Original Paper

Reducing the sulphate content of soda–lime–silica glasses with the aid of physical refining[1]

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Soda–lime–silica glasses from the float glass production sector have sulphate contents of ≈ 0.27 wt% SO_3. These sulphate contents contaminate the tin bath for the float process with sulphur. The thus-formed tin sulphides cause production faults by forming top-specks on the atmospheric surface of the glass ribbon.

The aim of the described experiments is a reduction of the sulphate content of such glass melts. For this purpose, within the scope of a physical refining process, the glass melts are rinsed with nitrogen in order to drive SO_3 (i.e. $SO_2 + \frac{1}{2} O_2$) from the melt and thus support the decomposition of sulphate. The sulphate content can thus be reduced to values of 0.11 to 0.13 wt% SO_3. Parallel to this, a shifting of the Fe^{3+}/Fe^{2+} ratio in favour of the bivalent iron is observed. It is thus possible to supervise the success of the physical refining process directly in the melt with the help of oxygen ion sensitive probes.

Verminderung des Sulfatgehaltes von Kalk–Natronsilicatgläsern mit Hilfe der physikalischen Läuterung

Kalk–Natronsilicatgläser aus der Flachglasproduktion weisen Sulfatgehalte von etwa 0,27 Masse-% SO_3 auf. Diese Sulfatgehalte verunreinigen das Zinnbad des Floatprozesses mit Schwefel. Die entstehenden Zinnsulfide verursachen Produktionsfehler, indem sie „top-specks" auf der Oberseite des Glasbandes bilden.

Ziel der hier beschriebenen Versuche ist die Verminderung des Sulfatgehaltes solcher Glasschmelzen. Dazu werden im Rahmen der physikalischen Läuterung Glasschmelzen mit Stickstoff gespült, um SO_3 (bzw. $SO_2 + \frac{1}{2} O_2$) aus der Schmelze auszutreiben und damit den Sulfatzerfall zu unterstützen. Der Sulfatgehalt kann so auf Werte von 0,11 bis 0,13 Masse-% SO_3 abgesenkt werden. Parallel dazu wird eine Verschiebung des Fe^{3+}/Fe^{2+}-Verhältnisses zugunsten des zweiwertigen Eisens beobachtet. Dadurch besteht die Möglichkeit, den Erfolg der physikalischen Läuterung direkt in der Schmelze mit Hilfe sauerstoffionensensitiver Sonden zu überprüfen.

1. Introduction

During the production of soda–lime–silica glass in the flat glass industry a chemical refining process is generally applied. For this purpose sodium sulphate is added to the batch. Through reaction of the sodium sulphate with the quartz sand at the melting temperature, gases are set free which contribute to the refining of the melt. Considerable proportions of the sulphate content (with "sulphate content", the total sulphur content expressed as SO_3 is meant) of the batch escape from the glass melt in this way. However, a certain proportion coming from the sodium sulphate does remain in the melt.

A reduction of the sulphate content of soda–lime–silica melts is desirable for technological reasons. However, this can only occur when the sodium sulphate has effected its refining action. In the following, experiments are described which aim to reduce the sulphate content of soda–lime–silica melts by physical refining.

Some physical properties of glasses and glass melts can be correlated with their sulphate content, e.g. the surface tension. Surface tension influences, amongst other things, the thickness of the molten glass floating on the tin bath in the float process [1 and 2].

A knowledge of the relationship between the sulphate content and the physical properties of glasses and glass melts, also the controlled variation of the sulphate content of glass melts, can contribute towards a corresponding reduction of production loss due to defects.

2. Sulphate in soda–lime–silica glasses

Sodium sulphate is added to the glass batch because at the relatively low temperature of 884 °C it forms a liquid phase which coats the grains of quartz and thus accelerates the melting of the batch [3 and 4]. The sodium sulphate itself is thermodynamically very stable and first decomposes at a temperature of 1850 °C [5]. Decomposition of the sulphate can, however, take place in the presence of silica with the formation of sodium metasilicate according to:

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[2] Now with: Carl Dellmann GmbH, Willich (FRG).

$$Na_2SO_4 + SiO_2 \rightleftarrows Na_2SiO_3 + SO_2 + \tfrac{1}{2}\,O_2$$

at a temperature > 1288 °C [6]. This decomposition was investigated by Schaeffer et al. [7] with an oxygen ion sensitive probe and an increase of p_{O_2} was observed at 1300 °C.

