Original Paper

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Influence of water dissolved in the structure of soda-lime-silica glass on melting, forming and properties: state-of-the-art and controversial issues

Report of the International Commission on Glass (ICG) Technical Committee 14 "Gases in Glass"

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The paper summarizes the information available about the water content of soda-lime-silica glass, the factors that influence it and the influence exerted by water in glass on redox and sulphur retention, on fining, on the melting and forming behaviour, workability and the physical and chemical properties of the melt. Such issues were discussed by the authors in their presentations at the first Forum on Water in Glass, organized in 1997 by Technical Committee 14 (TC 14 "Gases in Glass") of the International Commission on Glass (ICG). The present paper reports the conclusions of the final discussion, highlighting the issues on which consensus was reached (IR spectroscopy is suitable to monitor the water content; the water content of conventionally fired containers is 300 to 400 ppm and daily oscillations are moderate; water, redox and sulphur interact mutually; water lowers the viscosity; the influence of water content variations on the radiative thermal conductivity is moderate) and the still controversial issues (influence of water and hydroxides in the batch on the final water content; influence of water in the batch and atmosphere on the redox state of the glass; influence of oscillations of OH level on the workability; influence of OH level on ease of forming, product quality and strength).

Strukturell eingebundenes H₂O in Kalk-Natronsilicatglas – Einfluß auf das Schmelzen, die Formgebung und die Eigenschaften: Stand des Wissens und offene Fragen

Die Arbeit ist eine Darstellung des Stands der Kenntnisse über den Wassergehalt des Kalk-Natronsilicatglases, die Einflußgrößen, die den OH-Gehalt bestimmen und die Auswirkung des Wassergehalts auf den Redoxzustand und den Sulfatgehalt, die Läuterung, das Schmelz- und Formungsverhalten, die Verarbeitbarkeit und die chemischen und physikalischen Eigenschaften der Schmelze. Solche Themen wurden von den Autoren in Einzelberichten erörtet im Rahmen des ersten Forums über Wasser im Glas, das 1997 vom Technical Committee 14 (TC 14 "Gases in Glass") der International Commission on Glass (ICG) veranstaltet wurde. Die vorliegende Arbeit faßt die Schlußergebnisse der Debatte zusammen und hebt die Themen hervor, über die ein Konsens erreicht wurde (IR-spektroskopische Messungen eignen sich zur laufenden Kontrolle des Wassergehalts; der Wassergehalt von konventionell erschmolzenen Flaschen ist 300 bis 400 ppm, mit geringfügigen täglichen Schwankungen; Wasser, Schwefel und der Redoxzustand sind in stetiger Wechselwirkung; das gelöste Wasser erniedrigt die Viskosität; der Einfluß von Wassergehaltschwankungen auf die Strahlungswärmeleitfähigkeit ist gering). Die noch umstrittenen Themen werden ebenfalls behandelt (Einfluß von Wasser und Hydroxyden im Gemenge auf den Restwassergehalt im Produkt; Einfluß von Wasser im Gemenge und in der Schmelzatmosphäre auf den Redoxzustand des Glases; Einfluß von Schwankungen des OH-Niveaus auf die Verarbeitbarkeit; Einfluß des OH-Niveaus auf die Formgebung, Qualität und Festigkeit des Produkts).

1. Historical background: ICG TC 14 and the Forum on Water in Glass

In the last decade the interest of Technical Commitee 14 (TC 14 "Gases in glass") of the International Commission on Glass (ICG) has often focused on water in glass: two round robins for the determination of the water content of various glasses were performed and proposals for a standardized procedure for water analysis based on room temperature infrared (IR) spectroscopy were considered.

Franco Geotti-Bianchini; John T. Brown; Anne J. Faber; Heiko Hessenkemper; Sho Kobayashi; Ian H. Smith:

On 9 June, 1997 in Växjö (Sweden) TC 14 organized the "Forum on Water in Glass" during the conference "Fundamentals of Glass Science and Technology" of the European Society of Glass Science and Technology (ESG).

