

Impact of furnace atmosphere and organic contamination of recycled cullet on redox state and fining of glass melts

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The onset temperature of fining and the quantity of fining gases is not only determined by the amount of fining agents in soda-lime-silica batches, but also by the level of organic contaminants in the cullet or normal batch and the water vapor pressure in the furnace atmosphere. These conditions will also determine the redox state of the glass and residual sulfate or sulfide concentrations in the glass. Organic contaminants will form char during heating of the batch. This char partly reacts with CO₂ coming from the decomposition of the soda, limestone or dolomite forming carbon monoxide. Stable types of char or cokes or cullet-rich batches with only small amounts of carbonates will result in some carbon residues after the CO₂ evolution. This carbon partly reduces sulfates and ferric iron in the fresh melts. This results in sulfide and ferrous iron formation in these glass melts. At increasing temperatures in the melt, the sulfides and sulfates react together forming sulfur-containing gases between 1000 to 1250 °C. The sulfate retention decreases, finally the glass even may contain sulfur only in the sulfide form under very reduced conditions. In batches without reducing agents, sulfates in the melt start to decompose at temperatures exceeding 1400 °C. Small amounts of carbon and water vapor reduce the fining onset temperature.

Water vapor from the furnace atmosphere predominantly infiltrates the batch blanket during melting and foaming. The water will enhance the bubble and seed growth during fining. Water in the melt will influence the redox state of the final glass. Only in batches containing coarse raw materials or cullet, reducing or oxidizing gases from the furnace atmosphere infiltrate the batch blanket and these gases will respectively reduce and oxidize components like iron oxides, sulfate/sulfide or chromium oxides in the batch blanket interior.

Einfluß von Ofenatmosphäre und organischen Verunreinigungen der Recyclingscherben auf den Redoxzustand und die Läuterung der Glasschmelze

Die Anfangstemperatur der primären Läuterung und die Menge der während der Läuterung freigesetzten Gase werden nicht nur durch den Gehalt der Läuterungsmittel, sondern auch durch die organischen Bestandteile im Gemenge/Scherben und durch den Wasserdampfgehalt bestimmt. Diese Faktoren haben auch einen Einfluß auf den Redoxzustand des Glases und die Sulfat- oder Sulfidkonzentration im Glasprodukt. Organische Komponenten können Kohlenstoff während des Aufheizprozesses im Gemenge bilden. Dieser Kohlenstoff reagiert teilweise mit dem durch die karbonathaltigen Rohstoffe Soda, Kalkstein oder Dolomit freigesetzten CO₂. Stabile Kohlenstoffarten oder scherbenreiche Kalknatronglasgemenge mit nur wenig Karbonatrohstoffen ergeben nach der CO₂-Abgabe des Gemenges noch Kohlenstoffreste im Gemenge. Dieser Kohlenstoff reagiert mit dreiwertigem Eisen und Sulfat im Gemenge: in der frischen Schmelze werden Sulfide und zweiwertiges Eisen gebildet. Bei Temperaturen zwischen 1000 und 1250 °C reagieren Sulfate und Sulfide in der Schmelze miteinander, und es werden Schwefelgase freigesetzt. Die Sulfatkonzentration wird abgebaut, und unter sehr reduzierenden Bedingungen bleibt Schwefel nur noch in sulfidischer Form in dem Glas. In Gemengen ohne Reduktionsmittel fangen die Sulfate bei sehr hohen Temperaturen oberhalb 1400 °C an sich zu zersetzen. Bereits geringe Mengen an Kohlenstoff und Wasserdampf verringern die Sulfatzersetzungstemperaturen.

Wasserdampf aus der Ofenatmosphäre infiltriert das Gemenge vor allem beim Einschmelzprozeß und während der Schaumbildung. Wasser in der Schmelze beschleunigt das Wachsen der Blasen und Gispfen in der Schmelze und beeinflusst auch den Redoxzustand des Glases. Starke Oxidation oder Reduktion des Gemenges durch die Gase der Ofenatmosphäre findet nur statt bei grobkörnigen Rohstoffen oder Scherben. Nur dann können Sulfate/Sulfide, Eisenoxide oder Chromoxide im Gemenge durch diese Gase oxidiert oder reduziert werden.

Received 22 June 1998, revised manuscript 4 January 1999.

1. Introduction and objectives

The melting process of glass prepared from normal batch or batch plus recycled cullet often shows unexpected changes in redox state or in the colour and the fining behaviour, after:

- increasing the cullet ratios;
- changing the cullet source;
- conversion from air-gas/fuel oil to oxygen-gas/fuel oil firing;
- changes in burner settings and air/fuel or oxygen fuel ratios.

Currently, some important technological questions which need an answer are for instance:

- Is it possible to avoid reboil of sulfate-containing melts by proper furnace or batch composition control?
- In which way does the redox state and colour spectrum of the glass (melt) shift as the furnace atmosphere changes (important are water vapor concentration and oxygen concentration), especially important after a conversion from air to oxygen firing?
- Which parameters will stabilize the amber chromophore and why is the amber chromophore ($\text{Fe}^{3+}-\text{S}^{2-}$) in the molten glass less stable in an environment with a water vapor rich atmosphere compared to water vapor lean conditions?
- Can the fining behavior and even the nature of the fining gas in amber glass melts be explained and described?
- In which way can the glass manufacturers optimize their batch compositions and furnace operation (firing conditions, temperature, temperature profiles in furnace, etc.) for each kind of glass?

Often the colour changes dramatically, due to shifts in the redox state of the glass, displayed by shifts in the ferrous/ferric iron ratio ($\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio) (or the ratios of the valencies of other polyvalent colorizing ions) in the glass product. Also the sulfur retention, in the sulfate or sulfide form, is sensitive to the redox state of the batch and resulting glass (melt). In amber glass, an increase or sometimes also a decrease of the concentration of the $\text{Fe}^{3+}-\text{S}^{2-}$ chromophore responsible for the amber colour might be observed, after changing the cullet source or cullet fraction in the batch.

It is obvious [1 to 5] that organic components in the recycled cullet will decrease the concentration of chemically dissolved oxygen in the glass melt and will also increase the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in the final glass product.

The objective of this study is the determination of the impact of reducing species in the batch/cullet and the influence of the oxidation state and humidity of the furnace atmosphere on: the redox reactions in the batch, the fining reactions in the sulfate/sulfide containing soda-lime-silica melt and on the redox state plus the colour of the glass product.

Mathematical modeling of the gas exchange processes and modeling of chemical reactions based on thermodynamics and laboratory simulation studies may show trends, but often lack a precise quantitative correlation with industrial melting. In this paper the effects of:

- organic contaminants in the batch or cullet,
 - the water vapor in the furnace atmosphere and
 - more or less reducing firing conditions
- on the redox state and sulfate/sulfide retention will be treated semi-quantitatively using modeling studies and melting test results.

2. Fluctuations in glass colour and fining behaviour

2.1 Different cullet colours

Usually, a cullet mixture is composed of glasses of different colors and redox states [6]. A shift in the composition of the cullet mixture frequently leads to an unexpected and often undesired change in the redox state and consequently a change of the color in the glass, molten from this cullet. For instance, the use of large amounts of green cullet in an amber glass furnace will give the glass product a greenish tint. In such case, the amber chromophore, in order to obtain the required dark amber colour, is often not sufficiently dominant, compared to the chromium (III) green colorizing effect. Especially, in amber glass molten in oxygen fired furnaces, the concentration of the $\text{Fe}^{3+}-\text{S}^{2-}$ chromophore will be relatively small and the green tint due to Cr^{3+} originating from the green cullet fraction may become dominant in the color spectrum.

Green cullet or a typical batch composition for melting green glass might lead to a *feuille morte* colored glass product when the (usually fluctuating) concentrations of organic contaminants in the cullet exceed a certain level.

By the application of redox sensors for test melts prepared from batch materials or mixed cullet [7 to 10], the redox state or reducing/oxidizing power of the mixed batch ingredients including filter dusts and cullet, before charging them into the furnace, can be characterized in order to make the proper batch redox corrections and to obtain the required glass color.

Apart from the batch ingredients, also furnace operating conditions like heating rate, batch blanket thickness, furnace atmosphere and local reducing gases touching the batch blanket or the melt may have a drastic impact on the redox state of the melt and the final glass.

In principle, the redox state and the presence of colorizing components (iron, chromium, cobalt, selenium, cerium, iron(III)-sulfides, etc.) will determine the final color of the glass and will have an impact on the radiative heat transfer rate in the glass melt, which is not only important for melting and conditioning processes [11], but which also determines the cooling rates during forming.

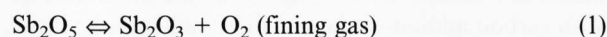
2.2 Fining

Most of the fining agents like: sulfates, antimony oxides and arsenic oxides, decompose by redox reactions at high (fining) temperatures in the molten glass, releasing the required fining gases (oxygen and/or SO₂ and even S₂). The redox state of the fresh melt, which arises just after the initial melting stage, controls the temperature at which the fining agent starts to decompose (fining onset temperature). This redox state is predominantly determined by the redox state of the batch components.

This redox state of the batch also influences the total amount of fining agent effectively available (which is the fining agent in the active state like sulfate, pentavalent antimony or pentavalent arsenic required for primary fining, instead of the more reduced forms of these components), determining the quantity of the released fining gases.

As an example, trivalent antimony in the fresh melt will be stable at reducing conditions, but this form is inactive in the primary fining process. In this state, antimony oxide cannot release oxygen and thus the seeds in the melt will hardly grow¹⁾ because of the limited availability of the fining gas, O₂, in this case.

A melt to be prepared with antimony oxide as a fining agent should be prepared from a relatively strongly oxidized (using antimonates and nitrates in the batch) batch, in order to obtain the pentavalent (Sb⁵⁺) antimony in the fresh glass melt. On increasing temperature the pentavalent antimony will produce oxygen as a fining gas according to:



above ±1250 to 1300 °C.

Also the sulfate fining¹⁾ efficiency, determined by the rate of bubble removal from the molten glass, will also strongly depend on the redox state of the melt. Often there is an optimum redox range for sulfate fining: reducing conditions promote the sulfate decomposition at lower temperature levels causing unfavourable strong foaming of the high viscous batch melts. Fining by sulfates at strongly oxidizing conditions requires very high temperatures (1450 to 1530 °C) before decomposition starts and these extremely high temperature levels are often not met in the glass melting tanks.