The literature yields data giving a maximum solubility of sulphate in soda–lime–silica glasses of up to 1.1 wt% SO_3 [8 and 9]. However, these data are of doubtful value as they were determined at unknown partial pressures of oxygen and sulphur dioxide. Holmquist [10] determined a solubility of 0.11 wt% SO_3 at controlled p_{O_2} and p_{SO_2} values in 20 Na_2O · 80 SiO_2 (wt%) melts.

The solubility of sulphate in glass melts is dependent on the redox condition of the glass melt [11 to 13] (figure 1). The redox condition is expressed here by the $(Fe^{3+}/Fe^{2+})^2$ ratio. It can be observed that with decreasing oxygen partial pressure the SO_3 content also decreases and that the Fe^{3+}/Fe^{2+} ratio is shifted towards the bivalent iron. In figure 1 the $(Fe^{3+}/Fe^{2+})^2$ ratio is shown in a linear plot. If p_{SO_2} is increased in a silicate melt then the sulphate decomposition can be stopped [14]. If there is even more SO_2 available than can be dissolved in the described melt, a Na_2SO_4 layer (gall) is formed as a second liquid phase. It is not miscible with the glass melt and forms a supernatant liquid because of its lower density.

The melting time and the silica content of the glass melt are also important for the sulphate solubility [15]. Hence, a diffusion of sulphate from silica-rich areas in glass melts to areas of lower silica concentrations has been described [16].

Nowadays, flat glass melts as a rule have SO_3 contents of 0.2 to 0.4 wt% [17].

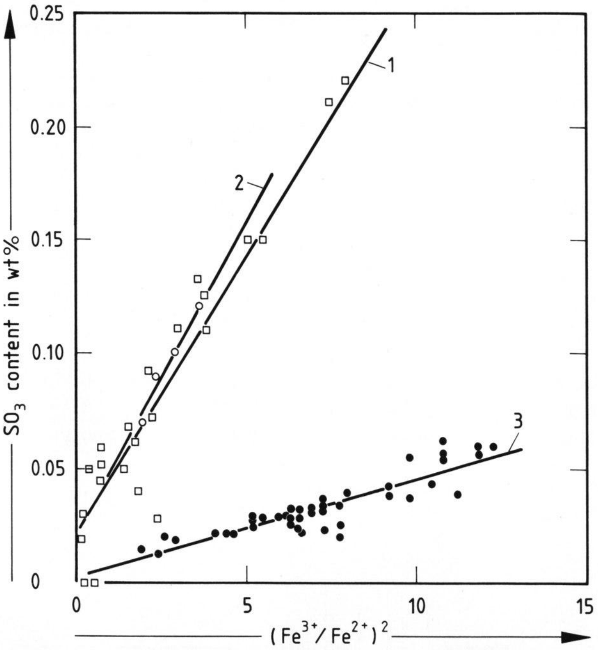

Figure 1. SO_3 content as a function of the redox condition of silicate glasses: curve 1 after [11], curve 2 after [12], curve 3 = E glass, Gevetex, Herzogenrath (FRG), after [13].

Table 1. Solubilities at 1400 °C and diffusion coefficients at 1200 and 1400 °C of different gases in glass melts

	gas solubility at 1400 °C in cm³/cm³ melt (gas in standard state)	diffusion coefficient in m²/s	
		at 1200 °C	at 1400 °C
He	$3.48 \cdot 10^{-3}$ [24]	$1.15 \cdot 10^{-8}$ [27]	$1.64 \cdot 10^{-8}$ [29]
N_2	$3.5 \cdot 10^{-4}$ [25] to $4.2 \cdot 10^{-4}$ [26]	$9 \cdot 10^{-11}$ [28]	$4.3 \cdot 10^{-10}$ [28]
O_2	0.2 to 1.0 [27]	$6.4 \cdot 10^{-11}$ [29]	$2 \cdot 10^{-10}$ [27]
$SO_3$³)	0.012 to 0.051 [27]	$1.3 \cdot 10^{-11}$ [28]	$1 \cdot 10^{-8}$ [27]

³) These are literature data, which does not necessarily mean that SO_3 is stable at the temperatures stated.

