REDOX AND SULPHUR REACTIONS IN GLASS MELTING PROCESSES

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For about 95 wt.% of all industrially produced glasses, sulphate is added to the batch for several reasons, the most important task of sulphates is to remove small bubbles and seeds from the melt. The chemistry of the sulphates during heating of the batch and melting determines the foaming behaviour, the fining efficiency and the final colour of the glass product.

Fluctuations in sulphate addition and redox state of the batch ingredients including recycled cullet, may lead to changes in glass colour even beyond the required specifications. The paper describes the chemistry of sulphur species during batch melting and glass melt fining. The impact of process conditions and the batch composition on the redox state and sulphur reactions in the batch blanket and molten glass will be shown. These reactions and the redox state of the batch will determine the efficiency of bubble removal and the final colour of the glass product.

INTRODUCTION

During the heating process of a mixture of glass forming raw materials, chemical reactions, involving decomposition of carbonates and reactions between raw material grains, take place which lead to the formation of primary melts.

During further heating of the batch, most raw material grains such as sand or alumina compounds react with these melts or dissolve in the primary melts until all components are completely molten.

Some raw materials or contaminants in the batch react with other raw materials absorbing or releasing oxygen. Such reactions are called redox reactions.

Reducing components will absorb oxygen from other compounds in the batch or melt: polyvalent ions will be converted to the reduced forms, for instance sulphates will react with a reductor into sulphur dioxide, sulphur or sulphides and ferric iron can be reduced to ferrous iron. Since, the valency state of polyvalent ions determines the transmission spectrum of the glass and the availability of oxygen during melting and fining, the presence of reducing agents in the batch will effect the rate of degassing and the colour of the glass product.

The redox state of a glass product can be characterized by the ratio of ferrous/ferric iron or the sulphate or sulphide residue in the glass. This redox state depends on:

- redox state of the batch [1 - 3], determined by the presence of reducing agents such as: carbon, sulphides, ferrous iron, organic contaminants, metals or by the level of oxidants in the batch, examples are: nitrates, sulphates, antimonates, arsenates, cerium(IV) oxide.

- the maximum fining temperature: generally residual sulphur concentrations will decrease as fining temperatures increase, this is especially the case for oxidized melts;

- the redox of the furnace atmosphere: gases may react with the batch ingredients during batch heating. Reducing gases will substract oxygen from a batch consisting of coarse grains and cullet. Oxygen infiltration may oxidize reducing batch components during the heating stages;

- the water vapor pressure (p_{H_2O}) in the furnace atmosphere: during batch heating and during fining, large amounts of water infiltrate the batch or melt. This water will indirectly effect the release of reducing or oxidizing gases or sulphur components from the batch or melt and therefore water vapor influences the redox state and sulphur residue in the glass product;

- the glass composition: the presence of sodium in most glass melts will increase the sulphate solubility [3, 4], the sulphate residue in the glass products increases also with the basicity [5] of the glass composition. An increase of the Na_2O content by 1% on expense of the SiO_2 content in a container glass composition, may increase the sulphate residue relatively by 25%.

The redox state of the final glass product, expressed as iron redox ratio: Fe^{2+}/Fe^{3+} is a function of $(T_{max}$, redox batch, p_{H_2O}, $[Na_2O]$ in the glass, basicity, batch grain size) but also the sulphate or sulphide retention depends on the same factors.

This paper will describe laboratory tests for investigating the sulphate and redox chemistry during batch melting and fining of the melts, using glass melt oxygen (equilibrium) pressure sensoring, evolved gas analysis (CO, O_2, SO_2, S_2 release) and the analysis of residual sulphur in the glass after melting at different conditions.

THEORETICAL BACKGROUND ON SULPHATE CHEMISTRY IN GLASS MELTING OPERATIONS

Sulphur, most often in the most oxidized form as sulphate, is added on purpose to the raw materials to aid the removal of dissolved gases and small seeds from the glass melt or to oxidize the melt. Addition of sodium sulphate to a glass forming batch enhances melting kinetics also by the formation of early melting phases in the batch blanket with a low surface tension, this low surface tension will improve the wetting of the silica sands by the early formed agressive melts.

In some glasses, a certain level of sulphate retention is required also, because it is expected for instance to reduce the breakage frequency of glass fibers during drawing.

In amber glass, sulphide is necessary to form together with the most oxidized form of iron: Fe^{3+}, the iron(III) sulphide, amber chromophore: $Fe^{3+}-S^{2-}$, absorbing light predominantly at wavelengths of about 410 - 420 nanometer [6] and giving the glass the typical amber-brown color.

Sulphates are added as sodium sulphate, calcium sulphate or filter dusts originating from flue gas filters, located downstream scrubbers. Sulphur compounds such as SO_2 and SO_3 in the flue gases are absorbed by soda or lime based powders injected in these scrubbers. The filter dusts contain among other components, sulphates such as sodium and/or calcium sulphates. But in some cases, sulphur compounds are impurities in the raw materials or sulphur is added as sulphide in the form of blast furnace slags (from iron / steel production) or as pyrite.

A very small amount of sulphate added to the batch will react with the sand grains forming sodium silicates and SO_2 gas at temperature levels of 800 - 1000 °C.

