the effects of the sources of SO_3 on foaming, two glasses in which SO_3 comes mainly from clay (G10) or mainly from Na_2SO_4 (0,282% SO_3, G4), are melted. At 10 min., G4 contains 40% foam covered area whereas for G10 it was 80%, i.e. when the total SO_3 contents of the glasses are the same, SO_3 coming from clays produces more foam at the beginning of melting, compared to SO_3 coming from Na_2SO_4. However, at 30 min. G10 is practically foam free whereas the surface of G4 still contains 20% foam. It was also observed that the foam on G4 contains unmelted batch particles whereas foam on G10 consists of a thin layer of small bubbles without any batch particles.

In the batches with a constant level of Na_2SO_4 (0,052% SO_3), when clays with increasing SO_3 contents are used (G2,5,7,10,11), it is observed that the amount of foam increases while the foam structure changes (Fig.1). At lower values of SO_3 from clay (C1, C2) foam contains unmelted batch particles (G2,5). In G7, however, which incorporates C3, the structure of the foam is different than the other two glasses (G2,5) consisting of a thin layer of small bubbles without any unmelted batch particles, meaning that even in 10 minutes the batch containing clay with higher SO_3 melts rapidly. Observing the structures of foam on all experimental melts reveals that 0,47% can be defined as the threshold value for SO_3 concentration of clay at which the structural transformation in foam starts. In G10 and 11 the glass surface is 80% and 70% covered also with a thin foam layer consisting of tiny bubbles without any batch particles. Although the foam covered area is high at the beginning in G10, the amount of this foam decreases down to 5% in 20 minutes and to 2% in 30 minutes, showing a very high rate. However, in G11, in 20 minutes the amount of this layer goes down to 20%. From the experiments conducted with increasing SO_3 of clay, it is seen that after certain point, where in this case it is 0,72% SO_3 of clay, the rate of foam disappearance slows down.

Results on foaming behavior indicate that the solubility of SO_3 in E-glass changes depending on the source of SO_3. When SO_3 is introduced into the batch from clay, the SO_3 loss during the initial melting gets higher as the SO_3 level in clay increases, and as a result, an increase in the amount of foam at the beginning of melting occurs. The ease of melting observed after a certain threshold value of SO_3 in clay is due to the agitation effect of higher SO_3 loss. Fast disappearance of foam is suspected to be due to the higher hotspot solubility of SO_3 when it is introduced into E-glass batch in the structure of clay. It dissolves into the melt easily, and even in 30 minutes, glass becomes foam free. But this effect slows down when the SO_3 in clay increases as the melt gets saturated.