3. Solubility and diffusion of different gases in soda–lime–silica melts

Gases which are introduced into glass melts can be physically dissolved in these melts. On the one hand, the solubility is determined by the dimension of the gas atom or molecule to be dissolved. On the other hand, the number and size of voids in the corresponding glass melt, which are available for assimilation of the gases present, are decisive [18]. Starting from a pure silica melt, alkali ions decrease the number of mentioned voids for the gases, so that with increasing alkaline oxide content the solubility of gases in a glass melt decreases [19].

An increase of temperature [19] and pressure [20 to 23] increases the solubility of the gas, whereby the influence of pressure outweighs the influence of temperature; because, not only are the available voids filled to a higher degree, but the gases are in a position to create new voids. The result is a reduction in the density of such treated glasses.

The solubility of helium in glass melts (table 1) is relatively high, compared to e.g. nitrogen. This is caused by the different radii of the atoms and molecules, respectively (r_{He} = 80 pm, r_{N_2} = 145 pm). However, the solubility of N_2 is hardly influenced by the alkali ion content of the melt, because, due to its large molecular radius, N_2 can only fill such voids which are too large for alkali ions [19 and 22].

If one compares the solubility data for O_2 and SO_3 with those of N_2 and He, the relatively high solubilities of O_2 and SO_3 quoted for these large dimension molecules, point to a possible or partly observed chemical solubility, which is superimposed on the physical solubility.

Considering the diffusion coefficients in table 1, it is remarkable that for the large molecules SO_3, N_2 and O_2, they increase sharply with increasing temperature; while the values for the small helium atom change only insignificantly. It can thus be concluded

Table 2. Composition of the glasses used in the experiments (in wt%)

oxide	colourless glass	green glass I	green glass II
SiO_2	71.37	70.88	70.76
Al_2O_3	0.55	0.53	0.52
TiO_2	0.05	0.05	0.05
CaO	9.66	9.71	9.62
MgO	3.87	3.97	4.03
Na_2O	13.32	13.42	13.41
K_2O	0.19	0.04	0.04
SO_3	0.27	0.26	0.25
FeO	0.020	0.124	0.170
Fe_2O_3[4])	0.104	0.553	0.750
Total	99.38	99.41	99.43

[4]) Total iron content, expressed as Fe_2O_3.