At very oxidizing conditions the rest of the added sulphate is very stable until very high temperatures have been reached. For instance, without any reducing component in a soda-lime silica batch (similar to tableware, or oxidized float glass or very oxidized flint glass batches) in air-fuel fired glass furnaces, thermal sulphate decomposition at initial SO_3 levels < 0.5 wt.% starts only at temperatures above 1450 °C. Higher water vapor pressures as encountered with oxygen firing, will decrease the sulphate decomposition onset temperature by about 30 - 50 °C when melting these oxidized batches.

Batches containing reducing components, such as carbon compounds, ferrous iron (Fe^{2+}), organic contaminants, sulphide containing slags and sulphides will release much more gaseous sulphur components in the temperature range of 900 - 1400 °C. In the vicinity of reducing components, sulphur can be present not only as a sulphate in the S^{6+}-state but also as S^{4+} (SO_2), S^0 (S_2) or S^{2-}, (sulphide). However, the sulphur is only stable in the batch and melt as *sulphide* or *sulphate*. In mildly reduced batches using ferrous iron or carbon compounds as reductors, a large part of sulphates will form SO_2 gas during heating of the batch blanket. The residual sulphate level in the glass will decrease by lowering the oxidation state of the batch till very strong reducing conditions are met. Then, at sufficiently reducing circumstances, the redox state allows the formation of stable sulphides in the melt which will lead to an increase of sulphur retention (as sulphide) and in the presence of some residual ferric iron, the amber chromophore will be formed in the glass during cooling [7].

Organic components added to the batch, for instance present as contamination in the recycled cullet, will partly evaporate or will be oxidized by oxygen in the batch pores or by oxygen infiltrating the batch. However, part of the organic material may form coal. Carbon compounds such as coke or activated carbon, directly added to the batch or obtained by the char formation of the organic contaminants partly reacts with CO_2 to form CO, this reaction is called the Boudouard reaction.

During the carbonate decomposition, CO_2 gas is released from the batch blanket. According to the Boudouard reaction mechanism this CO_2 gas partly reacts with:
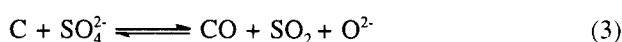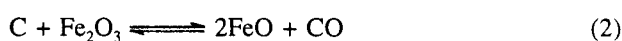a)   carbon added to the batch [8] or
b)   carbon formed by char formation from organic contaminants in the cullet:

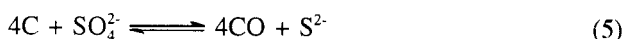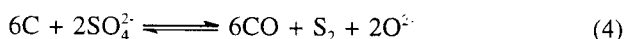$$C + CO_2 \rightleftharpoons 2\,CO \tag{1}$$

Figure 1 shows the release of gases during the heating of a soda lime silica batch containing sulphates and carbon.

The carbonate decomposition starts at about 600 °C and this reaction is accompanied by the Boudouard reaction forming CO till 900 °C. SO_2 formation starts at ± 950 °C: different stages of SO_2 release till 1300 °C can be observed from figure 1.

Carbon in a melting batch can lead to reactions as:

$$C + Fe_2O_3 \rightleftharpoons 2\,FeO + CO \tag{2}$$

$$C + SO_4^{2-} \rightleftharpoons CO + SO_2 + O^{2-} \tag{3}$$

$$6C + 2SO_4^{2-} \rightleftharpoons 6CO + S_2 + 2O^{2-} \qquad (4)$$

$$4C + SO_4^{2-} \rightleftharpoons 4CO + S^{2-} \qquad (5)$$

Similar reactions with CO can take place, in the case that CO is not directly released from the batch blanket. CO is often present in the gas bubbles in the batch blanket.

The presence of sulphide in very reduced glasses is the consequence of reaction 5.

Reactions (3-5) take place at temperature levels of 900 - 1050 °C. The first part of the SO_2 emission curve in figure 1 is caused by reaction (3) or a reaction between CO and SO_4^{2-}.
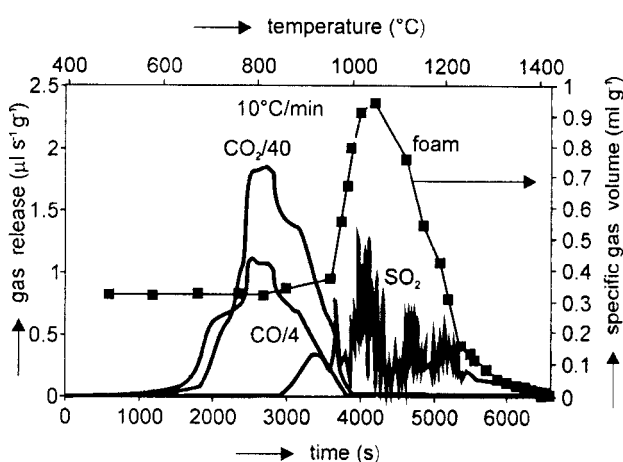

Figure 1. Gas release during the heating of a soda-lime silica batch containing sand, soda, limestone, 1 wt.% sodium sulphate and 0.2 wt.% carbon compounds.

The reactivity of the carbon compounds and temperature range at which the carbon compounds will react depends on the sizes of the powder particles and the crystalline structure of the carbon compounds. More than 50 % of the carbon compounds may react with CO_2, to form CO at temperatures of 600 - 950 °C, the directly released CO will hardly effect the redox state of the batch melt. CO in closed pores in the batch blanket reacts with sulphates and leads to SO_2 or even S_2 formation. Barton and Chopinet [2] demonstrated that the redox state and sulphate retention in the final glass depends on the size of the carbon powder: the addition of a finer coke powder instead of a coarse powder caused a lower sulphate retention and a higher ferrous iron level in the final glass.