The aim was to highlight the technological relevance of water in glass, to improve exchange of information and co-operation between experts and to better define some critical areas where the present knowledge was not fully satisfactory. An Organizing Committee including F. Geotti-Bianchini (Forum chairman); A. J. Faber; H. Kobayashi and I. Smith (TC 14 chairman) finalized the program and designated the invited speakers. The Forum was attended by 50 participants from 15 countries. The following presentations were dedicated to the water content of soda-lime-silica glass and its influence on properties:

F. Geotti-Bianchini (SSV, Murano, Italy): Water content of industrial soda lime glass and influence on viscosity, workability, high temperature absorption and heat transfer [1];
H. Hessenkemper (University of Freiberg, Germany): Influence of water in glass on melting, forming and glass properties [2];
A. J. Faber, R. Beerkens, P. Laimböck (TNO, The Netherlands): Influence of oxy-fuel atmosphere on redox state and melting of industrial glasses [3];
J. Brown (Corning Inc., USA) and H. Kobayashi (Praxair Inc., USA): Benefits of high water content in glass. Industrial experience and theoretical considerations [4].

Essentially, the presentations covered the following issues:

- water content of industrial soda-lime-silica glass (mainly containers and float) and the factors that influence it;
- correlations between the water content, redox conditions and sulfate addition;
- possible influence of the water content on the fining behaviour, the melting behaviour, the forming behaviour, workability and physical properties.

No proceedings of the meeting were published. This paper was produced, at the request of TC 14, in order to summarize and to record the outcome of the discussion, highlighting both the consensus issues and the issues on which no full agreement could be reached in the course of the discussion.

2. Introduction

Soda-lime-silica glass articles include containers, float glass, tableware, technical glass, fibers and decorative articles. It has been known since the sixties that the hydroxyl content of the melt has a significant influence on its spectral absorption, viscosity and other physical properties. Therefore, in principle one can predict that variations of the OH level may affect both the melting and the forming behaviour of industrial glasses. However, for many decades the only available literature was dedicated to experiments on laboratory melted glasses. Only recently have some authors focussed their attention on the water content of industrial glass with the aim of investigating some production problems called by engineers "bad workability" or "unsteady forming behaviour" and to understand the melting and forming behaviour of oxyfuel fired glass with its high OH level [5 to 10]. The Forum on Water in Glass offered the chance to discuss these issues, presenting new evidence about current research.

3. Consensus issues

There was general agreement on the following issues.

3.1 IR spectroscopy is suitable to monitor the water content.

The water content of a given glass can be determined by IR spectroscopy [11], by various degassing procedures [12 to 14], by Nuclear Magnetic Resonance [13, 15 and 16] or by Nuclear Reaction Analysis [14, 16 and 17]. At present the latter methods appear to be more suitable for basic research or for the determination of extinction coefficients for spectroscopic measurements. The vast majority of studies dedicated to industrial soda-lime-silica glass are based on IR spectroscopy: a technique which is reproducibile, easy to use and suitable for routine control. In [17] a standard IR spectroscopic procedure recommended by TC 14 is described. Water is incorporated in the glass structure as hydroxyl or silanol, $Si-OH$, groups. In this study its concentration is expressed in terms of parts per million water by weight.

3.2 The water content of industrially produced, conventionally fired soda-lime-silica glass ranges between 300 and 400 ppm. Oscillations within a given production are moderate.

The saturation solubility of water in soda-lime-silica glass is about 1200 ppm [18]. Container glass, float glass and household and technical glass melted in furnaces heated by the combustion of gas (or oil) and air contain between 300 and 400 ppm. For a given batch and tank the water content of the final article is mainly the result of equilibria reached at the hot spot. This is reasonable in view of the fact that in industrial tanks the melt/atmosphere exchanges are promoted by convection, whose extent increases with temperature.

