Ceramics-Silikáty 61 (2), 119-126 (2017)
www.ceramics-silikaty.cz
doi: 10.13168/cs.2017.0006

INFLUENCE OF FINING AGENTS ON GLASS MELTING: A REVIEW, PART 1

[#]MIROSLAVA HUJOVÁ, MIROSLAVA VERNEROVÁ

Laboratory of Inorganic Materials, Joint Workplace of the University of Chemistry and Technology Prague,
Technická 5, 166 28 Prague 6,
and the Institute of Rock Structure and Mechanics of the ASCR, v.v.i.,
V Holešovičkách 41, 182 09 Prague 8, Czech Republic

[#]E-mail: Miroslava.Hujova@vscht.cz

Submitted October 12, 2016; accepted January 12, 2017

Keywords: Glass melting, Sodium sulphate, Chemical reactions, Gas evolution, Dissolution, Fining, Foaming, Bubble nucleation

Glass melting is significantly influenced by two processes: the dissolution of particles and the fining of glass. Because these processes are time- and energy-consuming in industry, fining agents are used. Although much literature has been reported about the use of fining agents, no extensive overview of such literature has yet been published. In this paper, we provide such a review, targeting articles that describe the influence of fining agents on (i) the dissolution of particles, (ii) the bubble nucleation and removal, (iii) colour of glass at reduced melting conditions, and (iv) the foaming of glass. We cover the history of fining agent usage from the earliest research in the field to the most recent cutting-edge discoveries. The advantages and disadvantages of all the traditional fining agents are described, with attention paid to the most widely used agent, sodium sulphate. In addition, sodium sulphate is considered as a surface-active compound and colouring substance. Furthermore, we include the influence of redox conditions on the process of fining. We believe that our review provides an ideal introduction to the use of fining agents, both for researchers and industry professionals.

INTRODUCTION

Different types of fining agents, namely selected oxides and salts have been used to enhance the bubble removal from industrial and many special glasses for a long time. Their effect is generally assigned to gases or vapours evolved only at high temperatures in the glass melt, to diffusion of the relevant gases or vapours in growing bubbles and to the consequent increase of bubble separation from the melt by the buoyancy force. The antimony oxide with alkali nitrates as an oxidizing agent, sodium chloride evaporating intensively at melting temperatures and particularly sodium sulphate – either itself or with reducing agents – are preferential examples of these substances. Nevertheless, several further effects of fining agents were observed during glass melting which affect the partial melting phenomena and consequently, the melting efficiency. The effects evoked by the additions of sodium sulphate fining combinations most completely elucidate the behaviour of fining agents:

- additions of sodium sulphate prevent the agglomeration of batch particles, particularly sand particles, and consequently, the slowing down their dissolution in the melt [1-17],
- sodium sulphate and other fining agents react with other batch components during the initial stages of glass melting and produce new chemical compounds, including gases, depending on the glass batch composition, oxidation-reduction state of the melt and atmosphere above the melt [17-35],
- the reactions of sulphate and other fining compounds in the melt affect the glass colour and other properties of glass [35-40].

Further effects of the sodium sulphate on glass melting:

- the gases released in the melt during the later stages of the melting process accelerate the bubble removal phenomenon (fining) by their diffusion into the growing bubbles,
- if the melt becomes supersaturated by refining gases or vapours, new bubbles are nucleated during the later stages of glass melting on bubble inhomogeneities and prolong the bubble removal,
- the primary bubbles supplied by fining gases and the secondary bubbles coming from reactions between fining components and atmosphere cause melt foaming which slows down glass heating and worsens glass quality.

This article will focus on the recent knowledge in the phenomena bound with the presence of fining agents and relevant gas evolution in the melt with respect to the efficiency of the glass melting.