Sulphate reacting with carbon compounds, at a sufficiently strong reducing power of the added carbon in the temperature range between 800 - 1000 °C, will lead to the formation of sulphides - reaction (5). As stated

before, also the organic contaminants in the raw materials, but especially in the recycled external cullet, may form coal or coke, which reduces the batch. Depending on the level of sulphate reduction, the sulphate/sulphide ratio can change from very large values to very low numbers.

At moderately reducing conditions and further heating, all formed sulphides will react with the excess of sulphates still present in the fresh melt. The sulphides consume not only sulphates but also dissolved oxygen present in the batch or melt or converts ferric iron into ferrous iron. The Fe^{2+}-level will increase and the oxygen equilibrium pressure will decrease at increasing sulphide levels.

The sulphate-sulphide reaction rate depends on the mixing of the sulphate and sulphide rich parts of the melt at temperature levels of 1000 - 1300 °C. Above this temperature range, only sulphate is left but at a low concentration level.

Addition of even more carbon compounds leads to the formation of larger amounts of sulphide in the batch melt, finally reacting in the mixing melt with the residual sulphate. Then sulphate retention will decrease further. During this reaction in glass melts at a viscosity of about 50 - 200 Pas, large amounts of SO_2 gas (or even S_2) gas can be formed which can produce a foam in a rather high viscous molten glass.

At a certain level of carbon (or other reductors) addition, a surplus of sulphides are formed between 700 - 1000 °C and during further heating and mixing of the sulphide rich melt with sulphate rich parts, all the sulphate will be reacting away and only sulphides will remain.

For soda lime glass batches, a sulphide excess relative to sulphate in the melt can be obtained at such strong reducing conditions that more than 70 % of the iron is available in the ferrous state. The residual ferric iron forms iron(III) sulphides in the glass, this complex is responsible for the amber colouring.

Thus, very oxidized melts need very high temperatures for the onset of sulphate decomposition required for the release of fining gases (SO_2 and O_2), consequently the sulphate retention will be very high (> 0.15 wt.% SO_3) after melting at normal temperatures. For reduced melts, most of the sulphates will react between 900 - 1300 °C (first with carbon or CO gas later with the intermediate sulphide) releasing SO_2 or S_2 gas: the sulphur retention will be very low (0.03 - 0.08 wt.% SO_3). In very reduced melt, after reactions of sulphides with sulphates, forming S_2 and SO_2 up to 1300 °C, the remaining sulphur will be dissolved as very stable sulphides and the sulphur retention can be rather high (0.05 - 0.15 wt.% SO_3 in the form of S^{2-}). At these conditions, the Fe^{3+} -S^{2-} complex will be formed during cooling [7].

OXYGEN PRESSURE IN MELT

After the main melting stages which are almost completed at 1100 - 1200 °C for a soda-lime-silica batch, the equilibrium oxygen vapor pressure of the dissolved oxygen in the melts have been measured in our laboratory using the Rapidox sensors [9]. Due to the release of oxygen at increasing temperatures, by the reduction of ferric iron or sulphate into respectively ferrous iron and SO_2 or the formation of sulphur and sulphide, the level of dissolved oxygen in the melt increases.

For almost all batches one can find an increasing oxygen equilibrium pressure (often called p_{O_2}) at increasing temperature regardless of the redox state. However, the measured p_{O_2}-level at one temperature depends very much on redox state of the prepared batch. Figure 2 shows measured p_{O_2}-values for soda-lime-silica melts containing 0.045 mol.% iron oxides, adding 1.0 wt.% sodium sulphate and different levels of carbon compounds (active carbon powder, grain sizes < 5 micrometer) to the 600 - 700 gram batches. The oxygen equilibrium pressure values were measured between 1200-1400 °C in a laboratory furnace. The crucible filled with batch is directly inserted in the furnace preheated at 1100 °C. The atmosphere is air with 1 - 2 volume % water vapor.
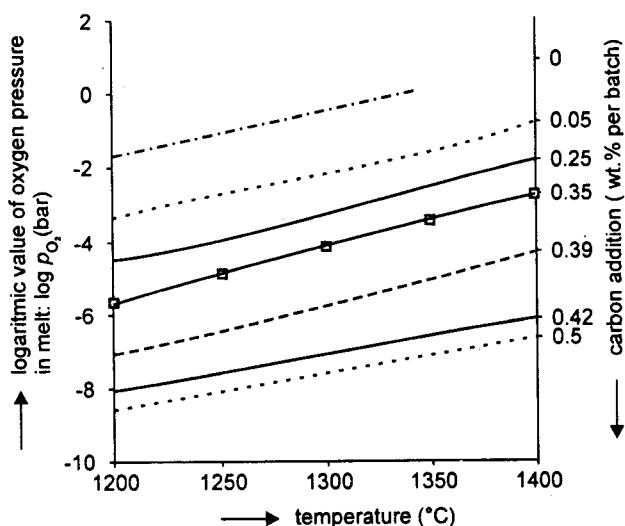

Figure 2. Oxygen equilibrium pressures measured with Rapidox sensors in melts prepared from batches with different active coal levels.
Raw materials – pure sand, pure soda and pure limestone and 0.045 mol.% Fe_2O_3 and 0 till 0.4 mol.% SO_3; coal size – 30 μm; Glass – SiO_2-Na_2O-CaO 73.0-16-10.6 mol.%

In this case, a small increase from 0.39 wt.% active coal addition to 0.42 wt.% coal, leads to a sudden drop in the oxygen equilibrium pressures measured in the melt. The colour changes from bluish green to light brown and the absorption at 415 nm increases suddenly by this small increment in active coal addition. The reducing effect of the cokes depends on heating rate, type of cokes and size of batch and coke grains.