According to Kobayashi [4], the final water concentration results from a dynamic balance of water originating from the atmosphere and diffusing through the melt

surface (which is dependant on the production rate and melter area) and water losses due to stripping (whose extent is proportional to the volume of fining gases released). The water content changes drastically when the melting atmosphere (in particular the water partial pressure) changes, e.g. in the case of electrical or oxyfuel melting (with 150 to 200 and 500 to 600 ppm, respectively) [1, 3, 4 and 7]. This however has no drastic consequences because the machine operation can be adapted to the different situation when the whole firing process is modified. Tricky situations may arise when sudden changes occur (within hours) on a given line. Sudden oscillations of the order of ± 100 ppm water would be very dangerous, therefore Geotti-Bianchini investigated if they may occur in practice [1, 7]. Extensive monitoring of industrial cases shows that for a glass produced in a given furnace with a given colour and redox state the water content does not oscillate significantly with time (± 10 ppm daily) in spite of variations in pull rate, furnace temperature, atmospheric humidity, cullet quantity and type added. Also the OH level of industrial articles produced at a given time from various feeders of a given furnace is extremely consistent (± 5 ppm), even when each line is differently conditioned. This suggests that when a given OH level is reached at the hot spot, little change occurs during glass cooling, probably due to a significantly reduced convection flow when compared to the melter.

3.3 The water content, redox conditions and sulphur chemistry interact mutually.

The water content of sulphate-fined glass varies mainly as a function of the redox state, reaching a maximum at the minimum of solubility of sulphur compounds, i.e. at the border between oxidized glasses (which contain mainly sulphates) and reduced glasses (containing mostly sulphides and the amber chromophore). This conclusion was reached independently by Geotti-Bianchini and De Riu [7] who studied a variety of container and float glasses melted from batches with widely ranging redox conditions and by TNO researchers on the basis of melting experiments of sulphate-containing batches in various melt atmospheres [3 and 19]. Different chemical mechanisms are invoked by the two groups in order to justify the observed interactions between water, redox and sulphur compounds.

Geotti-Bianchini and De Riu [7] explain the observed behaviour with a mechanism originally described by Hanke and Scholze [20], assuming that while sulphur escapes from the melt in gaseous form (both in reducing and oxidizing conditions) water from the atmosphere is incorporated into the melt.

Faber et al. [3] observed the fining and gas content behaviour of sulphate-fined glasses with different redox states and colours (flint, green and amber) melted in atmospheres with widely ranging H_2O contents. The water

partial pressure in the atmosphere influences the sulphur retention and redox equilibria in the melt. An increase of p_{H_2O} promotes sulphur losses, regardless of the redox conditions, so that oxidized glasses become more reduced and reduced glasses more oxidized. The mechanism proposed by Faber is based on detailed studies of bubble and foam growth, supported by a thermodynamic based model of bubble formation and evolution developed by Laimböck [19]. According to this model in sulphate-fined glass the exchanges with the atmosphere are particularly active in the foam layer formed as the batch melts.

3.4 The water content lowers the viscosity.

According to a literature review by Geotti-Bianchini and De Riu [7] in the range between $10^{7.6}$ and 10^{13} dPa s an increase of the water content by 100 ppm decreases the viscosity, lowering the isochomal temperatures by 2 to 4 K. According to recent experimental measurements by Faber [3] on amber glass melted electrically and with oxyfuel ($+600$ ppm H_2O) the decrease of T_g was 1.1 K/100 ppm. Geotti-Bianchini and De Riu measured a similar viscosity decrease (1.3 K/100 ppm) for flint glass melted with conventional gas and oxyfuel/gas ($+225$ ppm H_2O) [1 and 7]. The lower than expected values of the viscosity decrease are probably in agreement with the fact that further water additions to "wet" glass produce smaller effects than the first additions to "dry" glass [7]. In the range up to gob forming and melting temperatures (down to 10^3 and 10^2 dPa s, respectively) there is a lack of published evidence. Experiments in this range performed with controlled atmosphere to avoid changes of OH level by interdiffusion during the test were reported by Faber [3]: the decrease of the isochomal temperature between 1000 and 1200 °C was between 1.5 and 3 K/100 ppm.