Since the redox state also determines the glass color (the transmission spectrum in the VIS and NIR ranges) and other properties, like the mechanical strength [12], which is extremely important for fiber glass production, the redox state range of the batch should always be very accurately controlled.

¹⁾ During the primary stage of fining, the released fining gases will diffuse into small bubbles, subsequently these bubbles will grow and this will drastically increase the ascension rate of the bubbles towards the surface of the melt.

3. Factors determining redox state and fining efficiency

Qualitatively, the effects of:

- organic materials in the batch,
- different glass colors in the cullet, exhibiting different oxidation or reduction power,
- more or less reducing/oxidizing firing conditions

on the redox state (color) and fining behaviour are relatively well understood.

However, the nonlinearity of relations and complexity of the influencing factors limit the quantitative understanding of the relations between the following factors, on the one hand:

- the maximum melting temperature;
- the amount and kind of organic components in batch and cullet;
- the heating rate of batch;
- the particle sizes of batch ingredients, important are the particle sizes of the cullet (fine cullet always appears to act more reducing than coarse cullet) and coke;
- the glass composition;
- the furnace atmosphere,

and on the other hand the final redox state and the color of the glass (melt). These factors also control the efficiency of bubble removal and might be important in the reboil phenomena encountered during changes of redox state.

The reaction mechanisms at which reducing agents interact with sulfates in the batch blanket depend on temperature, other reaction partners (CO₂, polyvalent ions) and the redox state. In section 4 these reactions will be discussed.

Nowadays recycled cullet is sometimes pulverized in the container glass industry to avoid the presence of coarse, very slowly dissolving ceramic pieces or stones in the melt. However, the industrial practice has frequently shown foaming problems using large quantities of such pulverized cullet if contaminated with organic impurities. Moreover in such cases, the final glass color might be unstable, due to the temporarily strong reducing effects of the fluctuating levels of organic materials in the fine cullet. Changing from air-gas or air-fuel oil to oxygen-gas or oxygen-fuel oil firing will increase the water vapor pressure above batch blankets and melts by a factor 3. After such conversions, glass producers found changes in the redox state (Fe²⁺/Fe³⁺ ratio) and thus in the glass color and in the sulfate retention without changing batch compositions.

In some cases, the foaming tendency increases after conversion of the combustion system to oxygen firing. The increased water vapor level seems to promote the evolution of gas from the melt and may cause extra foam formation, limiting the heat transfer from the combustion space into the melt. These observations ask for

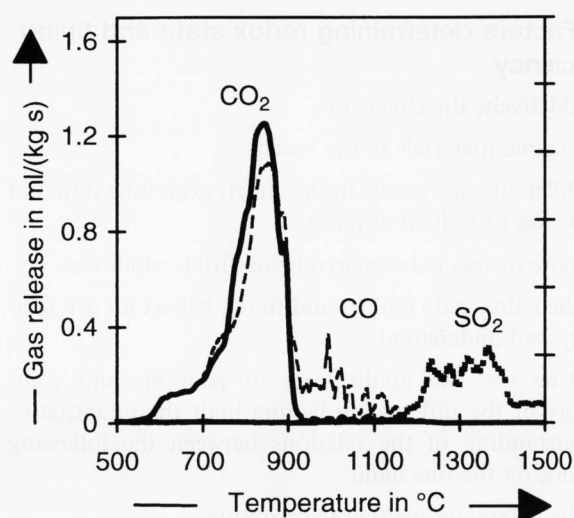


Figure 1. Gas release from sulfate and cokes containing batch and cullet mixture for soda-lime-silica glass during heating and melting. Simultaneous CO and CO₂ release between 600 to 900 °C.

batch changes, like adaptations in the quantity of fining agents and changes in the reducing or oxidizing components added to the raw material mixture.

Glass producers are always searching (empirically) for an optimum of the redox state and an optimum level of required fining agent. However, today with often very fast changing conditions and requirements (cullet recycling, required reduction of the SO₂ emissions, filter dust recycling, oxygen firing, higher glass quality standards) a more basic approach is required for finding the answers to these major technological questions.

4. Redox reaction mechanisms in batches containing iron, sulfates and organic contaminants

During the heating of the batch mixture, including the recycled glass cullet, chemical reactions take place. Fusion reactions of the batch ingredients will cause the formation of primary liquid phases and the release of batch gases like water vapor and CO₂. Only, when an exchange of gas species is possible, reactions with furnace atmosphere components may influence the sulfate decomposition process and the reduction or oxidation of other batch components like iron oxides, organic contaminants or cokes.

4.1 Water infiltration

Results of experimental work will show that during the premelting stage, water from the furnace atmosphere is partly absorbed by the first liquid phases. 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 to the stirring action, caused by the increased bubble ascent. Water infiltration (mixing of the saturated surface layers with the bulk of the melt) is also promoted by foaming and also the free convection of the melt, caused by temperature differences in the melting tank. In industrial 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 ($C_{H_2O}^s$ in mg water per kg glass) depends on the water vapor pressure (p_{H_2O} in bar) above the melt: $C_{H_2O}^s = L_{H_2O} \cdot p_{H_2O}^{1/2}$. For common soda-lime-silica glass melting at about 1500 °C, the maximum solubility value L_{H_2O} is determined here on a value of about 1100 mg/kg glass per bar water vapor pressure, in close agreement with data derived from the literature [13 to 15].

4.2 Reactions with carbon-containing components

During the carbonate decomposition, CO₂ gas is released from the batch blanket. According to the Boudouard reaction mechanism this CO₂ gas partly reacts with a) carbon added to the batch [16] or b) carbon formed by char formation from organic contaminants in the cullet:



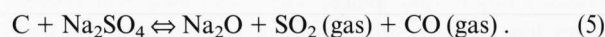
This reaction shifts to the right side at increasing temperature, especially above 750 °C. Indeed, the authors' laboratory studies of melting soda-lime-silica batches with carbon additions, showed the simultaneous release of CO₂ and CO during the decomposition stage of the carbonates (dolomite, soda, limestone) in the temperature range of 500 to 1000 °C. Figure 1 shows the release of gases from such a batch during the initial reaction and melting stages.

Active carbon reacts relatively fast with the CO₂ from the carbonates. The major part of the gaseous CO will be removed from the batch and reaction (2) continuously shifts to the right side. However, the much more stable graphite only reacts at higher temperatures. The active surface area of graphite is probably smaller compared to the reacting surface area of active carbon. The overall reactivity of cokes also depends on the cokes grain sizes [3].

At higher temperature levels the batch grains start to sinter and the grains will become interconnected by viscous melting phases. The CO gas which is formed can hardly escape from the melt and the Boudouard reaction may stop due to the high CO vapor pressures, but more probably because the end of the carbonate decomposition stages will be reached at these high temperatures. The CO gas which cannot directly escape from the batch mass may react with sulfate or polyvalent ions. Thus, the graphite cannot always completely react with CO₂ and starts to react with other components like sulfates or

iron oxides in the batch blanket. Especially, at low temperatures the reactivity of graphite is much smaller compared to the reactivity of active carbon.

The high viscous primary melts plus the bubbles may form a batch foam. The entrapped CO gas or the non-reacted carbon can react with the fining agent sodium sulfate, forming SO₂ gas or sulfides in the melt/batch like respectively:



The CO and SO₂ gases will cause batch expansion or form a foamy mass with the partly molten high viscous material.

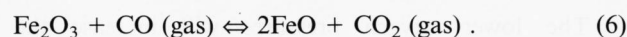
Organic contaminants in the batch, or more importantly, in the recycled cullet can partly vaporize during heating when the batch blanket still contains sufficient open pores. But these organic compounds may also pyrolyse, forming char and reduced gas components in the batch blanket.

The different evaporation and pyrolysis behaviour during heating of the variety of organic components in the cullet, causes fluctuations in the residual char contents and char structure (dependent on the size and kind of organic compounds), and therefore it influences the reducing power of these compounds for the melt. The oxidation of organic contaminants with components in the furnace atmosphere depends on the kind of organic material. The organic material which shows the lowest reactivity in the batch and the lowest evaporation rates from the batch blanket will lead to the most reduced glass melt.

Differences in the redox state of the melt can still be found, even for batch and cullet with exactly the same chemical oxygen demand (COD) of these different batch/cullet mixtures, measured at low temperatures [10].

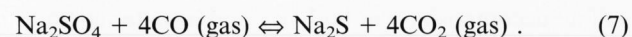
Especially sugars can form a stable char in the batch. This char can partly react with CO₂ by the Boudouard reaction at lower temperatures (600 to 1000 °C). But the residual carbon fraction, which did not react in earlier stages with the CO₂ according to the Boudouard reaction, will reduce the sulfate in the batch especially after all the CO₂ has been released, according to reaction (4) and (5), or after the batch blanket is covered by layers of melt. In the case of cullet-rich batches (>90% cullet) with only very small amounts of carbonates (soda, lime, dolomite), the total CO₂ release will be limited. Then the Boudouard reaction hardly converts all the carbon into CO gas. In such cases, the residual carbon will reduce some of the glass compounds like the sulfates and ferric iron, Fe³⁺.

Even a melt, prepared from a batch without reducing components, can show chemical reduction by reactions with mildly reducing atmospheres (CO-rich), like reaction (3), when the reducing gases from the flames can infiltrate the batch blanket:



Thus, part of the ferric iron in the batch blanket or melt will be reduced into ferrous iron and also the stability of sulfates in the melt will decrease. The sulfate will start to decompose, due to the reducing effect of the reactive CO (or other reducing gases, like hydrocarbons or soot).

Besides, at very reducing firing conditions, sodium sulfates in the batch or melt might react according to reaction (4) or:



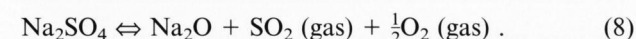
In fact the carbon has transferred the reducing power to the sulfur species by forming stable sulfides in the melt or to the iron oxides by forming the reduced ferrous iron form. At very reduced conditions, sulfur will be present in the sulfide state. Together with the residual oxidized part of the iron, ferric iron (Fe³⁺), this sulfide will form the rather stable amber chromophore in the glass.