The slope of the log p_{O_2} versus temperature curve changes also, the slope for the curves with coal addition > 0.4 wt.% is about 35 % smaller than the slope at more oxidizing conditions. This observation indicates that the increased release of oxygen when increasing temperature, is caused by a different reaction for a batch containing more than 0.4 wt.% of this carbon, compared to carbon lean batches.

For other coke types or coke grain sizes this effect might also be observed but at lower or higher levels of carbon addition. The heating rate of the batch, the mixing of the batch ingredients and infiltration of gases such as CO or water vapor from the furnace atmosphere will effect the reaction of carbon compounds during heating of the batch and thus it will determine which part of the carbon compounds (or CO) reacts with ferric iron or with the sulphates. Therefore, changes in furnace atmosphere and heating rate can influence the sulphide formation and ferric/ferrous iron ratio during batch heating and melting. This is one of the main reasons for differences encountered when comparing redox states of industrial melts, expressed as Fe^{2+}/Fe^{3+} ratio in the glass or the equilibrium pressure of dissolved oxygen with observations from laboratory melts, using exactly the same raw materials.

Figure 2 shows that a relatively small increase in carbon compound addition can decrease the p_{O_2} level with one order of magnitude. Here, the colour of the glass changes from bluish-green to light amber colour which becomes darker at further increasing carbon compound additions. Figure 3 shows the residual sulphur contents in the final glass depending on the Fe^{2+}/Fe^{3+} ratios for the melts presented in figure 2.

Note the minor influence of the iron content on sulphur retention in figure 3.

The minimum in the sulphur solubility curve is very distinct and this minimum is located at a redox state value at which sulphur is most stable as SO_2 or S_2: species which hardly dissolve in the glass melt.

The sulphate retention at the oxidized side for $Fe^{2+}/Fe_{total} < 0.65$ will decrease when temperature increases or at higher water vapor concentration in the furnace atmosphere. The sulphide retention appears to be less sensitive for temperature.

Figure 4 shows the sudden change in transmission spectra at coal additions between 0.39 and 0.5 wt.% in the batch. Without any iron, the absorption at 420 nanometers is almost zero which is explained by the absence of the iron(III)-sulphide chromophor.
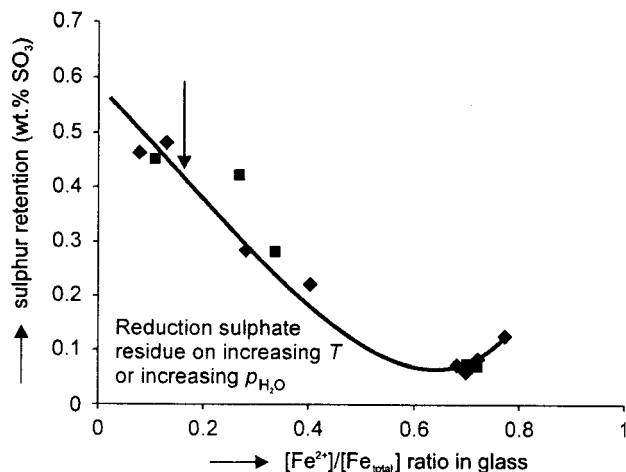
Figure 3. Sulphur retention after melting soda-lime-silica batches with sulphate addition and iron oxides (expressed as Fe_2O_3) to the batch. Melting in air at a maximum of 1400 °C.
Glass – SiO_2-Na_2O-CaO 73-16-10.6 mol.% (+ 0-0.4 mol.% SO_3); ■ + 0.135 mol.% Fe_2O_3 in glass, ◆ + 0.045 mol.% Fe_2O_3 in glass
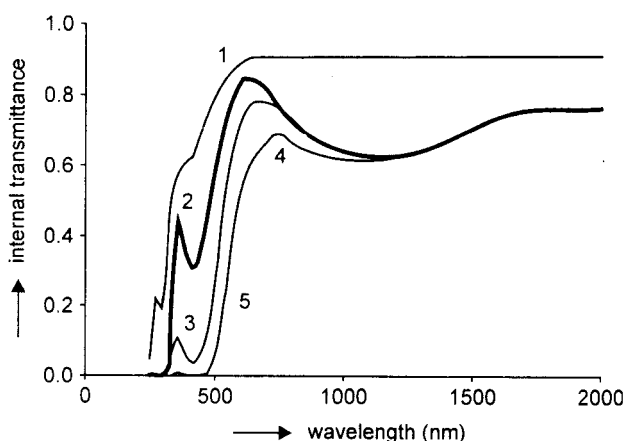

Figure 4. Measured transmission spectra of 2 mm thick glass samples prepared from sulphate containing batches and different active coal additions.
1 - 0.5 wt.% coal and no Fe_2O_3 addition; 2 - blue, 0.39 wt.% cokes and 0.045 mol-% Fe_2O_3; 3 - light amber, 0.42 wt.% coal and 0.045 mol.% Fe_2O_3; 4 - dark amber, 0.5 wt.% coal and 0.045 mol.% Fe_2O_3; 5 - dark amber, as 4 but only 50 % of the sulphate addition (curves 4 and 5 are identical)