3.5 The influence of water content variations on the radiative thermal conductivity is moderate (within some percent).

The high temperature spectral curves of industrial soda lime glass are described by Endrys et al. [9] and by Blazek [21]. The spectral absorption coefficient α_λ (in cm^{-1}) is defined by the equation:

$$\alpha_\lambda = \frac{1}{d} \ln(\tau_0/\tau_\lambda) \tag{1}$$

where d is the sample thickness in cm; τ_λ the measured spectral transmittance; and τ_0 the spectral transmittance of a sample with $\alpha_\lambda = 0$.

The spectral behaviour changes with temperature. Above T_g the melt structure becomes more open and consequently the absorption bands of the chromophores change. Considering the complexity of the spectral curves, it is useful to summarize the tendency of the melt to transmit energy by radiation with the help of a single parameter obtained by integrating the whole curve, i.e. the radiative thermal conductivity, k_r, defined as:

$$k_r = \int \frac{1}{\alpha_\lambda} \frac{dP_\lambda}{dT} d\lambda \qquad (2)$$

where α_λ is the spectral absorption coefficient, P_λ Planck's radiation function, dP_λ/dT its derivative versus temperature, and λ the wavelength.

The purpose of k_r is to quantify the glass transparency with a single parameter. For a clear, a half-white and a dark green container glass with increasing iron contents at 1200 °C the k_r values are respectively 150, 10 and 5 W/(m K). The relevant spectral range is 0.4 to 4.5 µm. Beyond this wavelength the whole silicate network absorbs and the absorption coefficient is assumed to be infinite, regardless of glass composition, while below 0.4 µm the value of the weighting function dP_λ/dT is negligible. For container glass the main chromophores within this range are Fe^{2+}, Cr^{3+} and OH. In order to correctly appreciate their relative relevance, it must be noticed that in equation (2) the absorption coefficient appears as $1/\alpha_\lambda$. In a plot of α versus λ for a clear glass, with a low iron and chromium content, the most significant feature is the presence of the hydroxyl bands between 2.6 and 4.5 µm (with α = 3 to 4 cm^{-1} as compared to less than 1 cm^{-1} in the 0.4 to 2.6 µm range). Apparently one would expect that the influence of a given variation of the OH bands will cause major variations of the k_r value. However, in plots of $1/\alpha_\lambda$ versus λ the situation is reversed: for a good part of the relevant spectral range (i.e. between 0.4 and 2.6 µm) the value of $1/\alpha_\lambda$ is larger than in the OH band range (2.6 to 4.5 µm) and therefore the influence of variations of OH bands on the overall k_r value is less dramatic than expected. According to Endrys, Geotti and De Riu [9], at 1200 °C an increase of the water content by 150 ppm decreases the k_r value by 0.4 % for clear glass (Fe_2O_{3tot} = 0.03 wt%), by 3 % for a half-white glass (Fe_2O_{3tot} = 0.16 wt%) and by 4−5 % for coloured glasses (green, amber and yellow-green, $Fe_2O_{3tot} \geq$ 0.3 wt%). In view of the wavelength dependence of the weighting function dP_λ/dT (with a maximum shifting towards smaller wavelengths as temperature increases), the relative variations of k_r values brought about by a given OH content increase decrease as temperature increases.

Therefore, the effects of OH level variations are more relevant at forming than at melting temperatures. According to Faber [3] at 800 °C for amber glass a 50 % OH increase decreases the k_r value by 10 % and the difference can no longer be neglected. The calculated examples given above refer to large water content varia-

tions, corresponding to the difference between conventional and oxyfuel fired glass. Daily oscillations of OH level within a given production, which by common agreement are within ±10 ppm, cause proportionally smaller oscillations of k_r values (well below 1 %).

4. Controversial issues

The following issues can be considered as still controversial and require further studies.

4.1 Influence of water and hydroxides in raw materials and batch on the final water content

While it is well established that batch moisture influences the kinetics of batch dissolution, there is no full consensus on the influence of hydrates and moisture in the batch on the final water content of the melt. According to comprehensive experiments reported by Götz [22] such parameter responds only to the water partial pressure in the furnace atmosphere, regardless of batch moisture.