The organic contaminants, or coal in the cullet may also partly react with oxygen, if present in the local furnace atmosphere above the batch/cullet blanket. Only when the cullet allows sufficient infiltration of the oxygen from the furnace atmosphere such oxidation processes might take place.

4.3 Fining reactions enhanced by water

The fining agent in the glass melt partly decomposes during the primary fining stage. For most fining agents, sulfate, antimony oxide, arsenic oxide or cerium oxide, the decomposition reaction is a redox reaction. For a strongly oxidized melt, oxygen is one of the most important fining gases and during fining the melt will release and loose oxygen and will thus become more reduced. The presence of dissolved water in the melt will accelerate bubble growth rates because of two reasons:

- Water molecules diffuse rather fast from the melt into the bubbles, contributing to the increase of the total gas volume in the bubbles;
- Water vapor dilutes the other gases in the bubbles, reducing the vapor pressures of these gases including the fining gases. The reduction of the vapor pressures of the fining gases will shift the fining reaction equilibrium to the gas-producing side like:

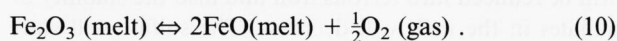


The sulfate decomposition equilibrium constant (only glass composition and temperature dependent) for constant sodium oxide activity in the melt is defined as:

$$K_s = p\text{SO}_2 \cdot p\text{O}_2^{1/2} / [\text{SO}_4^{2-}]. \quad (9)$$

Equation (9) shows that a decrease of the partial vapor pressures $p\text{SO}_2$ or $p\text{O}_2$ will cause a decrease in the residual sulfate concentration: $[\text{SO}_4^{2-}]$.

The lower oxygen pressures will increase the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in the melt as well, caused by a shift of the reaction (10) to the right side:

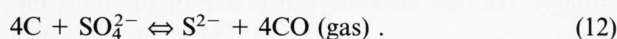
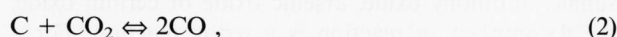
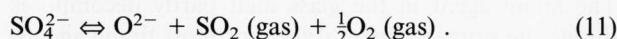


Dissolved water decreases the sulfate decomposition temperature. At these temperature levels water will promote the formation of oxygen by the enhanced sulfate decomposition. Initially this will shift the reaction (10) to the left side. However, at increasing temperatures, as sulfate decomposition in both dry and in water-containing melts will take place, dissolved water will decrease the oxygen pressure in the bubbles and melt and the redox state in the case of sulfate-containing batches without reducing agents.

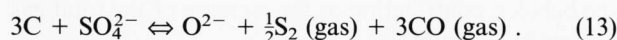
In the case of strongly reduced melts, the behavior can be different, gases like S_2 can be formed during the fining or degassing stage and the melt will lose reduced species, thus becoming more oxidized. Water vapor may even react with sulfides forming H_2S gas, the release of H_2S will make the melt less reducing.

4.4 Redox reactions in batch blanket and melt

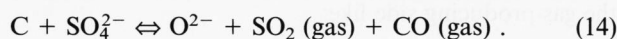
The following scheme of reactions, all relevant for the final redox state of the melt and some important for the fining processes, can take place during melting of soda-lime-silica glass from batch and cullet:



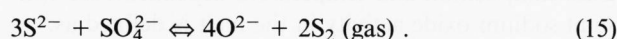
Reaction equilibria (4) and (5) are special cases of respectively the given equations (12) and (11). Other important reactions forming sulfur gases are:



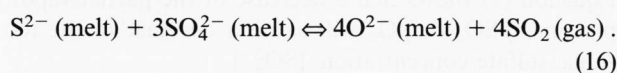
At moderate carbon levels, reactions of sulfates similar to reaction (5) take place, given in the more general form as:



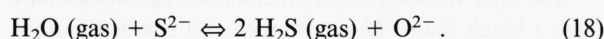
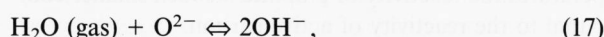
For very reduced melts, containing mainly sulfur in the sulfide form, the residual sulfate at increasing temperatures, is consumed by reactions such as:



For mildly reduced melts, containing sulfur partly in sulfide and mainly in sulfate form:



And including water vapor absorption:



During the heating of the batch, reactions (2), (10), (11) to (18) will determine the redox state and the total sulfur content but also the sulfide and sulfate levels after the primary melting process. During fining, reactions (10), (11), (15), (16) and the reverse reaction (17) (water vapor release) might take place. The glass melt will release gases like oxygen, sulfur dioxide, water vapor and also S_2 gas, under reduced conditions.

In the case of oxidized or very mildly reduced soda-lime-silica melting, sulfate will be the most important sulfur compound in the fresh melt starting to decompose above about 1400°C, depending on the concentration of sulfate and the redox state of the melt.

For more reduced batches, sulfate and sulfide will both be dissolved in the melts up to 1100 to 1250°C, due to reactions like reaction (12). Above this temperature level, sulfate and sulfide heavily react, forming SO_2 and/or S_2 gas or foams, depending on the ratio sulfide/sulfate.

In the case of a rather low ratio sulfide/sulfate (mildly reduced melt), the sulfide will completely react during further heating before all the sulfate has disappeared from the melt. After the removal of the sulfide from the melt, this melt will contain a very low sulfate concentration, which will not decompose anymore until very high temperatures (>1550°C) are reached. For most green container glasses, this condition applies. As found experimentally, at rather low temperatures (1000 to 1250°C) the major part of sulfides and sulfates react and form fining gases: SO_2 and/or S_2 . Above 1250°C the total sulfur solubility decreases by further sulfide-sulfate reactions. The minimum sulfur solubility according to the Budd curve decreases as temperature increases. The reaction of sulfides with sulfates depends on diffusion and mixing of sulfate and sulfide rich parts of the melt and on the thermodynamics of these reactions.

Fining gas release at rather low temperatures and high glass melt viscosities may form stiff foam layers. The fining stops as the sulfide has completely been reacted away and the residual sulfate level becomes too low (smaller than ± 0.15 wt% in normal soda-lime-silica glasses) to obtain further decomposition.

In very reduced melts containing some sulfate but also a sulfide excess, the sulfate portion will be completely reacted away at about 1250°C or somewhat higher temperatures, by reactions (15) and (16). As soon as this sulfate has been converted into sulfides plus sulfur gases, only sulfide will remain in the melt. The sulfide solubility increases at increasing temperatures [17]. At least at lower temperatures (<500°C), the residual sulfide will form together with ferric iron, the $\text{Fe}^{3+}-\text{S}^{2-}$ chromophore, responsible for the amber

coloring. Since the sulfide solubility increases at further heating and as soon as the sulfate has been completely removed, the sulfur gas formation and fining will probably stop at further increasing temperatures, although H_2S can be formed by sulfide-water reactions in a melt containing dissolved water.

The prediction of the redox state and sulfate/sulfide retention of the final glass product is a very difficult task without proper understanding of the kinetics and thermodynamics of the exchange of gases with the furnace atmosphere and with the bubbles during the melting and primary fining stages or during the cooling process [18].

5. Reducing power of recycled cullet and effect on the redox state of the molten glass

Large amounts of reducing components will promote the decomposition of fining agents like sodium sulfates, at low temperatures. The gas bubbles may form a foam in a high viscous melt and sulfates are almost lost before the required fining in a low viscous, high-temperature melt can take place.

Due to redox reactions of polyvalent ions, the redox state of the batch components will directly influence the valency states of these polyvalent ions like iron, sulfur or chromium dissolved in the glass(melt). Different valency states of polyvalent ions will absorb the light in the glass at different wavelengths. Thus, the color of the final glass depends on the valency states of the different polyvalent species. In amber glass, ferric iron (Fe(III)) and sulfide are responsible for the amber coloring (dominant light absorption at about 425 nm). In emerald green glass, chromium(III) absorbs light at 450 and 650 nm coloring the glass emerald green. Ferrous iron in chemically reduced glasses without sulfides colors the glass blue-green, having a broad absorption band with a maximum at 1050 nm.

The characterization of the reducing power of the recycled cullet is extremely important for proper composition corrections to be applied to the batch. However, not only the redox state of the batch but also the operating conditions (size of cullet/batch grains, gas atmosphere, melting rate) are important for the final redox state of the products obtained. This section will focus mainly on frequent and reliable characterization of the redox state of cullet only or of normal batch, including cullet.

Analyzing the redox state of the glass (melt) in the feeder by oxygen sensors (oxygen activity as a measure for the redox state) or analysis of the redox ratio, $[\text{Fe}^{2+}]/[\text{Fe}_{\text{total}}]$, in the glass products, will give important information on changing redox conditions, but often this information will be obtained too late for making fast proper corrections of the batch redox.

A practical useful method for the determination of the reducing power of cullet is the analysis of the oxygen activity or oxygen equilibrium pressure, at a fixed tem-

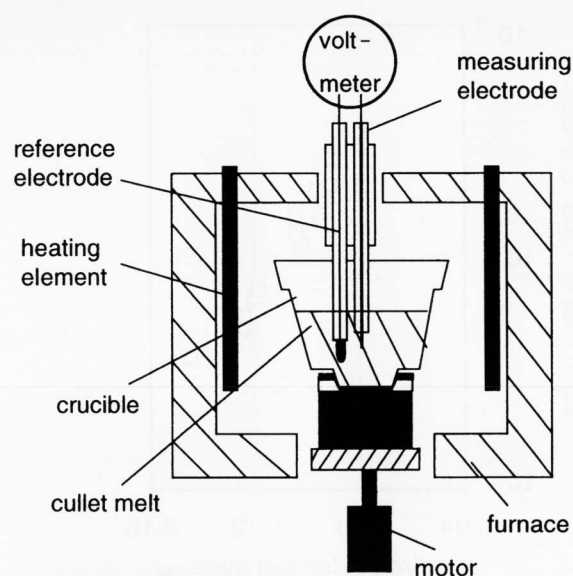


Figure 2. Schematic presentation of equipment for measuring the partial oxygen equilibrium pressure (or oxygen activity) of a cullet/batch melt.

perature, of a test melt [19] prepared from a representative sample of the cullet before charging this material into the furnace. A freshly molten glass portion sampled just beneath the batch blanket can also be used to characterize the redox state of the fresh melt.