Sand dissolution

The glass-making process consists of three main stages: melting, fining, and homogenization. These stages overlap and influence each other. Melting is finished when all the residual solid particles are dissolved. The silica particles, or sand, are the major component for the most of commonly used glasses. However, sand particles are hard to be completely dissolved. The dissolution of silica grains is therefore crucial for glass homogeneity and for energy costs of glass melting. Therefore, this phenomenon has been studied by many researchers.

Hrma and colleagues provided a brief history of batch melting studies [1]. This article provides a review of the research activity from the beginnings of glass melting studies to cutting-edge discoveries. At first, studies were primarily focused on the mechanism and kinetics of batch reactions. However, since 1960, mainly sand dissolution has been studied. The principle of sand dissolution has been described as a two-step process. In the first step, mainly the fine silica particles are dissolving during the early batch melting, where the reactions in batch primarily occur. However, the dissolution of residual grains is later controlled by diffusion, the important process in the glass melting in terms of time and energy consumption. The diffusion is influenced by various aspects; (i) the buoyant segregation [2-4], (ii) particle agglomeration, (iii) the formation of bubbles [5], [6] and (iv) the clustering of particles [7].

The melting and fining of glass may be enhanced by several methods. One of them is the usage of minor chemical additives. Their function is based on the decrease of reaction temperatures, which results in the formation of low-melting eutectics during the early batch melting stage. In the batch of soda-lime-silica glasses, such an eutectic is formed before Na_2CO_3 melts and positively affects their reactions. The melting accelerators also lower the glass melt viscosity which enhances convection in the melt [8].

Taylor and Rowan [9] studied various combinations of the system Na_2SO_4–Na_2CO_3–$CaCO_3$–SiO_2 by the DTA, TGA and XRD methods to explain the role of Na_2SO_4 in the reactions of soda-lime-silica glass. If the system contained $CaCO_3$ and SiO_2 (apart from Na_2CO_3–$CaCO_3$–SiO_2), wollastonite ($CaSiO_3$) emerged in the melt between 850-950°C. This phase was formed even more easily when sodium sulphate was added. However, when carbon was added to such a batch, the wollastonite peak disappeared. The explanation lies in the conversion of sulphate to sulphite.

The glass melting reactions in one-component, two-component and multicomponent systems (commercial container glass batch) using DTA, TGA and XRD were studied by Hong and Speyer [10], [11].

The studies discussed the role of accelerants, namely sodium sulphate, nitrate and chloride, as well as the different sizes of silica grains used (45-250 μm). In the case of both, the two-component system (soda ash – silica) and multi-component system, sodium chloride was the most effective melting accelerant. It was able to lower the temperature of CO_2 release by 80°C. The soda ash fused and reacted with quartz yielding the metasilicate or disilicate. The reason is the formation of a eutectic melt between soda ash and NaCl.

The addition of sodium sulphate to the binary system enhanced the solid-state reaction between soda ash and silica at low temperatures. However, sodium sulphate has a limited solubility in a silicate melt. Its further addition supresses another metasilicate/disilicate formation by coating residual silica grains. The role of sodium sulphate as a surfactant was confirmed by the shift of the CO_2 release to higher temperatures.

In the multicomponent system, sodium sulphate only had a minor effect as a reaction accelerant. The DTA curves of 0.3 and 1.0 wt. % sodium sulphate mixtures are almost the same as that of the glass batch without additives. The role of Na_2SO_4 as a surfactant in the two-component system is eliminated in the multicomponent system by the addition of other batch materials.

Because of sulphate's limited solubility in silicate melts and its minor effect as a reaction accelerant, its usage is restricted to fining enhancement. This is achieved by the formation of SO_3 respectively SO_2 and O_2, which either forms bubbles or dissolve depending on the partial pressure of oxygen in the melt.

Němec and colleagues have studied the role of sulphur compounds in glass melting. One of their concerns is about the influence of sulphates on sand dissolution, particularly when combined with a reducing agent. Němec found out that the dissolution of sand particles and the gas nucleation and bubble removal (fining) are closely connected. The gases which are evolved from the glass batch can nucleate in the form of bubbles at a solid-melt or melt-melt interface [12].