Recent experiments reported by Faber [3] and Geotti-Bianchini [1] essentially confirm the conclusions reached by Götz [22]. Faber [3] tested the influence of varying by up to 25 % the moisture content of industrial batches and observed a significant impact on carryover and flue gas emissions but no significant effect on the water or SO_3 content of the final glass. Geotti-Bianchini [1] reported some experiments introducing hydroxides into industrial batches without any significant effect on the final OH or SO_3 content. Such results are in agreement with the fact that in industrial tanks, in view of the strong convection, the exchanges with the atmosphere are particularly active and therefore tend to obliterate possible differences of OH concentration arising before the hot spot.

According to Hessenkemper [2] the introduction of up to 1.5 wt% calcium hydroxide in the batch of flint glass caused an increase in water content by up to 50 ppm (over several months), modifying the flow patterns, melt temperatures and energy consumption. Moreover, in a recent study of viscosity oscillations in the feeder the instability of forming behaviour observed was attributed by Roger, Hessenkemper, Roth [23] to the unsteady OH content of recycled filter dusts with excess hydroxides.

According to Kobayashi [4], even for a constant water content in the final glass, the OH level of the melt may vary along the line. This hypothesis should be checked by sampling glass at different stages of the melting process along the furnace. Further investigations (including an accurate monitoring of how the OH level responds to batch ingredients) are necessary to clarify the exact role of hydroxyls in influencing both the viscosity and the melt behaviour from doghouse to gob.

On the other hand, according to reports by Geotti-Bianchini [1] and Hessenkemper [2] there is agreement on the conclusion that the addition of foreign cullet is

not directly correlated with the final OH content in industrial melts. A significant correlation with the amount of cullet added was observed only when the organic contamination of cullet influenced the iron redox ratio and the sulfate content [1].

4.2 Possibility that the redox conditions of the glass may be influenced by the H₂O concentration in the batch, atmosphere and the glass

Some recent papers suggest that during the initial stages of melting, water in the batch and atmosphere may exert a direct reducing action on ferric ions [24 and 25], independant of contributions due to the presence of sulphur compounds. If confirmed, this mechanism would explain the redox state and colour instabilities often observed in conjunction with the use of hydroxides by Roger, Hessenkemper, Roth [23] and which Krauß et al. [26] attribute instead to the concurrent use of foreign cullet with an unsteady reducing power due to organic impurities.

According to Hessenkemper [2 and 8] the introduction of hydroxides into an industrial batch modified the sulphur and Fe^{3+} content of amber glass, causing colour instability. According to Kobayashi [4] no direct reaction between OH and Fe ions takes place, however water vapour influences the carbon and sulphur losses. In this context the oxidizing effect of atmospheres rich in water vapour on reduced glasses reported by Faber [3] is explained by Kobayashi [4] with a mechanism of carbon loss associated with the reaction:

$$H_2O + C \rightarrow CO + H_2 \,.$$
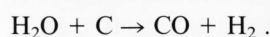
On the basis of melting experiments with atmospheres reproducing the electrical, gas/air and oxyfuel firing, Faber [3 and 19] concluded that the much larger water partial pressure of oxyfuel-fired furnaces exerts a slightly reducing effect on oxidized glasses and an oxidizing effect on reduced glasses. The most spectacular effect is associated with sulphur losses, causing loss of amber colour due to removal of S^{2-}.

The mechanism is based on a model describing bubble evolution and predicting that the partial pressures of both SO_2 and O_2 decrease as a result of dilution with water vapour. According to this model the influence of water in the atmosphere on the final redox conditions is a secondary effect due to its influence on sulphur chemistry and fining, not associated with direct redox interactions of water with polyvalent ions.

4.3 Influence of variations of the radiative thermal conductivity produced by oscillations of OH level and redox on workability

In spite of decades of investigations, there is still no consensus about the best way to describe in scientific terms "workability problems", erratic variations of glass quality, strength and forming behaviour occasionally oc-

curing in container production. According to the theory of the "thermal history of glass" some uncontrolled variable in the melting process (batch, time/temperature schedule, atmosphere) occasionally alters some physicochemical parameters of the melt (e.g. colour and radiation conductivity, redox state, dissolved gases including water, chemically inhomogeneous layers, microparticles and phase separation) and therefore its rheology. According to the "technological" theory described by Geotti-Bianchini [10], no significant changes take place in the melt and workability problems occur due to poor reproducibility of the forming and handling process (temperature distribution in the feeder and gob, machine operation and timing, mould lubrication, on-line handling).