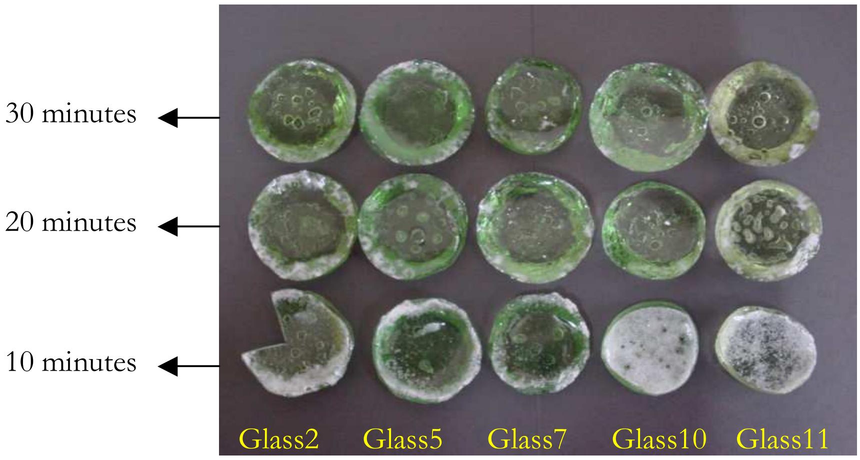

Figure 1: The Effect of SO_3 Level in Clay on Foaming Behavior of Glasses

3.2. Fining Behavior

The fining effect of the addition of Na_2SO_4 at two levels, to batches containing clays with different SO_3 contents, is investigated. When 0,052 % and 0,105 % SO_3 by Na_2SO_4 are added to the batches containing clays C1 and C3, the number of bubbles decreases compared to the batches that do not contain Na_2SO_4. When 0,052% of SO_3 is added by Na_2SO_4 in the same manner to the batch containing clay C4 (G9,10), the number of bubbles increases contrary to the cases with lower SO_3 containing clays. But in the final glass (with C4 at 90 minutes), the number of bubbles decreases by 30% which is again contrary to the other glasses, indicating a very high rate of fining due to the fining action of Na_2SO_4. But when SO_3 is increased in glass by higher Na_2SO_4 addition (0,282% SO_3), the number of bubbles increases by app. 22% compared to SO_3 increase of glass via clay at all fining times (G4,10).

When the amount of SO_3 in clay increases, although the number of bubbles decreases at early stages of fining (50-70 min.) at a certain threshold level, which is 0,47%, the rate of fining is the lowest (Fig. 2). When clay with 0,72% SO_3 is used, the number of bubbles increases at the beginning of fining but as the fining rate accelerates, the number of bubbles in the final glass (G10, at 90 min.) is low. Therefore, in terms of usable glass, clays that contain up to 0,72% SO_3 can be used in the batch since at 90 min. glasses that contain clays with varying amounts of SO_3 have almost the same amount of bubbles (Fig. 2).

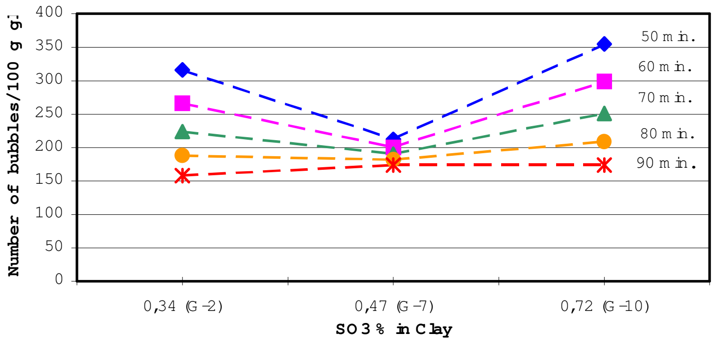

Figure 2: The Effect of SO_3 Level in Clay on Fining Behavior of Glasses

The results about fining behavior also show that, as the solubility of SO_3 increases, the number of bubbles decreases at the threshold level. This is when the glass starts to get saturated with SO_3. After this point, as the melt cannot dissolve SO_3 any more, the number of bubbles increases in the glass and certain amount of sodium sulfate becomes necessary for complete fining.

4. CONCLUSION

In this work, the effect of structural SO_3 of clay on melting and fining behavior of E-Glass is studied. It is found out that even though the amount of foam increases as the SO_3 content of clay increases, the structure of the foam changes from foamy appearance with unmelted batch particles to a thin layer containing tiny bubbles without any batch particles after a certain threshold value (0,47%). After this level melting eases and the rate of disappearance of foam is the fastest at 0,72% SO_3 in clay. When the SO_3 content of clay is further increased, foam disappearance rate slows down.

When high SO_3 containing clays are used in the batch, sodium sulfate is much more effective as far as the rate of fining is concerned. At all levels of SO_3 in clay, the number of bubbles does not change in the final glass due to the fining agent action of sodium sulfate. Therefore clays, which contain SO_3 in the range of 0,4 – 0,7% can be used safely, 0,47% SO_3 giving the best results. In all cases a certain amount of Na_2SO_4, is necessary for fining of E-glass.

[1] Paul Rudolf Laimbock, in *Foaming of Glass Melts* (Teschnische Universiteit Eindhoven, Eindhoven, 1998).