The absorption at 1050 nanometer caused by the ferrous iron in the glass is similar for glasses prepared from the batches 3, 4 and 5, which leads to the conclusion that the ferrous iron contents in these glasses are probably similar. However, the sulphide levels are very different. The results so far, demonstrated the effect of the batch redox state on the redox state of the glass, on the oxygen equilibrium pressure of the melt, on the colour of an iron containing soda-lime-silica glass and on

the sulphate/sulphide retention. Curves 4 and 5 in figure 4 are exactly the same, thus at these cokes levels, an increase in sulfate addition to the batch hardly caused a change in the colour of the glass. But also the maximum applied fining temperature, the oxidation state of furnace atmosphere and the humidity of the atmosphere will determine the final redox state of the glass, thus the colour and sulphate or sulphide retention.

MAXIMUM MELTING OR FINING TEMPERATURE

Chopinet and Barton [10] found a strong reduction in sulphate retention in oxidized or mildly reduced sodium borosilicate glass melts as temperature increases. However, for more reduced melts at lower Fe^{3+}/Fe^{2+} values, sulphur retention is only weakly dependent on the melting temperature.

Figure 5 shows the effect of the maximum temperature on the Fe^{2+}/Fe^{3+} ratio determined in the glasses prepared in the laboratory, using pure soda, silica sand and limestone plus 1 wt.% sodium sulphate and ± 0.1 wt.% (= 0.04 mol.%) Fe_2O_3 in the batch. Figure 6 presents for the same glasses the sulphur retention depending on temperature. The Simpson number [11] of the batch is rather high (> +20) for sulphate containing batches without reducing agents, a negative Simpson number corresponds to a batch containing relatively large quantities of coke.

At increasing temperature Fe_2O_3 is often converted into FeO, increasing the Fe^{2+}/Fe_{total} ratio.

The effect of the maximum temperature on sulphate retention is especially important for very oxidized glass compositions, at these conditions the sulphate decomposition:

$$SO_4^{2-} \rightleftharpoons 1/2O_2 + SO_2 + O^{2-} \tag{6}$$
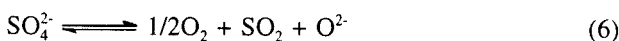
is the most important reaction. This reaction produces oxygen and sulphur dioxide as fining gases and therefore may lead to some re-oxidation of the ferrous (Fe^{2+}) iron.

In mildly reduced glasses, most of the sulphide and sulphate residues still present in the melt after the first melting stages, will react between 900 and 1300 °C by mixing of the sulphide rich parts with the sulphate rich sections of the melt. At 1300 °C only sulphate or only sulphide will be left in the melt. At further increasing temperatures the remaining sulphates or the remaining sulphides will hardly react unless very high temperatures are reached. For instance for a soda-lime-silica melt with only 0.05 wt.% SO_3 in the sulphate form, temperatures above 1550 °C are required to obtain thermal decomposition of this low level of residual sulphate. Thus temperature has only a moderate impact on sulphur retention in such reduced glass melts (redox number: about 0).
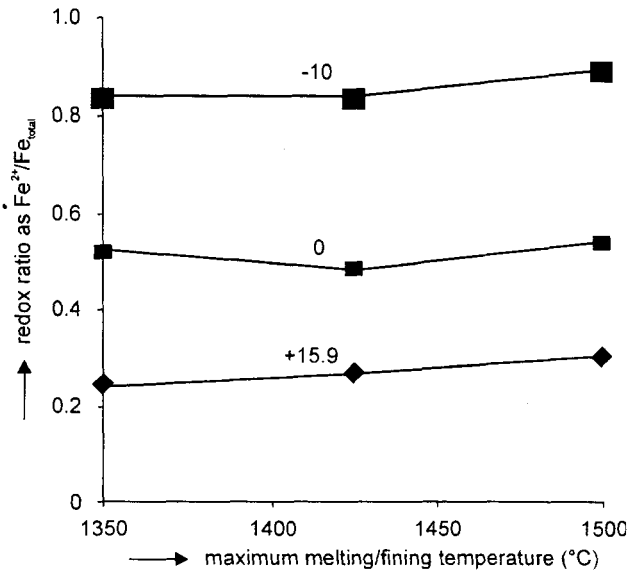
Figure 5. Redox ratio (Fe^{2+}/Fe_{total}) in soda lime silica glass depending on Simpson redox number of the batch and on the maximum temperature. Melts prepared in almost dry air. Parameter is the redox number - conditions; Glass - SiO_2-Na_2O--CaO 73.9-16-10 mol.%
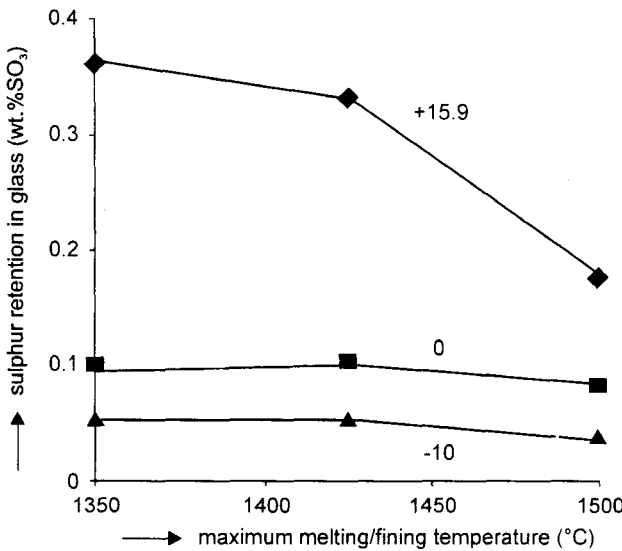