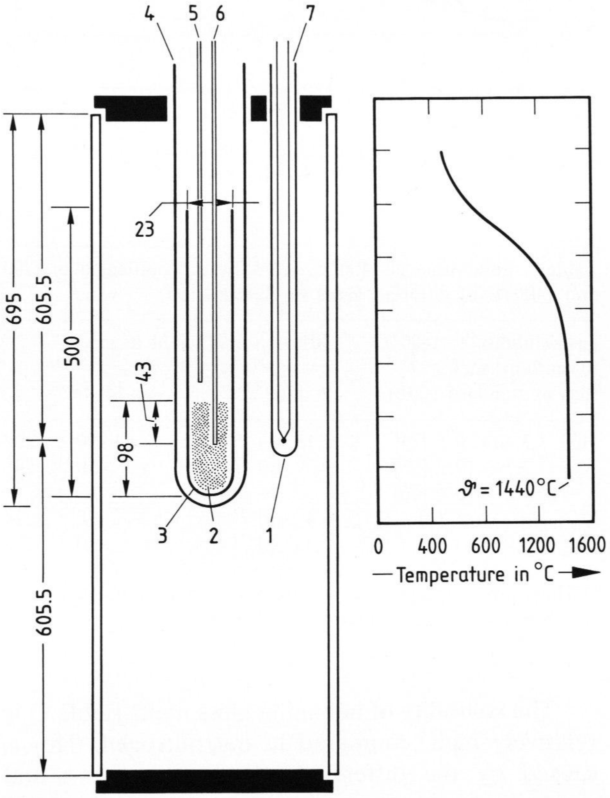

Figure 2. Experimental arrangement for rinsing of glass melts in a tube furnace with a temperature profile for an experimental temperature of 1440 °C. 1 = protective tube of the thermocouple, 2 = glass melt in a ceramic crucible, 3 = inner crucible, 4 = outer crucible, 5 = ceramic capillary tube for feeding the atmosphere into the furnace, 6 = ceramic capillary for rinsing the melt, 7 = thermocouple Pt 90 Rh/10/Pt. All dimensions of the experimental arrangement are given in mm.

that with increasing temperature the large voids in a glass melt expand faster than the small ones.

Based on the observation of refining processes, several authors decribed the behaviour of gases in gas bubbles present in glass melts. For example, there is no change in volume of a nitrogen-containing bubble [30] in a glass melt over a period of 30 h. Because a N_2 bubble is, however, not in equilibrium with the other gases of a glass melt, an increase in bubble size is to be expected.

If gas bubbles contain several gases, e.g., O_2 and SO_2, a rapid shrinking can be observed. At a ratio of $SO_2 : O_2 = 2 : 1$ they dissolve completely. However, there is also the possibility of allowing SO_2-containing bubbles to shrink by disproportionation into $Na_2SO_4 + \frac{1}{2} S_2$, whereby the reaction products form by dealkalization of the surface of the bubbles [21].

4. Conclusions from the literature survey

According to the literature survey, it is certain that the SO_4^{2-} ion in the glass melt is in equilibrium with SO_3, i.e., $SO_2 + \frac{1}{2} O_2$ physically dissolved in the melt. In order to reduce the sulphate content of the glass melt, it appears to be possible to reduce the SO_3 content ($SO_2 + \frac{1}{2} O_2$ content) and to support the decomposition of sodium sulphate according to the equation:

$$(SO_4)^{2-} \rightleftarrows O^{2-} + SO_2 + \tfrac{1}{2} O_2 \, .$$

The following experiments investigate the possibility of reducing the SO_3 content ($SO_2 + \frac{1}{2} O_2$ content) of the glass melt by giving the physically dissolved SO_3 the chance to diffuse into SO_3-free bubbles. These bubbles are introduced into the melt by a physical refining process.

5. Experiments in order to reduce the sulphate content of soda-lime-silica melts by physical refining

5.1. Used glasses

The glasses used for the described experiments come from the float glass production sector. They differ according to their iron oxide contents and are defined as "colourless glass", "green glass I" and "green glass II". The "colourless glass" has a total iron oxide content of 0.10 wt% Fe_2O_3, which increases in "green glass I" to 0.55 wt% Fe_2O_3 and in "green glass II" to 0.75 wt% Fe_2O_3. This occurs mainly at the cost of the SiO_2 content which is reduced from 71.4 wt% in "colourless glass" to 70.8 wt% in "green glass II". The glasses have a Na_2O content of 13.4 and a CaO content of 9.7 wt%, respectively. SO_3 concentrations between 0.25 and 0.27 wt% were analysed (table 2).

5.2. Experimental equipment and procedure

The glasses were melted in a vertical tube furnace heated to a temperature of 1440 °C (figure 2). A corundum tube closed at one end was installed as a crucible in the tube furnace. This outer crucible served as a protective tube for a second crucible which held 100 g (= 40 ml) of molten glass. During the 2.5 to 3 h heating-up period from room temperature to the experimental temperature, a nitrogen atmosphere was fed in through a corundum capillary tube. All ceramic parts were manufactured from Degussit AL 23 (Degussa AG, Frankfurt (FRG)).

After reaching the experimental temperature, a second corundum capillary was immersed 43 mm deep into the glass melt, through which 2.5 ml nitrogen/min was passed through as a rinsing gas. The nitrogen was taken from pressurised gas cylinders and the flow rate of the rinsing gas supervised with floating-cone flow meters. After completion of the rinsing phase, the capillary tube used for the introduction of the rinsing gas was extracted from the melt and the glass kept at the experiment temperature for a further 6 h in order to obtain a bubble-free melt. This was then cooled to room temperature over a period of 8 h.