The evolution of gases connected with sulphates decomposition has two different effects. The micro-stirring, which is caused by the mentioned gas nucleation on the solid surface, and the macro-stirring, caused by the foaming of the melt. On the one hand, the nucleation of bubbles on sand grains slows their dissolution by reducing the free surface of grains. However, as published in [13], [14], sulphates under reducing conditions may enhance sand dissolution. As the decomposition occurs earlier during the glass melting, both stirring effects reduce the diffusion layer around the grain, enhancing its dissolution.

Another beneficial and currently used role of sodium sulphate is to prevent the flotation of silica grains. The bubbles of evolved gas adhere to the surface of silica grains and lift them to the surface where a non-melted layer is formed. Flotation becomes more intensive at higher temperatures as a result of lower viscosity. Na_2SO_4 reduces the surface tension and thus improves the wetting of solid surfaces by the melt [8], [15].

The positive effect of sulphur compounds is expected in the prevention of sand particle agglomeration and clustering. The fact that silica grains are forced to form clusters by rising bubbles was observed by Hrma [7]. The study describes the incorporation of solid silica into molten high-alumina borosilicate glass during glass-batch melting as a function of the grain size. Whereas tiny grains formed a bubbly melt, very large grains formed slowly dissolving clusters. Silica clusters may further agglomerate and eventually create a continuous crust. These crusts were observed by glass makers in the electric melting furnace [16], but no thorough study has been conducted yet.

The interaction of sodium sulphate with carbon as a function of particles dispersity was studied by Minko [17]. The study considered three different combinations of the system Na_2SO_4+C+SiO_2 with various dispersity of sulphate and coal particles. It was found that the flotation of silica depended on the dispersity of the sulphate and coal. The largest amount of melt was formed when fine coal and sulphate were used. The most uniform product was obtained with a coarse sulphate and fine coal. However, the temperature for complete melting was too low.

The dissolution of hard-to-melt particles (silica, alumina) is primarily controlled by diffusion. Since in the early melting stages the surrounding melt around the particles is quite viscous, diffusion and therefore the dissolution process is significantly slowed. For the enhancement of dissolution, melting accelerants may be used, primarily sodium sulphate and sodium chloride. Their presence in melt may cause the formation of easily melting eutectics, which further enhance the melting process. Furthermore, sodium sulphate may act as a surface-active compound, which coats the residual grains. Reducing conditions connected with sodium sulphate further enhances the grain dissolution as micro- and macro-stirring of the melt occur. However, apart from the melting enhancing compounds, the grain size itself needs to be carefully considered. Too coarse or too fine grains may result in the agglomeration and cluster formation of particles in the melt.

Fining agents and their interaction with glass melts during initial stages of glass melting

The choice of a fining agent during glass melting is quite limited. The fining agent has to be a compound stabile up to high temperatures. After reaching a certain temperature, it should decompose, react or evaporate while creating a fining gas or vapour. A sustainable fining compound should not be toxic, should not worsen the glass quality or colour and its solubility in a melt should be sufficient. Its volatility during non-fining temperatures should be as low as possible.

Nowadays, the most widespread fining agent is sodium sulphate. In cases, where a volatile function of the compound is needed, alkali halogenates are used. For this purpose, nowadays only sodium chloride is useable due to environmental issues. The examples of oxidational compounds are alkali nitrates. Nitrates can release oxygen during chemical reactions in the early stage of melting and so they oxidize the lower forms of oxides in melts. Oxides of arsenic and antimony are used with nitrates. Some other oxides, like CeO_2, are also used to a minor extent [12], [18].