Figure 6. Sulphur retention in soda lime silica glass depending on redox state of the batch (carbon addition) and on maximum temperature.
Melts prepared in almost dry air. Parameter is Simpson number [11]. Glass - SiO_2-Na_2O-CaO-Fe_2O_3 73.9-16-10-0.1 mol.%

♦ - oxidized glasses, ■ - neutral glasses, ▲ - mildly reduced glasses

WATER INFILTRATION

Results of experimental work [3] show that during the premelting stage, water from the furnace atmosphere is partly absorbed by the first liquid phases. Water can partly react with carbon in the batch at relatively low temperatures, producing CO and hydrogen gases and therefore reducing the amount of cokes in the batch. The final quantity of absorbed water depends on the water vapor pressure and the glass melt composition. Exchange of water vapor between the furnace atmosphere and the glass melt is rather limited in the case of a motionless melt. During fining and foaming at high temperatures, water infiltration is extra promoted by the convection of the melt due the stirring action caused by the increased bubble ascension in the melt. Water infiltration (mixing of the saturated surface layers with the bulk of the melt) is also promoted by foaming and by the convection of the melt in industrial melting tanks.

In fossil fuel fired tank furnaces, the dissolved water concentration in the melt after fining, appears to be about 70 % of the saturation value. The saturation value $(C_{H_2O}^c e$ in mg water per kg glass) depends on the water vapor pressure $(p_{H_2O}$ in bar) above the melt: $C_{H_2O}^c = L_{H_2O} \cdot p_{H_2O}^{1/2}$. For common soda-lime-silica glass melting at about 1500 °C, the maximum solubility value L_{H_2O} is determined to be 1100 mg kg^{-1} glass per bar water vapor pressure, in agreement with data derived from the literature [12 - 14].

Generally, the presence of water in the melt will decrease the sulphate retention because of the following principle: The presence of dissolved water in the melt will accelerate bubble growth rates during fining because of two reasons: Dissolved water diffuses to the bubbles and will contribute directly to the bubble growth and water vapor will dilute the other gases in the bubble. The reduction of the vapor pressures of the fining gases will shift the fining reaction equilibrium given by equation (6) to the *gas producing side*.

For instance, the sulphate decomposition equilibrium constant (glass composition and temperature dependent) for constant sodium oxide activity in the melt is defined as:

$$K_S = \frac{p_{SO_2} \, p_{O_2}^{1/2}}{[SO_4^{2-}]} \qquad (7)$$

Equation (7), shows that a decrease of the partial vapor pressures p_{SO_2} or p_{O_2} in the bubbles, caused by the dilution of water vapor will cause a *decrease* in the residual equilibrium sulphate concentration: $[SO_4^{2-}]$.

The lower oxygen pressures in the bubbles and melt will increase the Fe^{2+}/Fe^{3+} ratio in the melt as well, caused by a shift of the reaction (2) to the right side:

$$Fe_2O_3 \text{ (melt)} \rightleftharpoons 2 \, FeO \text{ (melt)} + 1/2 \, O_2 \text{ (gas)} \qquad (8)$$
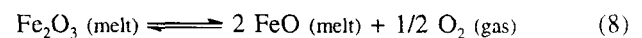
Thus at a certain temperature level, dissolved water in the molten glass decreases sulphate stability and therefore

decreases the sulphate decomposition temperature. At these temperature levels and oxidation states, water will promote the formation of oxygen by the enhanced sulphate decomposition. Small bubbles will encounter additional growth, because of this enhanced sulphate decomposition and because of the extra water dissolved in the melt, diffusing into these small seeds or bubbles.

Since water infiltration in the batch might reduce the level of residual coke in the batch it can have an oxidizing effect, but at the other hand because water can also dilute the oxygen pressure in the bubbles of the melt it can have a reducing effect after all. For more oxidized batches, a higher water vapor level generally has a reducing effect on the final glass. For mildly reduced batch compositions, water vapor may have (but this depends also on kind of reducing agent in batch and heating rate) an oxidizing effect.
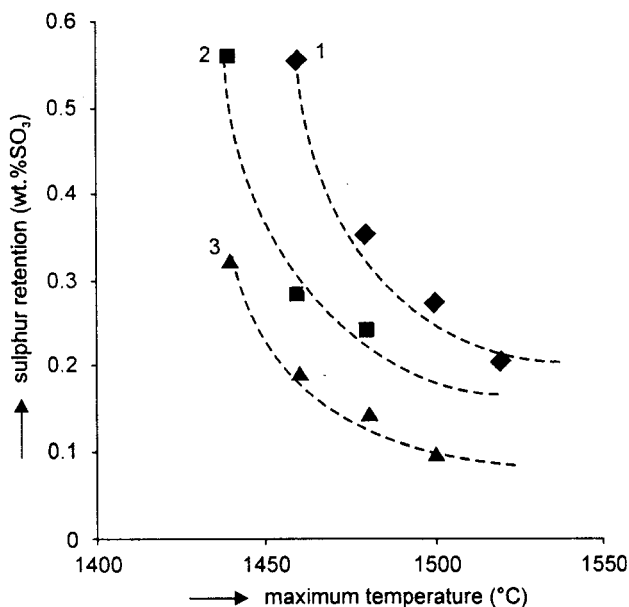
Water vapor will dilute the sulphur gas in the bubbles, and water may even react with sulphides forming H_2S gas. It is expected that the infiltration of water in these melts during melting and foaming will decrease the sulphide retention.