The cullet or the sampled glass can be remelted in a laboratory furnace. In air, the cullet should be remelted relatively fast, in order to limit the oxidation of the organic contaminants by air oxygen before a melt layer covers the melting cullet. At further heating, this layer prevents further infiltration of oxygen into the material. The oxygen activity of the prepared melt is measured by the application of an electrochemical sensor dipped in the cullet melt. The electrochemical potential between the measuring platinum or iridium electrode, dipped in the molten cullet, and a reference electrode, in equilibrium with air or a metal/metal oxide system and connected to the melt by stabilized zirconia, is directly related to the oxygen equilibrium pressure of the melt [7 to 10 and 20]. Figure 2 shows the equipment for analyzing the oxygen activity of a melt.

Now, the redox state of the cullet, which is important for glass melting, is characterized by the measured oxygen activity or oxygen equilibrium pressure of a melt, for example at 1300 °C, prepared from a representative sample of cullet [10]. The redox state can be characterized by the partial oxygen equilibrium pressure of the melt, $p\text{O}_2$ (melt), at a given temperature or the measured EMF value at this temperature, in this case 1300 °C.

Figure 3 shows the relation between the measured oxygen activity of different laboratory cullet premelts and the final redox ratio ($= \text{Fe}^{2+}/\text{Fe}_{\text{total}}$) of the obtained production glass. The graph shows an almost, although not completely straight correlation. This dependence of the $\text{Fe}^{2+}/\text{Fe}_{\text{total}}$ ratio in the glass product on the oxygen

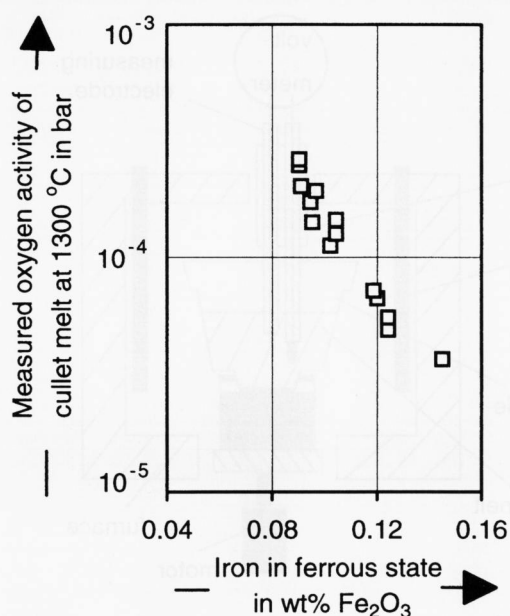


Figure 3. Correlation between measured oxygen activity in cullet melt and the final redox ratio of iron ($= Fe^{2+}/Fe_{total}$) in the glass prepared from this cullet.

activity of the cullet melt might change after changing furnace atmosphere, melting capacity, cullet ratio and kind of glass. Thus, the given relation in figure 3 cannot be applied in general. The relation between the Fe^{2+}/Fe_{total} ratio in the final glass versus oxygen activity of the cullet melt, which is also dependent of the glass furnace situation, has to be determined for each particular glass melting process.

Depending on the kind of organic contaminants, a part of the organic components can vaporize during heating, the remaining part will form carbon-rich residues. Figure 4 shows the impact of the presence of different organic contaminants on the oxygen activity of the cullet melt as measured by the oxygen activity sensor. Plastics behave more reducing than the same amount of paper in the melting process. In most container glass plants, several types of recycled cullet are used, including coarse cullet, pulverized mixed cullet, flat and flint glass cullet, etc. In a series of industrial measurements, the oxidation state of representative samples of several different French cullet types were characterized by oxygen activity measurements at 1300 °C. Some typical results of these measurements are depicted in figure 5. As can be seen in this figure, the redox state of the various cullet types differs considerably. In particular, the reducing behavior of pulverized recycled cullet can be noted. During the heating process, the fine-powdered cullet starts to sinter together and the volatile organic reducing components and CO gas inside the powder blanket cannot freely be released and will react with Fe^{3+} and sulfates in the batch or melt. Using coarse cullet, the open structure in the cullet blanket allows the vaporization of the reducing species in the open atmosphere. Thus the organic components in fine cullet behave more reducing

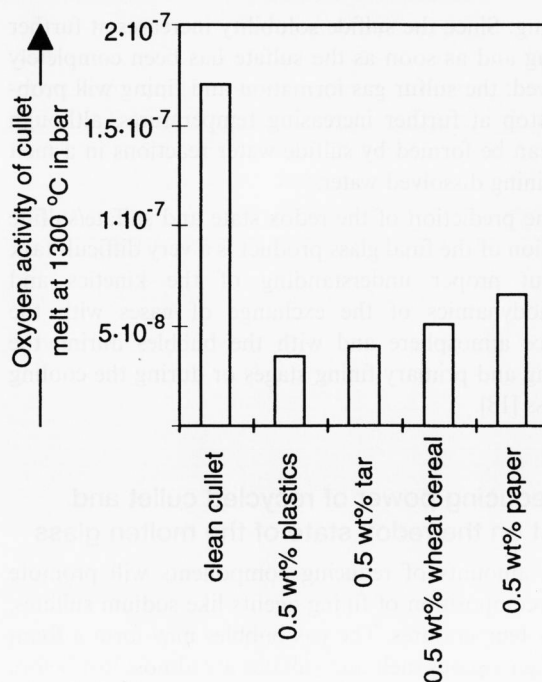


Figure 4. Impact of 0.5 wt% addition of a contaminant to the redox state of the glass melt expressed as oxygen activity at 1300 °C.

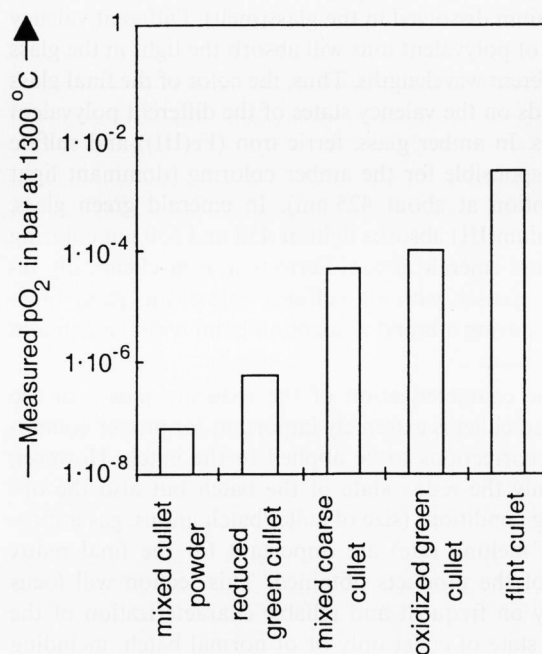


Figure 5. Measured pO_2 (bar) at 1300 °C in melts of different cullet types. The mixed powder cullet leads to a feuille morte glass. Melting the mixed coarse cullet gives a dark green glass.

than in the coarse cullet. The char or CO residues entrapped in the batch or melt finally react with the batch components forming ferrous iron and sulfides.

Computer programmes based on thermodynamics are used to evaluate or optimize redox correction procedures, like the addition of extra sulfate to the batch or

a change of the cullet percentage in these batches. The results of some exemplary calculations for a realistic batch composition are presented in figure 6. This figure shows the calculated effects on the redox state (iron redox ratio of produced glass) after increasing sulfate additions to a typical industrial glass batch (for oxidized green container glass), consisting of 80% cullet and 20% primary raw materials (sand, soda, limestone and chromite). In this figure the required sulfate addition (X -axis) for obtaining a certain Fe^{2+}/Fe_{total} ratio (Y -axis) in the glass can be derived, starting from three different redox states of the cullet: with the pO_2 (at 1300°C) in the cullet melt at a level of $1 \cdot 10^{-7}$ or $1 \cdot 10^{-6}$ or $1 \cdot 10^{-5}$ bar, respectively. It can be derived from figure 6 that the required amount of sulfate to obtain a certain Fe^{2+}/Fe_{total} ratio in the glass product very much depends on the redox state of the given cullet.

6. Water vapor absorption by molten glass

The maximum solubility of water species in glass melts at 1 bar water vapor pressure depends on the glass composition [13] and slightly on temperature [14 and 15]. Figure 7 shows the here measured dissolved water concentration in molten soda-lime-silica glass melt as a function of water vapor pressure, by bubbling of the melt with different gas compositions and measuring the absorption in the IR-spectrum at a wavelength of 2.78 μm (typical for dissolved water assuming an extinction coefficient for H_2O of $41 l \cdot mol^{-1} \cdot cm^{-1}$ [13]). According to extrapolation of almost linear relation between the square root of the water vapor pressure and measured water content, the maximum water solubility at 1 bar water vapor pressure at 1480°C is about 1023 mg/kg glass (in mol%: 16Na₂O, 10CaO and 74SiO₂). The water solubility is determined by bubbling the melt with steam air mixtures and measuring the absorption at 2.78 μm in the glass product. In this case, water is probably dissolved in the form of free water and hydroxyl groups. Scholze et al. [13] measured a maximum water solubility at 1480°C of 1105 mg/kg glass for approximately the same composition (in mol%: 15.5Na₂O, 10.7CaO and 73.8SiO₂). McGinnis and Shelby [15] found for a typical float glass melt at 1400°C, a maximum water solubility at 1 bar water vapor pressure of about 1100 to 1200 mg/kg glass melt. The solubility of water increases only slightly with temperature.

During heating and melting of an initially dry soda-lime-silica batch, the water vapor pressure above the batch has been adjusted to different levels during the different stages of the laboratory melting tests. Table 1 shows the different stages during the heating/melting process, the composition of the simulated furnace atmosphere and the absorbed water concentrations during these different stages.