In the framework of a comprehensive research program Geotti-Bianchini [1] tried to find evidence of the "thermal history" theory by collecting a wide range of problematic and control samples and by comparing their physicochemical parameters, in the expectation that the differences would be larger than the normally observed oscillation range. Analysis of samples from the "good" and "bad" workability periods highlighted differences in chemical composition, OH level, redox state, colour and presence of inhomogeneous layers always within the variation range normally accepted for production sampled from a given line at different times [7]. In particular, the differences in water content and Fe^{2+}/Fe_{tot} ratio were within 10 to 20 ppm, respectively within 0.005, corresponding to differences of isochomal temperature well within 1 K in the forming range and of radiation thermal conductivity well within 1 %. In conclusion, no evidence confirming the theory of the "thermal history of the glass" was found by studying workability problems [1 and 7]. Therefore, the production problems observed are likely to be associated with poor control of the forming technology.

Geotti-Bianchini also reported the results of a mathematical model, dynamically describing the forming process, developed by Dall'Igna [1 and 27]. The model was applied to two glasses with identical chemical composition and colour, having different spectral behaviour in the range 2.6 to 4.5 µm, corresponding to a purposely exaggerated OH increase of 500 ppm. The difference in the cooling time (calculated time from gob to finishing mould) was within 0.02 s, i.e. much smaller than the differences caused by changing the glass colour from green to amber (0.1 s) and comparable to the differences caused by the above-mentioned commonly accepted oscillations of glass composition [28].

According to Hessenkemper [2], in container production even small differences of OH level and redox can cause catastrophic consequences due to a range of "multiplication" effects. A mathematical model of the forming process shows that for a constant machine setting even small changes of the radiation thermal conductivity may cause small but detectable temperature differences in the mould (modifying both the stresses

and the stress relaxation rates in the glass surface and ultimately the extent of surface damage and strength) and in the glass (affecting the viscosity and therefore the final wall thickness). If the forming process is analyzed dynamically, for short times even small differences of heat transfer rate may cause large temperature (and therefore viscosity) differences. Some production processes are more tolerant, others (particularly fast jobs on light containers) may easily fall into a critical range. The above described mechanism of the forming process is supported by some experimental evidence collected by measuring the surface temperature of moulds with fast pyrometers and the temperature, OH and Fe^{2+} content of the melt flowing in feeders thanks to a combination of IR and pyrometric sensors [2 and 8]. According to experiments performed by Hessenkemper in industrial plants [2], an increase of the OH content may in some cases be beneficial for the production speed by increasing the cooling efficiency, in other instances it may cause process instability, bringing the system closer to critical situations.

Finally, Hessenkemper [2] recalled the experience of Yue and Brückner [29], who analysed in detail the chemical and rheological aspects of a case of poor workability. The differences between the "good" and "poor" workability sample were comparable to the daily occurring oscillations: 2 ppm OH and 0.04 for the ratio Fe^{2+}/Fe_{tot}. Such differences were predicted to cause catastrophic variations of the critical deformation rate, in qualitative agreement with systematic studies of the influence of large variations of redox state on melt rheology published by Hessenkemper, Brückner [30]. Moreover, on the basis of measurements with the Sheljubskii-Christiansen technique, the "poor workability" sample was shown to have a worse chemical inhomogeneity, a further factor which according to Yue and Brückner [29] might affect rheology.

In summary, in spite of the general agreement on the typical oscillation levels of Fe^{2+}, OH, k_r and chemical composition observed, opposite conclusions are reached by different authors as concerns their influence on the process variability. It is necessary to check the accuracy of the models and to improve the knowledge of high temperature properties. Moreover, once shown with experiments based on samples with extreme differences of OH and Fe^{2+} content and colour that such parameters can influence rheology [30], the next more difficult task will be defining acceptable oscillation levels, above which the forming behaviour can be upset. The influence of chemical inhomogeneities detected by the Sheljubskii experiments on rheology is still to be defined.