Figure 8 shows qualitatively the impact of water in the very reduced melt on the decrease of S^{2-} level and the Fe^{3+} concentration in this melt. Increasing water vapor level in the bubbles will decrease S_2 (or H_2S) pressure and the S_2 producing reaction shifts to the right side, consuming oxygen which may lead to an increase in the Fe^{2+} level in the melt.

Figure 9 shows measured sulphur retention after melting in dry and water vapor containing atmosphere. Generally, sulphur retention drips as water vapor pressure increases.
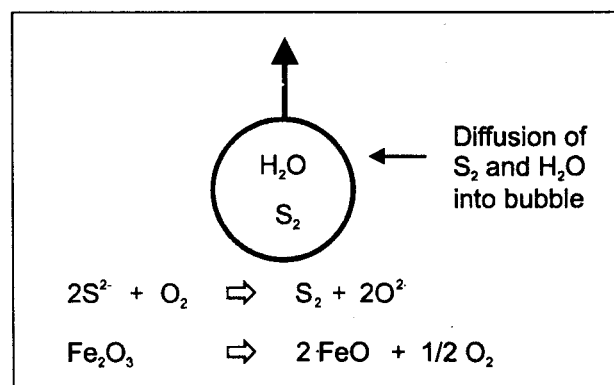

Figure 7. The effect of water vapor pressure on the sulphate retention in a oxidised soda-lime-silica glass SiO_2 - Na_2O - CaO 75 - 15 - 10 mol.%

▲ - almost dry air atmosphere, ■ - water vapor pressure = = 0.20 bar, ▲ - water vapor pressure = 0.55 bar

Figure 8. Bubble dilution by water vapor in amber glass melt.

However, at increasing temperatures, as sulphate decomposition both in dry as in water containing melts will take place during primary fining, dissolved water will decrease the oxygen pressure in the bubbles and therefore, in the case of sulphate containing batches without reducing agents, will decrease the redox state (the p_{O2} level).

In the case of strongly reduced melts, the behaviour can be different, instead of SO_2 and oxygen, gases like S_2 can be formed during the fining or degassing stage.
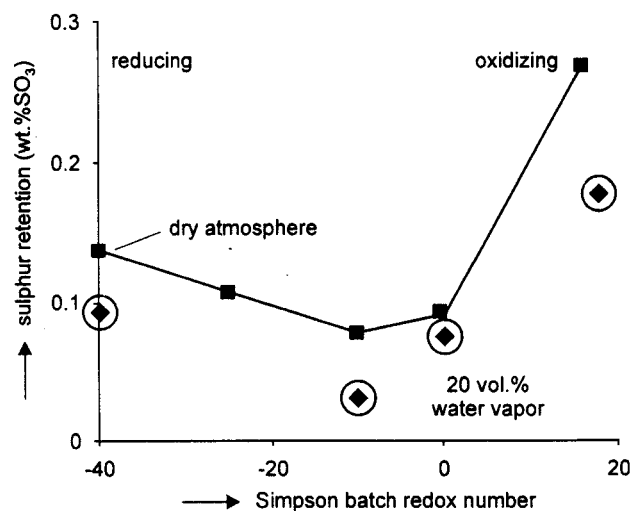

Figure 9. Effect of water vapor pressure and batch redox state on sulphur retention after melting a soda-lime-silica batch at 1500 °C.
Glass - SiO_2-Na_2O-CaO 75-15-10 mol%

INFILTRATION OF OXIDIZING GASES OR REDUCING GASES

Laboratory melting studies for mixed coarse cullet, typically applied for green glass production show for these quantities of small sized laboratory glass melts the importance of the partial oxygen pressure in the furnace atmosphere on the colour, sulphur retention and ferric/ferrous ratio in the glass product.

Table 1 shows the results of melting tests with 2 different cullet batches, some containing only fine or some only coarse cullet, with some addition of carbon compounds (active coal), molten in different atmospheres.

The fine cullet will start to sinter at temperatures above about 700 °C: the oxygen from the furnace atmposhere will hardly penetrate into the cullet mixture after this sintering process. The table shows that the colour of the glass, molten from fine cullet plus coke, in an atmosphere without oxygen will be amber due to formation of sulphides still present in the final product. The ferrous/ferric ratio exceeds the 80 % level. Exactly the same fine cullet, with carbon addition, molten in an atmosphere with a small partial oxygen pressure already becomes more oxidizing and the final sulphide level is not sufficient for full-amber colouring.

The oxidizing effect of oxygen in the furnace atmosphere is much more important for coarse cullet, even up to temperatures above 700 °C. The final glass is green, there is no or hardly any sulphide left in the glass and the ferrous/ferric ratio is relatively low compared to the glass prepared from fine cullet in the same atmosphere.