Directly after melting of a sulfate-containing soda-lime-silica batch, without reducing components, the analyzed water content in the glass before fining and

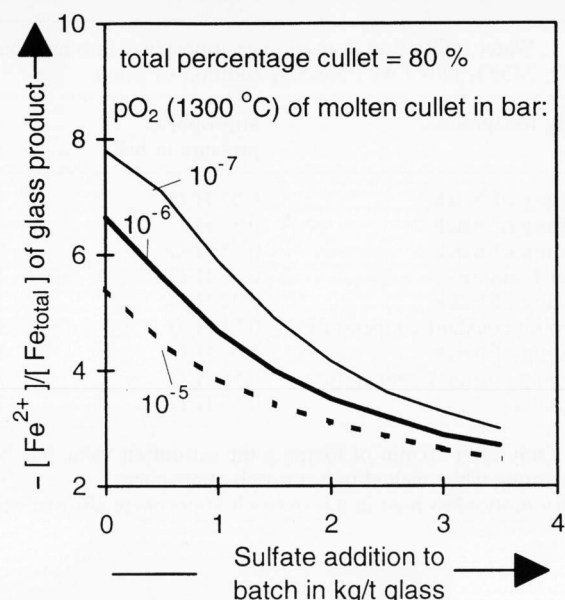


Figure 6. Graph showing the required amount of sodium sulfate addition for three different types of cullet (parameter oxygen activity of cullet melt) for obtaining the desired redox ratio in the glass product.

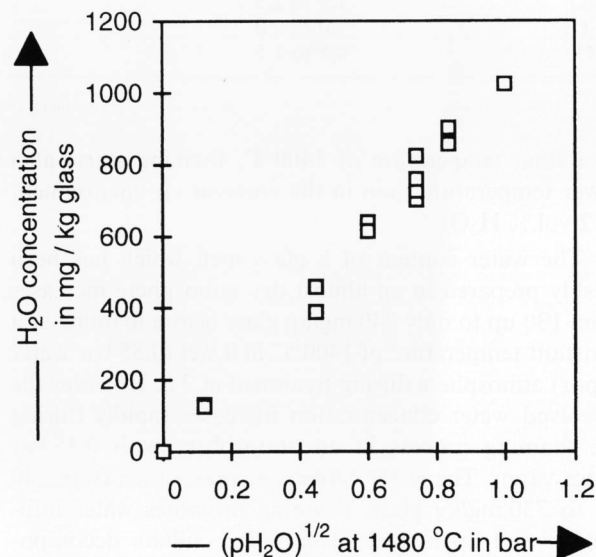


Figure 7. Maximum water solubility in soda-lime-silica glass melt as a function of water vapor pressure (square root) at 1480°C. Glass composition (in mol%): 16Na₂O, 10CaO, 74SiO₂.

foaming is 130 mg per kg glass for ambient atmospheres (1 to 1.5 vol.% water vapor), but about 600 mg/kg glass for melting in atmospheres containing 55 vol.% water vapor. Water infiltration is only moderate at 1400°C for a motionless melt without foaming and bubble formation as indicated by the test nos. 5 and 6 in the table. However, after increasing the water vapor pressure up to 0.55 bar during heating of the batch and during melting

Table 1. Water infiltration from furnace atmosphere into melt/batch during melting and foaming/fining; base glass in mol%: 16Na₂O, 10CaO, 74SiO₂ plus 1 wt% Na₂SO₄ addition to batch

melting test/process	atmosphere pressure in bar	final temperature ϑ_f in °C	holding time in min at ϑ_f	water content in mg/kg
1. heating of batch	0.02 H ₂ O	1400	10	130
2. heating of batch	0.55 H ₂ O	1400	10	590
3. heating of batch	0.55 H ₂ O	1400	120	720
4. after foaming	0.55 H ₂ O	1480	60	740
5. heating of batch	0.02 H ₂ O	1400	10	130
keeping constant temperature	0.55 H ₂ O	1400	120	240
6. heating of batch	0.02 H ₂ O	1400	10	130
keeping constant temperature	0.55 H ₂ O	1400	120	240 ³
foaming	0.55 H ₂ O	1480	30	730

Note: Only after 30 min of foaming the saturation value has been reached. The melt is almost saturated with water before fining and foaming when melted in water-rich atmosphere.

³) A dry motionless melt in a water-rich atmosphere absorbs water very slowly.

Table 2. Average composition of cullet.

	content in wt%
SiO ₂	72 to 73
Na ₂ O	13 to 14
CaO	9.0 to 10
MgO	1.5 to 2.5
Al ₂ O ₃	1.0 to 2.0
K ₂ O	0.5 to 1.5

at a final temperature of 1400 °C, foaming starts at a lower temperature than in the ambient air environment (<2 vol.% H₂O).

The water content of a glass melt which has been freshly prepared in an almost dry atmosphere increases from 130 up to only 240 mg/kg glass before foaming at a constant temperature of 1400 °C in a wet (0.55 bar water vapor) atmosphere during treatment at 2 h. However the dissolved water concentration increases rapidly during the foaming process in an atmosphere with 0.55 bar water vapor. The water content increases then from 240 up to 730 mg/kg glass. Foaming promotes water infiltration and apparently also further sulfate decomposition, which increases the foam formation again.

After foaming of the sodium sulfate containing soda-lime-silica melt (without reducing agents in the batch), at 1480 °C in an ambient atmosphere (<2 vol.% water vapor), the residual SO₃ analyzed in the glass appeared to be 0.32 wt%. But after foaming in the 55 vol.% water vapor atmosphere, the sulfate retention has been reduced to 0.17 wt% (expressed as SO₃). Sulfate seems to become less stable in a water-rich melt prepared from a batch without reducing agents, which is expected from considerations given in section 4.3.

The water content of a melt prepared from a batch in a water vapor rich atmosphere, at $p_{\text{H}_2\text{O}} = 0.55$ bar, contains also a high level of dissolved water (590 mg/kg glass after 10 min and 720 mg/kg glass after 2 h). This

melt starts to foam at lower temperatures than melts prepared under dry or almost dry conditions. A dry glass, molten in ambient air will hardly absorb water after exposing the melt to an atmosphere with 55 vol.% water vapor. However as soon as the fining and foaming starts, water infiltration will be rather fast.

Table 1 clearly shows that infiltration of water from the furnace atmosphere into the batch blanket or melt mainly takes place during the primary melting stages and during the foaming stage. Hardly any water will be exchanged for the situation of a motionless melt. Convection due to foaming or stirring by bubbles seems to be necessary to obtain a water-rich melt during melting in a water vapor rich atmosphere.

Industrial melting tests with dry batch and a batch with 3 to 4 wt% water (60% cullet plus 40% normal batch) showed hardly any effect of batch humidity on the water concentration in the final glass, both batches being melted in the same furnace.

Table 2 shows average composition of cullet and table 3 the oxidizing effect of water vapor on cullet melts with and without extra reducing agents. From experiments 4 and 8 it appears that water enhances the release of reducing species (S₂, H₂S or SO₂) from the melt during fining, resulting in a more oxidized glass. Figure 8 depicts an explanation for the enhanced fining action of water for sulfate-containing oxidized melts as discussed in section 4.3. The increased level of sulfate decomposition releases extra oxygen which partly oxidizes the ferrous iron in the glass melt.

The diffusivity of water in soda-lime-silica glass melts is in the order of 10⁻⁹ m²/s at 1400 to 1500 °C [19], this means that during 4 h the water will infiltrate only 0.5 to 1 cm into a melt without any convection. But during foaming the water infiltration will be enhanced by the stirring action of the ascending bubbles and by the violent movements of the melt in the foam.

Table 3. Experimental conditions and properties of prepared glasses from cullet; cullet mixture: 50 wt% flint (clean), 38 wt% green and 12 wt% amber glass

cullet characterization	atmosphere pressure in bar	SO ₃ in wt%	[Fe ²⁺]/[Fe _{total}]	color
1. fine cullet (no additions)	1 N ₂	0.06	0.27	green
2. fine cullet + 0.06 wt% C	1 N ₂	0.06	0.84	amber
3. fine cullet + 0.06 wt% C	0.005 O ₂ /0.995 N ₂	0.02	0.73	dark green
4. fine cullet (no additions)	0.55 H ₂ O/0.45 N ₂	0.05	0.13	green
5. coarse cullet (no additions)	1 N ₂	0.07	0.24	green
6. coarse cullet + 0.06 wt% C	1 N ₂	0.05	0.80	amber
7. coarse cullet + 0.06 wt% C	0.005 O ₂ /0.995 N ₂	0.07	0.27	green
8. coarse cullet	0.55 H ₂ O/0.45 N ₂	0.06	0.10	green

Thus, for the same oxidized batch composition, more sulfate will decompose in a water-rich environment compared to dry conditions. The larger amounts of gases released from a fast-stripping water-rich melt (H₂O, SO₂, O₂) compared to the case of a water-lean melt make the melting process much more sensitive to foaming. For batch compositions with high levels of reducing agents, an increasing water vapor pressure seems to lead to a more oxidized melt.

7. Modeling of the effect of water vapor and glass composition on sulfate fining

The major redox reactions which take place during heating and melting have been shown in the previous sections.

Water vapor directly reacting with batch components or absorbed by the melt may also effect the redox state of the glass and the release of gases during fining. In water-rich melts, the gases in the bubbles will attain an equilibrium with the residual sulfate in the melt. In these melts, more SO₂ and O₂, acting as fining gases will be produced (but the vapor pressures of oxygen plus sulfur oxides in the bubbles will decrease), in order to maintain the equilibrium between SO₂ and O₂ in the bubbles and the sulfate in the melt, according to the reaction equilibrium equation (9). The sulfate retention in the glass will decrease.

The redox state of the final glass, the sulfate/sulfide retention and the quantity of gases released during fining mainly depend on:

- temperature in the fining zones of the melting tank;
- glass composition, especially basicity and sodium oxide concentration;
- redox number of the batch, determined by the effects of all oxidizing and reducing species together;
- reduction/oxidation of batch or melt by components from the furnace atmosphere;
- water infiltration in the melt, enhancing sulfate decomposition.
- release of CO₂ by carbonate decomposition, reacting with carbon.