Oxides used as fining agents

Arsenic (or antimony) oxide is the one of the most efficient chemical fining agents, especially when used in combination with alkali nitrates in a batch. The quantity of arsenic oxide used for fining is usually 0.1-1 wt.%. As the toxicity of arsenic and antimony is a problem, it is necessary to lower their volatility, which is high, especially, for lower oxidation forms. This is also an issue because of the consequential restricted efficiency of fining. Therefore, the higher concentration of alkali and alkaline earth oxides in the melt is important. These substances are able to support the formation and stability of higher oxidation states of As (Sb) which are less volatile and are the source of fining action.

One of the suggested mechanisms of fining is the reaction of trioxides with oxidants in the first step, e.g. nitrates, present in the melt, in the early stages of batch melting. The nitrate may convert a trivalent oxide into a pentavalent oxide as reaction (1) suggests. An analogous reaction is suggested for the reaction of antimony oxide with nitrate. Pentavalent oxide is then easily dissolved into the emerging melt.

$$4KNO_3 + 2As_2O_3 \rightarrow 2K_2O + 2As_2O_5 + 4NO + O_2 \quad (1)$$

After the decomposition of the batch, a melt is heated to high temperatures for complete fining. The decomposition of the present pentoxide providing the trivalent form takes place as the main part of fining (2). This reaction produces O_2 as the fining gas, which may either diffuse into the existing bubbles or to form completely new ones.

$$As_2O_5 \rightarrow As_2O_3 + O_2 \quad (2)$$

Instead of arsenic trioxide arsenic acid may be added into the batch, which is less volatile. Fining by arsenic (and antimony) compounds is irreplaceable for special applications, where a very high quality of glass or very high melting temperatures are needed. It is applied in the production of pharmaceutical glasses, display glasses and glass ceramics [19].

Cerium dioxide

One of the possible polyvalent elements used for fining is CeO_2, which can also be used as a chemical colorant. Other oxides used for this purpose in a less extensive way are, i.e.: MnO_2, Fe_2O_3, and Pb_3O_4 [20]. This group of fining agents acts as the source of oxygen, which may be released in decomposition reactions, for example (3).

$$4CeO_2 \rightarrow 2Ce_2O_3 + O_2 \qquad (3)$$

However, these oxides are mostly added for the other reasons than their fining action [19]. The presence of polyvalent elements in glass melts influences the colour of the resulting glass, which is discussed in a further chapter.

Halides

Halides are used when the decrease of glass viscosity is desired. Their disadvantage is especially in oxidizing atmospheres, where the replacement for oxygen gradually causes volatilization. Such an effect results in the inhomogeneity of the glass [19].

In the glass industry, mostly NaCl is used (b.p. 1413°C), because other halides are rather less soluble in molten glass and are less suitable environmentally. Even using NaCl is a problem, since this fining agent produces emissions of highly environmentally hazardous chlorides that may later form HCl gas.

Usage of NaCl may be preferred for glass types, which can be melted only at relatively high temperatures (e.g. borosilicate glasses). For such glasses the application of sulphates without NaCl is less effective, since the viscosity of the glass melt would be too high at fining temperatures [21]. NaCl further creates eutectics with hard-to-melt oxides, which therefore enhances glass melting.

Sulphates

From the all the alkali sulphates available, sodium sulphate is the most widely used in glass-making production, i.e. for the production of flat, container, electrochemical and other glass types. Its role is multi-faceted and may be described as:

a) source of Na_2O in the glass,

b) promoter of low-melting eutectics at the silicate-formation stage,

c) fining agent,

d) oxidizer via oxygen release in decomposition reaction,

e) surface active component.

At present, the main purpose in the usage of Na_2SO_4 in glass production is fining action. The other trend is the lowering of the sulphate/soda ratio as much as possible, due to the strict limits on SO_2 emissions [22].