Due to contact with the corundum crucibles and capillary tubes, the glass melts absorbed considerable quantities of Al_2O_3. This leads to an increase in the viscosity which was estimated by determining T_g in the rinsed samples. The increase in viscosity occurred mainly during the first 2 h of the rinsing time.

5.3. Methods of analysis

The chemical composition of the physically refined glass samples was determined by XRF. The SO_3 content was additionally corrected with a calibration curve, whereby sulphate, after previous reduction to sulphide, was determined titrimetrically via combustion in an oxygen atmosphere [31]. Random tests of the SO_3 content by means of Induction Coupled Plasma (ICP) confirmed the thus-obtained data. The dissolution of Al_2O_3 in the melt changed the concentration of the other elements. In order to exclude this influence, the analysis data were recalculated to the original Al_2O_3 content of the glass samples.

Furthermore, for the determination of the redox condition of the glasses, a wet chemical Fe^{3+}/Fe^{2+} analysis was carried out. Here the Fe^{2+} and the total iron contents were measured photometrically with orthophenanthroline at 510 nm against a calibration curve, after previous reduction.

6. Evaluation of the experimental results

In figure 3, the SO_3 content of the physically refined glass samples is plotted against the rinsing time. The results of the physical refining of the samples "colourless glass", "green glass I" and "green glass II" are compared. All samples were rinsed with 2.5 ml nitrogen/min in a nitrogen atmosphere. The reduction of the SO_3 contents in all three glass samples, from starting levels of 0.25 to 0.27 wt% to contents between 0.11 and 0.13 wt% SO_3, can be observed clearly.

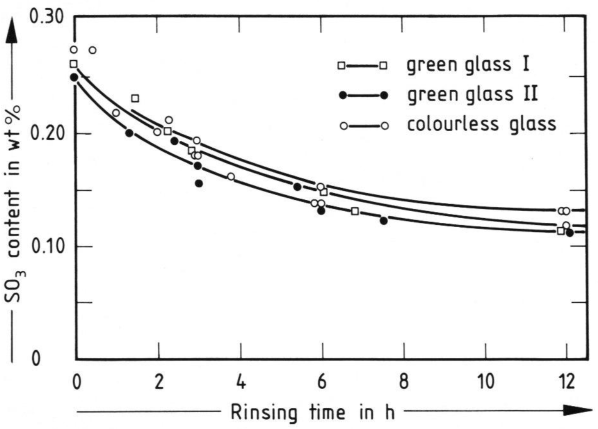

Figure 3. Decrease of the SO_3 content as a function of the rinsing time of the physical refining of colourless glass, green glass I and green glass II.

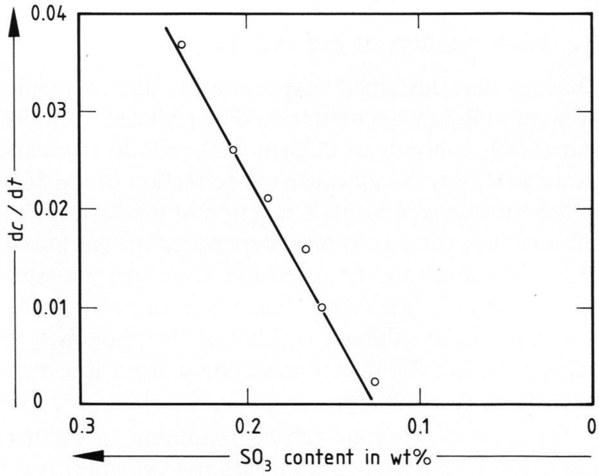

Figure 4. Change of the SO_3 content per time unit as a function of the SO_3 content of the colourless glass (slope $k = -0.235$).

Within the scope of further experiments, it could be demonstrated that with the use of other gases (e.g. helium), as well as by passing through larger amounts of gas/time unit, the SO_3 content can be insignificantly reduced further to levels between 0.11 and 0.08 wt%. In principle, the same shape of curve can be observed here.