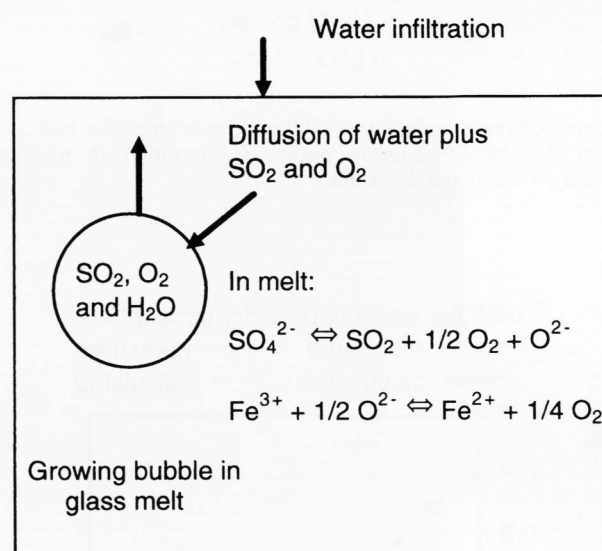


Figure 8. Schematic presentation of dilution of bubble contents by water vapor and shift in the sulfate reaction equilibrium in the melt at oxidized conditions. SO₂, O₂ and H₂O in the bubbles are almost in equilibrium with sulfate, Fe²⁺/Fe³⁺ and dissolved water, at the end of the fining process.

The developed model for the prediction of the redox state of the glass, sulfate/sulfide retention and fining behaviour is based on: a) the thermodynamics of all relevant reactions (2) to (18) plus b) the conservation equations for all relevant chemical elements: sulfur, oxygen, carbon, hydrogen, iron and c) the conservation of the electrical neutrality. In this model several assumptions are made: for instance a fast infiltration rate of water from the furnace atmosphere into the molten glass during fining. The water concentration in the melt is set equal to the saturation level or is set equal to an empirically derived fraction of the saturation level. This level is dependent on the water vapor pressure above the melt.

The model also assumes that primary fining starts as soon as the summation of equilibrium vapor pressures of the dissolved fining gases and water in the melt exceeds the 1 to 1.3 bar level (as the total gas pressure of

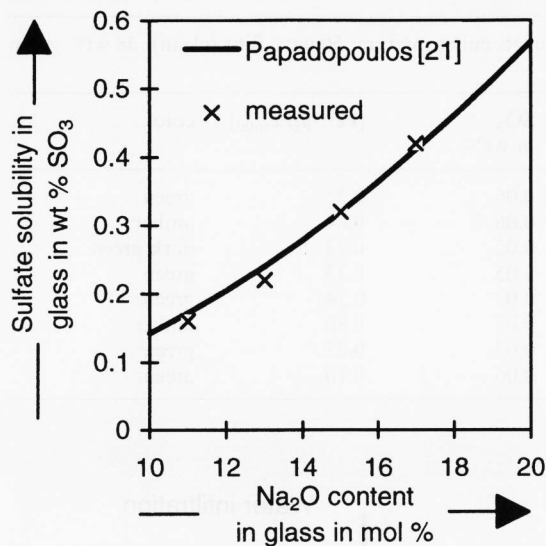


Figure 9. Maximum sulfate solubility in soda-lime-silica melt at 1480°C, without reducing agents. Composition in mol%: 75SiO₂, xNa₂O and 25-xCaO.

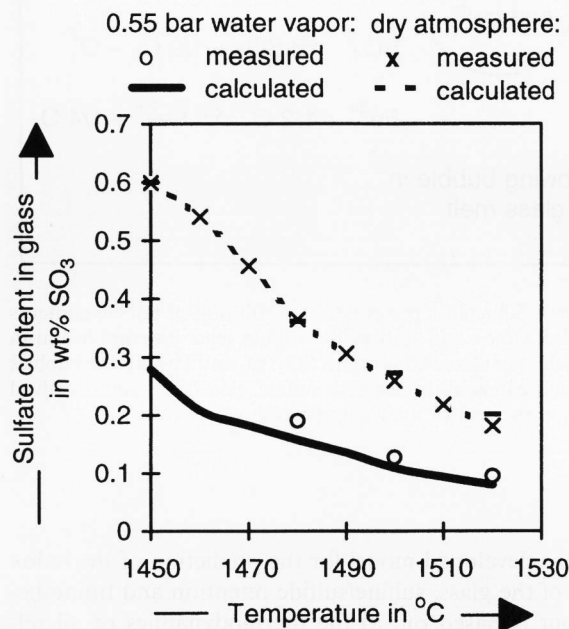


Figure 10. Sulfate residue in glass after melting a sulfate-containing soda-lime-silica batch without reducing agents at different temperature levels in an atmosphere with and without water vapor.

dissolved gases exceeds the atmospheric plus hydrostatic pressure plus surface tension contribution in the total internal bubble pressure, then the bubbles will steadily grow):

$$p_{O_2} + p_{SO_2} + p_{S_2} + p_{H_2S} + p_{H_2O} > 1.3 \text{ bar} . \quad (19)$$

In equation (19), the contribution of nitrogen and CO₂ gas are neglected, because these gases hardly contribute to the bubble contents at the end of the primary fining process. In reduced melts, containing dissolved water and sulfides, hydrogen sulfide gas can be released. Bubbles in foams of amber glass melts, sampled from an industrial oxygen-natural gas fired glass furnace, indeed contained this gas, i.e. hydrogen sulfide (H₂S).

At the end of the fining stage, oxygen in the bubbles will be at a chemical equilibrium with the physically and chemically dissolved oxygen in the melt which will determine the high-temperature redox reaction equilibria. This means that the ferrous/ferric ratio in the melt directly depends on the oxygen vapor concentration in the residual bubbles at the end of the fining stages. During the cooling process of the melt, redox reactions take place (in case of two or more polyvalent species in the melt), often changing the Fe²⁺/Fe_{total} ratio in the glass (melt) [4] or resorbing oxygen gas as the physically dissolved oxygen is converted into chemically dissolved oxygen.

During the cooling process, after primary fining, the glass melt can be assumed to behave as a closed system and is almost motionless. At that stage, shifts in the redox reaction equilibria are mainly determined by temperature and the presence of polyvalent ions in the melt and not by the exchange of gases to/from the furnace atmosphere. Small residual SO₂ bubbles can dissolve (refining) during the cooling of the melt if the redox state allows resorption of the SO₂ as sulfate or sulfide [18].

The effect of glass composition on the sulfate decomposition is calculated by the method proposed by Papadopoulos [21], the sulfate solubility depends on the basicity and, more than proportionally, on the sodium oxide content of the melt.

Figure 9 shows the modeled sulfate retention depending on sodium oxide concentration in the melt, in a soda-lime-silica glass after fining at 1480°C according to laboratory tests and calculations using the Papadopoulos approach. No reducing agent has been added to the batch and the melting atmosphere was ambient air. During fining the composition of the gas bubbles is assumed to be: 1/3 oxygen and 2/3 SO₂ (volume fractions), according to reaction:

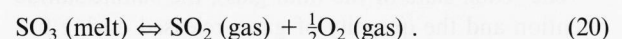


Figure 10 shows the modeled retention of sulfate in the soda-lime-silica glass without reducing components in the batch and after sulfate fining at different temperatures, depending on the water vapor pressure in the furnace atmosphere. The thermodynamic data presented by table 4 and derived from several literature sources [13, 22 to 24] have been used in this model. The melting test performed in different furnace atmospheres show a similar result. Figure 11 shows the results of the model calculations for the quantity of gases released during melting and fining of a soda-lime-silica plus 1 wt% sodium

Table 4: The standard reaction enthalpy and entropy of the chemical reactions in glass melts in the temperature range of 900 to 1500 °C

$$K = \exp\left(\frac{-\Delta G_r^0(T)}{RT}\right) = \exp\left(\frac{-(\Delta H_r^0 - T\Delta S_r^0)}{RT}\right)$$

ΔG_r^0 = standard reaction Gibbs energy at 1 bar in J/mol
 ΔH_r^0 = standard reaction enthalpy at 1 bar in J/mol
 ΔS_r^0 = standard reaction entropy at 1 bar in J/(mol · K)

reaction	ΔH_r^0 in kJ/mol	ΔS_r^0 in J/(mol · K)	ref.
1. $\text{SO}_4^{2-}(\text{melt}) \leftrightarrow \text{SO}_3(\text{gas}) + \text{O}^{2-}(\text{melt})$	325	103	from the authors' own experimental results
2. $\text{SO}_3(\text{gas}) \leftrightarrow \text{SO}_2(\text{gas}) + \frac{1}{2}\text{O}_2(\text{gas})$	96.3	90.9	[22]
3. $\text{SO}_2(\text{gas}) \leftrightarrow \frac{1}{2}\text{S}_2(\text{gas}) + \text{O}_2(\text{gas})$	361	72,5	[22]
4. $\frac{1}{2}\text{S}_2(\text{gas}) + \text{O}^{2-}(\text{melt}) \leftrightarrow \text{S}^{2-}(\text{melt}) + \frac{1}{2}\text{O}_2(\text{gas})$	379	198	[23]
5. $\text{Fe}^{3+}(\text{melt}) + \frac{1}{2}\text{O}^{2-}(\text{melt}) \leftrightarrow \text{Fe}^{2+}(\text{melt}) + \frac{1}{4}\text{O}_2(\text{gas})$	102	33	[24]
6. $\text{M}^{(x+k)+}(\text{melt}) + \frac{k}{2}\text{O}^{2-}(\text{melt}) \leftrightarrow \text{M}^{x+}(\text{melt}) + \frac{k}{4}\text{O}_2(\text{gas})$	–	–	
7. $\frac{1}{2}\text{H}_2\text{O}(\text{gas}) + \frac{1}{2}\text{O}^{2-}(\text{melt}) \leftrightarrow \text{OH}^-$	0	46.3	[13]
8. $\text{H}_2\text{O}(\text{gas}) \leftrightarrow \text{H}_2(\text{gas}) + \frac{1}{2}\text{O}_2(\text{gas})$	248	56.6	[22]
9. $\text{H}_2\text{S}(\text{gas}) \leftrightarrow \text{H}_2(\text{gas}) + \frac{1}{2}\text{S}_2(\text{gas})$	89.2	48.7	[22]

sulfate containing batch, depending on the equilibrium water vapor level in the furnace atmosphere. The presence of water seems to be very important for the temperature at which the fining starts and determines the increased quantity²⁾ of the released gases. Laboratory melting tests for sulfate-containing soda-lime-silica glass melts, without reducing components in the batch, show less seeds and blisters in the quenched glass samples after a few hours of melting in a very humid atmosphere, compared to melting at dry conditions.

Figure 12 shows the bubble growth rate calculated by the bubble behaviour model described elsewhere [25] for different situations: oxidized melts with different dissolved water concentrations (similar to the conditions of air firing versus oxygen firing), two temperature levels and different sulfate levels. The water in the melt contributes not only to the total quantity of released gases from the melt as shown by figure 11 but also to the required growth rate of single bubbles during the primary fining stages.