4.4 Influence of water content on ease of forming, product quality, glass strength. Physical properties other than spectral absorption and viscosity.

The modifications of production conditions and glass quality achieved when the melting process changes from conventional gas/air combustion to oxycombustion are described by various authors [4 to 6]. Brown and Kobayashi [5] reported improvements in process stability and pull, higher IS machine speed with good workability, improved ease of forming for difficult shapes, more efficient heat transfer to moulds and plungers, longer plunger life, less defects, shinier article surface and faster grinding and cutting with less breakage. Brown [6] attributed these improvements partly to the well-known variations of OH level, fining, spectral properties and viscosity and partly to changes of other physical properties such as latent heat and surface tension. The improved, faster forming behaviour is attributed to the diffusion-driven loss of OH from the outer surface layers during gob forming, causing a localized viscosity increase which improves the shape-holding capability ("skin effect of the gob") [6]. Such reports [5 and 6] are based on qualitative, empirical observations, supported by hypotheses based on OH level induced changes of physical properties postulated on the basis of literature reports. For a complete understanding of this issue more experimental data should be available about the changes of physical properties produced by OH level increases. At present besides the influence on viscosity, spectral absorption curves and radiation heat transfer, in the recent literature there is a lack of data about heat capacity, surface tension and surface concentration gradients. Geotti-Bianchini et al. [31] tried to obtain experimental evidence of Poole's skin effect theory by analysing with surface-sensitive techniques the near surface of the gob: the changes of chemical composition in terms of oxides versus bulk were quite moderate and confined to the outer 50 nm, hardly a thickness sufficient to modify the forming behaviour. A similar study should be performed on the H (or OH) depth profiles.

According to Faber [3] only a slight increase of the glass surface tension (within error) and no effect on the quality of production was observed in conjunction with the introduction of moistened batch. According to Faber [3] and Brown [4], no major effects of oxyfuel firing on the practical mechanical strength of containers were observed.

In this context, Hessenkemper [2] pointed out the influence of OH content changes on the heat transfer rate discussed above, affecting the temperature distribution, temperature gradients in the melt and convection cells due to density gradients during melting and quality and productivity during forming.

5. Conclusions

In the course of the discussion agreement was reached on several issues:

- The water content of conventionally fired soda-lime-silica glass is 300 to 400 ppm.
- The OH level increases to 500 to 600 ppm in case of oxycombustion and decreases to 150 to 200 ppm for electrical melting.

- For a given firing process (electrical, gas or oxyfuel) the main factor influencing the water content is the mutual interaction between water, sulphur and redox-active components in the glass.
- The theoretical (maximum) water content of a given glass melt (in equililibrium) is determined by the water vapour concentration in the atmosphere. The melting behaviour of the glass, characterized by batch melting kinetics, foaming behaviour and convection patterns, determines how far this equilibrium is reached in industrial furnaces.
- Furthermore, consensus was reached on the fact that daily water content oscillations are moderate (generally within ± 10 ppm), corresponding to moderate variations of the isochomal temperatures (≈ 0.1 K) and to moderate variations of the radiation thermal conductivity (within 0.1 %).

No full consensus was reached on some other issues:
- influence of water and hydroxides in the batch on the final water content and the redox state of the glass;
- influence of the OH (and Fe^{2+}) content of the melt on the forming behaviour (in particular radiation heat exchange), product quality and strength.

It is not an easy task to understand general laws and chemical reactions by analysing the glass melting process which is dynamically exposed to a range of temperatures and atmospheres. In particular, the production of container glass must accommodate large variations of raw materials (cullet, filter dusts) and pull. Many observed effects, such as fining, forming and strength problems can have a variety of alternative explanations. On the other hand, much ingenuity is required in order to plan laboratory experiments or computer models that can simulate the complexity of industrial reality.

For a more complete understanding of the still disputed issues further work still needs to be done, in particular the high temperature properties should be better investigated and the models improved.

6. References

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