The reaction order describing the decreasing SO_3 concentration during the physical refining process is determined with the test data for "colourless glass" as an example. If the concentration change/time unit (expressed as ($\mathrm{d}c/\mathrm{d}t$)) is plotted against the SO_3 concentration c, then a straight line with a slope of $\neq 0$ is obtained (figure 4).

Parallel to the decrease in the SO_3 content during the physical refining process, the Fe^{3+}/Fe^{2+} ratio is shifted towards the bivalent iron. If the representation of the $(Fe^{3+}/Fe^{2+})^2$ ratio, as applied in [11], is plotted against the SO_3 content, this relationship is found to be linear (figure 5).

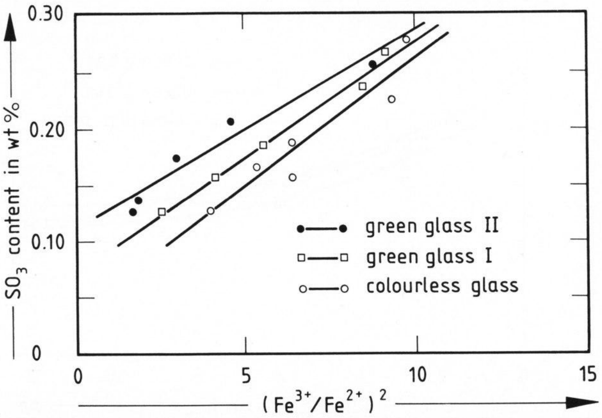

Figure 5. SO_3 contents of colourless glass, green glass I and green glass II as a function of the redox condition (expressed by the $(Fe^{3+}/Fe^{2+})^2$ ratio).

7. Interpretation of the results

During the described experiments, the sulphate content of float glass melts could be reduced from the initial SO_3 contents of 0.25 to 0.27 wt% to contents down to 0.11 wt%. Because the reduction of the SO_3 concentration represents a reaction of the first order, the reaction velocity is only dependent on the initial SO_3 concentration. Evaporation reactions are also reactions of the first order. It can be assumed that the lowering of the sulphate content of the glass melt is caused by transition of the sulphate from the melt into the gaseous phase.

Despite continuous physical refining, a further reduction of the SO_3 content was not possible. It is, therefore, assumed that the sulphate content is in equilibrium with the redox condition of the melt, i.e.:

$$(SO_4)^{2-} \rightleftarrows SO_3 + \tfrac{1}{2}\,O_2 + 2\,e^-$$

whereby SO_3, due to thermal dissociation, decomposes further into $SO_2 + \frac{1}{2}\,O_2$. The nitrogen used here contains remnants of oxygen which determine the oxygen content of the melt and thus its redox condition. If an oxygen-free nitrogen had been used for the rinsing of the glass melts, a further reduction of the SO_3 content would have been possible. However, if the melts contain polyvalent elements (e.g. iron), then the freed electrons resulting from the above reaction shift the ratio of the ions of the polyvalent elements to the ion with the lower valency state. For iron the following reaction can thus be assumed:

$$2\,Fe^{3+} + 2\,e^- \rightleftarrows 2\,Fe^{2+}\,.$$

Because of this interrelationship, the success of the physical refining process can be measured directly in the glass melt by means of oxygen ion sensitive probes.

8. Conclusion

The aim of the described experiments is a reduction of the sulphate content of glass melts. For this purpose the glass melts are subjected to a physical refining process at a temperature of 1440 °C and rinsed with nitrogen and other gases. The following observations are made:

a) The sulphate content of glass melts can be reduced by physical refining to values of 0.27 to 0.11 wt% SO_3, it is interpreted as a decomposition of sulphate.

b) The decrease of the sulphate content is described as a reaction of the first order, thus, the reaction velocity is only dependent on the initial SO_3 content.

c) Parallel to the decrease of the sulphate content a shifting of the Fe^{3+}/Fe^{2+} ratio in favour of the bivalent iron is observed which is caused by freed electrons resulting from the decomposition of sulphate.

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