8. Impact of oxygen level in furnace atmosphere on redox of cullet melt

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

²⁾ A decrease of the SO_3 solubility by 0.005 wt% will produce 0.3 l of gas per liter of glass melt at 1400 °C.

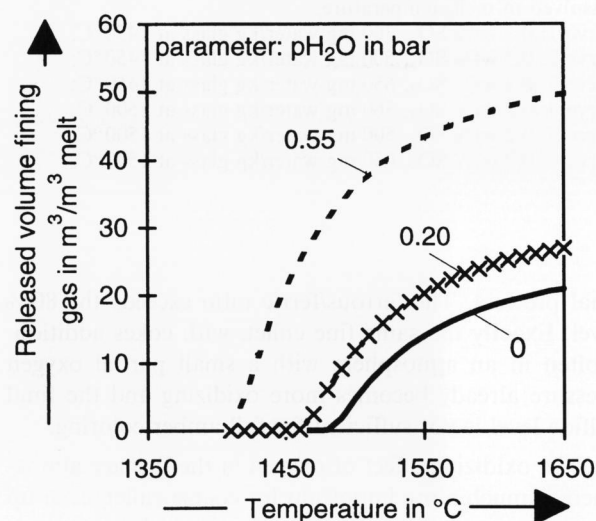


Figure 11. Total quantity of gas release from fining agent plus water in the melt as a function of temperature depending on the humidity of the furnace atmosphere.

Table 3 shows results of melting tests with different cullet batches, some containing only fine or some only coarse cullet, with or without cokes (active coal) addition and molten in different atmospheres. As already discussed fine cullet will start to sinter at temperatures above about 700 °C: the oxygen from the furnace atmosphere will hardly penetrate into the cullet mixture after this sintering process and CO gas can hardly escape. The table shows that the color of the glass, molten from fine cullet plus coke, in an atmosphere without oxygen will be amber due to formation of sulfides still present in the

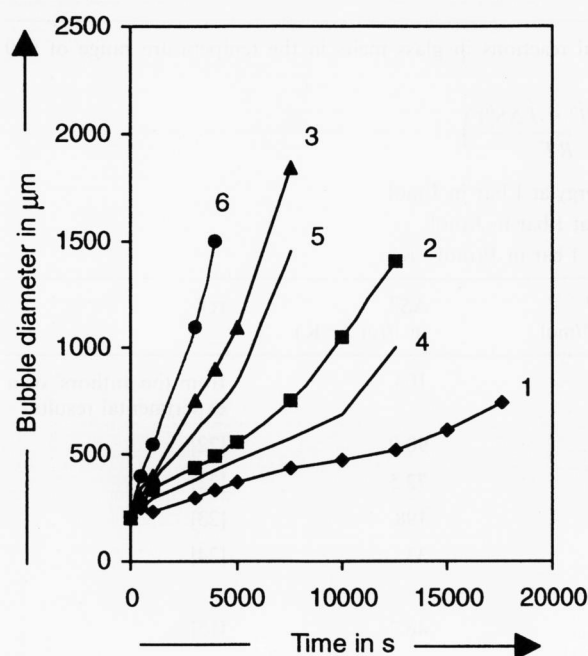


Figure 12. Growth of initially only nitrogen-containing bubble in sulfate-containing soda-lime-silica melt calculated with bubble behavior model for mildly reducing conditions: oxygen activity 10^{-4} bar at 1200°C . Parameters: sulfate content, water dissolved in melt, temperature;

curve 1: 0.3 wt% SO_3 , 360 mg water/kg glass at 1450°C ;

curve 2: 0.3 wt% SO_3 , 500 mg water/kg glass at 1450°C ;

curve 3: 0.3 wt% SO_3 , 650 mg water/kg glass at 1450°C ;

curve 4: 0.2 wt% SO_3 , 360 mg water/kg glass at 1500°C ;

curve 5: 0.2 wt% SO_3 , 500 mg water/kg glass at 1500°C ;

curve 6: 0.2 wt% SO_3 , 650 mg water/kg glass at 1500°C .

final product. The ferrous/ferric ratio exceeds the 80% level. Exactly the same fine cullet, with cokes addition, molten in an atmosphere with a small partial oxygen pressure already becomes more oxidizing and the final sulfide level is not sufficient for full-amber coloring.

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, thus there is no or hardly any sulfide left in the glass and the ferrous/ferric ratio is relatively low. 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.

Unfortunately, it is hardly possible to develop a model describing accurately the redox reactions between components from the furnace atmosphere like CO , C_xH_y , O_2 and components in the cullet or batch like carbon, sulfides, sulfates, ferric and ferrous iron during heating and melting of a batch blanket. The relations are very complex and the redox reactions are dependent on batch size itself and the size of the batch ingredients, determining the batch porosity. Usually important, but hardly defined or considered to be nonreproducible

parameters like cullet size, heating rate, infiltration rate of gases into the batch blanket etc. influence the kinetics of the relevant chemical processes.

9. Melting tests at simulated conditions

The results and the data from literature, presented in the previous sections show the complexity of the sulfate and redox chemistry during heating, melting, fining and cooling in the glass melting process.

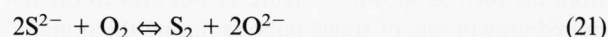
Often, the sulfate solubility in a glass melt as a function of redox state of the glass or redox state of the glass forming batch is given at only one temperature (at a level of 1400 to 1500°C), for only one glass composition, after melting in air or in a typical air fired glass furnace atmosphere (in vol. %: $0.5\text{--}3\text{O}_2$, 10 to 18CO_2 , 12 to $20\text{H}_2\text{O}$). But values for sulfate retentions or solubilities for the case of oxy-fuel fired furnaces, different glass compositions or at other temperature levels are hardly available.

Also quantitative information on the impact of different organic components or the influence of different coke qualities and their grain sizes on the reducing power in a glass melting batch is hardly known.

9.1 Redox state and sulfur solubility of melts in water vapor containing atmospheres

Generally, an increased water vapor pressure in a furnace atmosphere will increase the concentration of dissolved water species in the glass melt. In oxidized melts, water will decrease the SO_2 levels in the bubbles and additional sulfate will decompose to maintain the equilibrium as discussed earlier.

In very reduced melts, water vapor will reduce the sulfide concentration in the melt, this phenomenon has not yet been explained. Perhaps water and sulfides form H_2S gas which will be released from the melt. Water vapor diluting the bubble contents will decrease the oxygen and sulfur concentration in the bubbles and the reaction equilibrium:



is hardly changed by this dilution effect, because the $p\text{O}_2/p\text{S}_2$ ratio is unaffected. In melts prepared from batches with reducing agents, water will promote the release of SO_2 from the melt by decomposition of the residual sulfate, however during this decomposition also oxygen will be formed: for 2 moles SO_2 , 1 mole O_2 will be generated. In such a reduced melts, only a small part of this oxygen will diffuse into the bubbles at normal fining temperatures. Because the ratio $\text{SO}_2:\text{O}_2$ in the bubbles is much larger than the factor 2 in these melts, most of the oxygen produced by sulfate decomposition is absorbed by the reduced species in the melt. This oxygen will oxidize other polyvalent ions, like the ferrous

iron. Thus the oxidation state of the melt will increase due to the dissolved water, diffusing into the fining bubbles.

In amber glass compositions, lower sulfide concentrations were found after melting in a water vapor rich atmosphere, and the ratio ferrous/ferric iron in the amber glass seems to decrease (shifts to a more oxidizing state), with increasing water vapor level above the glass melt probably due to the H_2S formation.

However for melts prepared from oxidized or only very mildly reduced batches, water vapor may have a different effect. Figure 13 shows the measured sulfate retention after melting a batch, in a slightly oxidizing atmosphere without water vapor and in an atmosphere with about 20 vol.% water vapor. The batch is a sulfate-containing soda-lime-silica mixture with a small amount of coke. The Simpson redox number [26] for this batch is +1.5. The sulfate retention in this mildly reduced glass clearly depends on the water vapor pressure during melting and fining, this is also the case for more oxidized batch conditions. The analysis of the gases by EGA (evolved gas analysis) released from the batch during heating and melting in different atmospheres, similar as demonstrated for dry atmospheres in figure 1, may also give important information on reactions taking place between water vapor and batch components like carbon and sulfates.

9.2 Reducing versus oxidizing atmospheres

The sulfate retention and the redox state of the glass after melting an oxidized batch composition with silica sand, soda and limestone plus sodium sulfate have been determined. The impact of the atmosphere has been investigated studying the melting in ambient air, in pure nitrogen and in a dry nitrogen/CO mixture with about 0.5 vol.ppm CO. In the melting tests, 300 g of batch have been placed in a furnace preheated at 1200°C, the temperature has been raised by 20 K/min till the final temperature.

Figure 14 shows the sulfate retention measured in the melts of the three glasses prepared from the same batch, but melted in different furnace atmospheres at a maximum temperature of 1520°C. For the oxygen-containing atmospheres, the temperature dependency of the sulfate retention has been presented in figure 14 for a dry and a water vapor containing atmosphere in the furnace. The glass melted in the dry reducing atmosphere had only a slightly lower sulfate residue than in the case of melting in a dry oxygen rich atmosphere. However, the top surface layer (2 to 3 mm) of the melt included some amber cords, after melting in the CO-rich environment.