This means that the effect of the furnace atmosphere on the reduction or the oxidation of batch or cullet components, including the contaminants, depends very much on the grain sizes and cullet sizes.

Laboratory studies, melting a normal soda-lime-silica batch with grain sizes smaller than 1 mm during a few hours showed that reducing atmospheres, containing no oxygen or even CO-gas hardly influence the sulphate retention or the redox of the melt, apart from the thin top layer with a thickness of 1-3 mm which becomes more reduced. In the practice of industrial furnaces, with more convection in the melt and longer residence times, a thicker layer of melt may become reduced by reducing gases in the furnace atmosphere.

CONCLUSIONS

The sulphur and oxygen reactions in glass melts depend on a large number of factors, the most important are: the addition of reducing agents to the batch, the maximum melting/fining temperature and the water vapor pressure in the furnace during melting and fining. The fining mechanism of oxidized soda-lime-silica melts using sulphates as fining agents is based on the thermal decomposition of sulphate at temperatures above 1430 - 1450 °C. However, when adding reducing agent to the batch, part of the sulphates will react during the primary melting stages forming SO_2 gas and sulphides. At increasing temperatures the sulphate residues and formed sulphides react between 900-1300 °C forming SO_2 or even S_2 gas. This reactive fining (instead of thermal decomposition) takes place at relatively low temperatures forming bubbles at higher glass melt viscosities. This may lead to foamy melts.

In very reduced batches, almost all sulphates will be converted in SO_2, S_2 gas or sulphides. After cooling below 600 °C, the sulphide residues and the residual most oxidized state of iron (ferric iron) will form the so called amber chromophor [6].

Water infiltrating the melt during melting and foaming will decrease the sulphate and sulphide retention and especially in oxidized melts water infiltration accelerates the fining rate. Due to the lower sulphide retention and probably the extra reduction of ferric iron in water rich amber glass melts, the amber colouring might be less intensive compared to water lean amber melts.

Table 1. Sulphur retention and redox state of glass prepared from cullet at different conditions

Cullet characterization	atmosphere (bar)	SO_3 (wt.%)	Fe^{2+}/Fe_{tot} (-)	colour
1. fine cullet +0.06 wt.% C	1 N_2	0.06	0.84	amber
2. fine cullet +0.06 wt.% C	0.005 O_2 / 0.995 N_2	0.02	0.73	dark green
3. coarse cullet +0.06 wt.% C	1 N_2	0.05	0.80	amber
4. coarse cullet +0.06 wt.% C	0.005 O_2 / 0.995 N_2	0.07	0.27	green

Acknowledgements

References

1. Chopinet M.H., Massol J.J., Barton J.L.: Glastechnische Berichte Sonderband Kongreßvorträge pp. 596-601, Band 1, Hamburg 1983.
2. Barton J.L., Chopinet M.L.: Proceedings of the First International Conference on Advances in the Fusion of Glass, pp.30.1-30.8, The American Ceramic Society, New York 1988.
3. Laimböck P.: *Foaming of Glass Melts*, Thesis Eindhoven University of Technology, June 1998
4. Papadopoulos K.: Physics and Chemistry of Glasses *14*, 60 (1973).
5. Krämer F.: Glastech. Ber. *63K*, 252 (1990).
6. Douglas R.W., Zaman M.S.: Phys. Chem. of Glasses *10*, 125 (1969).
7. Müller M., Rüssel R., Kittel T.: VIS-NIR spektroskopische Untersuchungen bei hohen Temperaturen an Fe2+/Fe3+-enthaltenden Gläsern und Glasschmelzen
8. Flick C., Nölle G.: Glastechn. Ber. Glass Sci. Technol. *68*, 81 (1995).
9. Tonthat T., Ollier C.: Proc. 5th Int. Conf. Adv. in Fusion and Proc. of Glass, pp. 299-304, Toronto 1997.
10. Chopinet M.H., Barton J.L.: Collected papers of the XIV International Congress on Glass, vol.3, pp. 9-15, New Dehli 1986.
11. Simpson W., Myers D.D.: Glass Technol. *19*, 82 (1978).
12. Franz H., Scholze H.: Glastechn. Ber. *36*, 347 (1963).
13. Scholze H.: Glastechn. Ber. *32* , 314 (1959).
14. McGinnis P.B., Shelby J.E.: *Diffusion of water in float glass melts*, Report of the Centre for Glass Research New York State College of Ceramics at Alfred NY

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OXIDAČNĚ REDUKČNÍ STAV SKLA A REAKCE SÍRY VE SKLÁŘSKÉM TAVICÍM PROCESU

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Síran se přidává do vsázek přibližně 95 % průmyslově vyráběných skel. Jeho nejdůležitější funkcí je odstranit malé bublinky z taveniny. Chování síranů během ohřevu vsázky a tavení ovlivňuje pěnění, čeřicí schopnost skloviny a výslednou barvu výrobku. Nerovnoměrnost přídavku síranu do kmene a redox stav složek kmene včetně recyklovaných střepů může vést k nežádoucí změně barvy skla. Příspěvek popisuje chemické reakce síry v různých oxidačních stavech během procesu tavení vsázky a čeření skloviny. Je ukázán vliv tavicích podmínek a složení vsázky na redox stav skloviny a reakce síry ve vsázce a ve sklovině. Tyto reakce a redox stav vsázky určují účinnost čeřicího procesu a výslednou barvu výrobků.