Industrial measurements in a container glass furnace using large amounts of coarse recycled cullet (>80%) show a different trend. After changing the firing con-

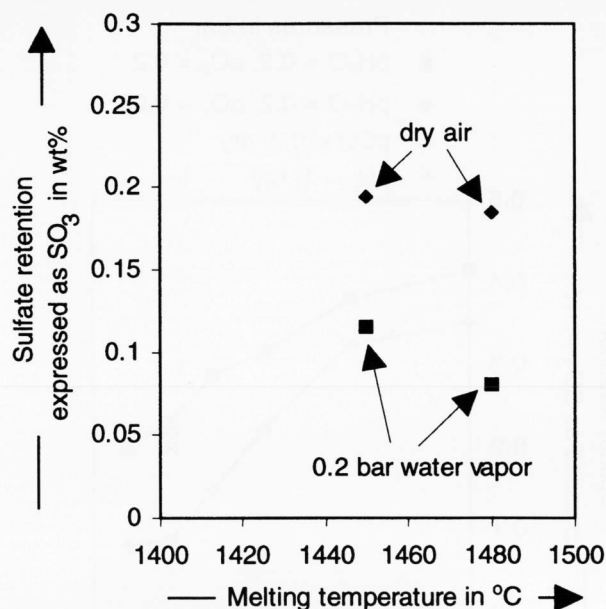


Figure 13. Sulfate retention after melting a sulfate-containing soda-lime-silica glass, molten from batch with 0.1 wt% carbon and 1 wt% sodium sulfate, at different water vapor pressures. Glass composition in mol%: 16Na₂O, 10CaO, 73.9SiO₂ plus SO₃

ditions and air/natural gas ratio in such a green container glass furnace, the CO level of the exhaust gases increased from 250 to 350 mg per m³ up to more than 1250 mg per m³. The SO_x emissions increased from about 1000 up to 2000 mg per m³ (8% oxygen, dry) flue gas. Sulfate becomes less stable as the atmosphere above the batch/coarse cullet blanket becomes more reducing. Additional sulfate addition to the batch appeared to be necessary to maintain the redox state and color of the glass within the required specification ranges.

The coarse cullet in the batch probably allows the infiltration of reducing gas species into the interior of the blanket. Because of the small quantities of soda and limestone in the cullet-rich batch, the CO₂ evolution is limited and hardly prevents the infiltration of the combustion gases. This leads to the conclusion that in batch blankets containing large quantities of coarse cullet, sulfate can be reduced by gases produced by an incomplete combustion and the redox state will become more reducing.

Table 3 shows that an oxidizing atmosphere (nitrogen plus oxygen) has a much more oxidizing effect on a mixture of coarse cullet with addition of a reducing component than for a fine cullet mixture containing the same reducing agent.

In batches with mainly normal raw materials as soda, lime, dolomite and sand grains, the reducing atmospheres only moderately change the average redox state and sulfate solubility of the obtained melt, as shown in figure 14.

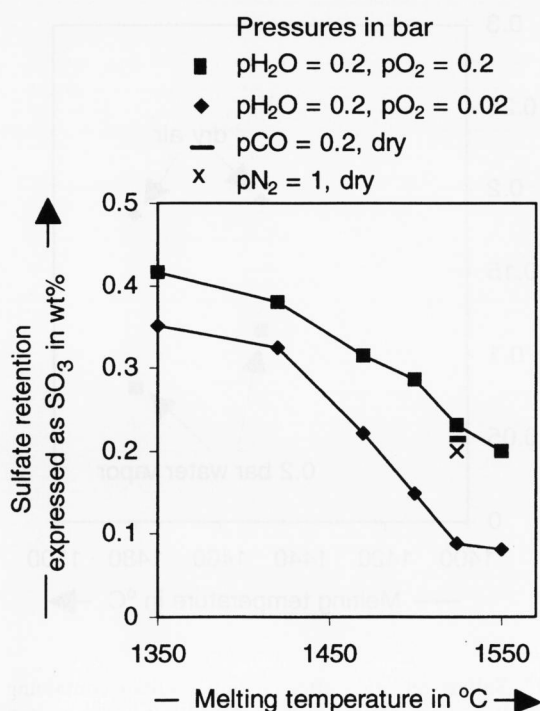


Figure 14. Effect of reducing vapors and water containing furnace atmosphere on sulfate retention for glass molten from sulfate containing soda-lime-silica batch without reducing agents. Glass composition (in mol%) 16Na₂O, 10CaO, 74SiO₂. At a maximum melting temperature of 1520 °C, only the water vapor in the furnace atmosphere, during heating and melting, has an impact on the sulfate retention.

Reducing atmospheres will effect the redox state of the top layer of a glass melt and will only have an impact on the redox state and sulfate retention in the bulk of the melt when using large quantities of coarse cullet or intensively stirring of the melt in a reducing atmosphere.

10. Control of redox state and fining processes applying cullet and changing firing conditions

From the previous sections, it is obvious that the redox state of the melt, the FeO concentration, sulfate and sulfide concentration in the melt, after the primary melting processes and in the final glass product, depend on the redox state of the batch, the heating rate, the exchange of gases with the furnace atmosphere and the batch composition (chemical composition and grain sizes).

For a proper control of the redox state, depending on the reducing power of the cullet contaminants, a representative quantity (30 to 50 kg) of recycled cullet is sampled from the cullet heap. The size of the cullet sample (without reducing the size of the cullet fragments), will be reduced down to about 500 g trying to achieve a representative sample composition.

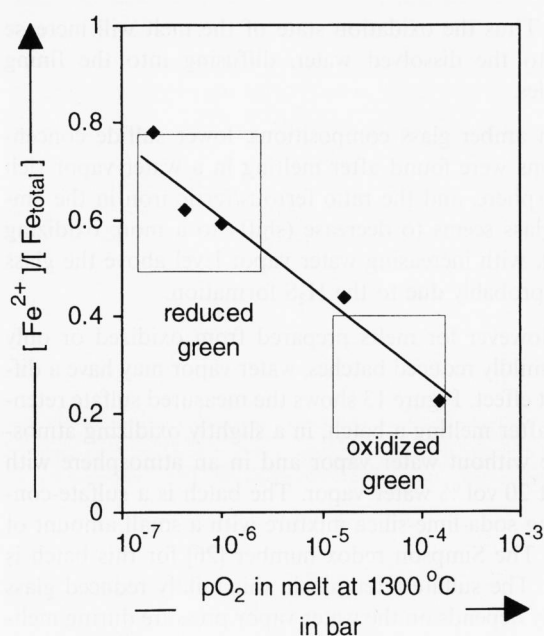


Figure 15. Correlation between redox ratio at room temperature and measured partial oxygen pressure of a melt at 1300 °C for the case of green container glass with total 0.27 to 0.28 wt% iron oxide (expressed as Fe₂O₃). Calculated thermodynamics of ferrous/ferric redox reaction: $[Fe^{2+}] \cdot p_{O_2}^{1/4} / [Fe^{3+}] = \exp \{ -104.000 / (R_g \cdot T) + 40 / R_g \}$ with T in K, $R_g = 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ and p_{O_2} in bar.

Another option is the sampling of about 500 g of fresh glass melt in the batch blanket area. The oxygen activity measured in melted cullet or remelted glass sample, at a certain temperature, can be used as a characteristic value for the redox state or reducing power including the effects of the organic components and the different redox states of the mixed glass types in the cullet.

In order to avoid uncontrolled losses of the reducing power due to oxidation of the organic components by oxygen in the furnace space, the cullet sample has to be melted in a crucible with very low porosity and the cullet should be heated as fast as possible, similar to industrial furnaces, within 30 to 40 min at 1300 to 1400 °C. The oxygen activity measured at a standard temperature by the previously mentioned electrochemical method [7 to 10] can be used for a reproducible correction of the redox state of the batch.

The PC programme predicts the redox-related properties of the produced glass, including iron redox ratio, optical properties and residual sulfate content taking into account the batch composition (raw materials and cullet) and the measured redox state of the recycled cullet (p_{O_2} at 1300 °C, as determined by the Rapidox system). The calculations involve minimization procedures of the Gibbs free energies for the redox equilibria of the different multivalent ions of iron, sulfur and chromium. Basically, the required thermodynamic data for these calculations, including enthalpy (ΔH),

entropy (ΔS) and solubility (L) of the different species (oxygen and sulfur dioxide), must be determined experimentally for each glass type. As an example, figure 15 shows the correlation between the $\text{Fe}^{2+}/\text{Fe}_{\text{total}}$ ratio in the glass product at room temperature and the $p\text{O}_2$ (1300 °C), determined for green container glass with an Fe_{total} content of about 0.27 to 0.28 wt%. Typical redox ranges for oxidized and reduced green glass are indicated in the figure.

In order to predict even more accurately the redox state of the glass to be obtained from a certain batch in a given furnace, it is recommended to simulate on laboratory scale the furnace atmosphere depending on the firing conditions in the industrial furnace. However, the exact simulation of the situation of industrial furnaces for melting of raw material and cullet batches is extremely difficult. The chemistry of batch melting and fining depends on batch blanket thickness, heating rate and furnace atmosphere plus the composition (size, chemical compounds, impurities) of the batch ingredients. Because the composition of the local furnace atmosphere above the batch blanket section in the industrial furnace is hardly known or even variable and also detailed information on the batch contaminants is often lacking, simulation of these conditions seems to be almost impossible.

Especially for coarse cullet, contaminated with organic components, the furnace atmosphere during heating and melting will have a rather large impact on the redox state of the final glass. Redox states of glasses or melts prepared from normal batches or fine cullet are less influenced by the reducing or oxidizing components atmosphere above the batch blanket. However, water vapor will infiltrate quite rapidly during melting and fining of glass melts. For all kinds of batch, water vapor in the atmosphere may drastically influence the final sulfate solubility and redox state of the glass. For batches with a very large quantity of reducing components, for instance in amber glass production, an increasing water vapor pressure during heating and fining will shift the redox state of the melt to the oxidized side. Batch corrections might be necessary at oxygen-firing conditions (high water vapor levels), applying smaller amounts of oxidizing agents or increasing reducing components in the batch like cokes or pyrites for such glass types.

In a batch blanket with small amounts of reducing agents like cokes, a small part of the sulfate might be converted into sulfides by reaction with the carbon, which has not been oxidized by CO_2 . During further heating of the fresh melt, the sulfides and sulfates can react and will form SO_2 gas below about 1300 °C. However, after complete removal of the sulfides, the residual sulfate level becomes relatively low. This sulfate will decompose only at very high temperatures. The presence of water vapor will increase the sulfate decomposition, but will also dilute the oxygen pressure in the bubbles. In such mildly reduced melt, dissolved water seems to act as a reducing agent. In the authors' laboratory stud-

ies and according to thermodynamic modeling, the same behaviour has been found for oxidized batches, without any reducing agents: a water-rich melt becomes more reducing (more ferrous iron) than a dry melt.

*

Some results of this study have been obtained by a cooperation with Dr. Hreglich of the Stazione Sperimentale del Vetro in Murano and Mr. Tonthat of BSN Emballage in Givros.

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