Before the fining by sodium sulphate takes place, dissolution in glass melt is required. The work [23] investigated the compositional dependence of sulphate solubility in glasses. The authors studied the ternary group of glasses SiO_2–MO–Na_2O (where the M stands for an alkaline earth metal). The experiments were conducted with MgO, $CaCO_3$, $BaCO_3$, and in conclusion, solubility increased in the order MgO<CaO<BaO. The solubility of sodium sulphate is also rising with the increasing MO content, generally, as the basicity of the glass increases [24]. Consequently, emerging sodium metasilicate becomes completely miscible in the glass melt.

In the fining process, the elimination of seeds from the glass melt is mainly performed by the ascent of bubbles to the surface. The bubbles originally contain gases coming from the batch reactions: mostly CO_2 from carbonate decomposition, a smaller amount of water vapour from the batch humidity and air coming from the original atmosphere. As the temperature increases, the sulphate decomposes and the arising amount of SO_3 quickly decomposes to SO_2 and O_2 gas. This escapes partially to the atmosphere and partially dissolves in the melt. All the dissolved gases including water vapour diffuse into the bubbles and substantially increase in size. The buoyancy force then causes their escape from the melt by rising. If the temperature is sufficiently high (more than 1450°C), the SO_3 supersaturates the melt and produces new bubbles. As a nucleation centre serves the melt inhomogeneity, the undissolved particles of the glass batch preferentially. If some bubbles remain present in the melt, as the temperature decreases they shrink and even complete disappear, since the solubility of the SO_3 present increases below 1400°C [25].

Reactions in oxidized melts are well defined. Sodium sulphate reacts with sand above 1200°C (4). This reaction is rather slow in comparison with the reaction of soda lime and sand [26].

$$\begin{aligned} &Na_2SO_4 + nSiO_2 \rightarrow Na_2O\cdot nSiO_2 + \\ &+ SO_2 + ½O_2 \end{aligned} \qquad (4)$$

The thermal decomposition of sodium sulphate then occurs above 1400°C, with a massive evolution of fining gas (5):

$$\begin{aligned} &Na_2SO_4\ (l) \rightarrow Na_2O\ (l) + \\ &+ SO_2\ (g) + ½O_2\ (g) \qquad \text{(above 1400°C)} \end{aligned} \qquad (5)$$

Reactions of sodium sulphate with carbon and with carbon monoxide are even more complicated, for example they are summarized in articles [11, 14, 30, 31]

The reduction of sulphate occurs in the early melting stages, in the range of 650-1000°C. Both, C (6) and CO (7) may act as a reducing agent [26]. The sulphide present further reacts with $CaCO_3$ (8) [22]:

$$Na_2SO_4 + 2C \rightarrow Na_2S + 2CO_2 \quad \text{(650-900°C)} \qquad (6)$$

$$Na_2SO_4 + 4CO \leftrightarrow 4CO_2 + Na_2S \quad \text{(700-1000°C)} \qquad (7)$$

$$Na_2S + CaCO_3 \rightarrow CaS + Na_2CO_3 \quad \text{(740-800°C)} \qquad (8)$$

Further, the complex reactions in reduced batches may lead to sulphur deposits in primary bubbles occurring in a glass (9 and 10):

$$\begin{aligned}&N_2SO_4 + CaS + 2SiO_2 \rightarrow Na_2SiO_3\\&+ CaSiO_3 + SO_2 + S \qquad (865°C)\end{aligned} \tag{9}$$

$$\begin{aligned}&Na_2SO_4 + Na_2S + 2SiO_2 \rightarrow\\&\rightarrow 2Na_2SiO_3 + SO_2 + S \qquad (865°C)\end{aligned} \tag{10}$$

Both sulphides and sulphates form eutectics at lower temperatures [22], enhancing the creation of the melt and the dissolution of sand particles (11-14):

$$Na_2S - Na_2SO_4 \qquad (740°C) \tag{11}$$

$$Na_2S - Na_2CO_3 \qquad (756°C) \tag{12}$$

$$Na_2SO_4 - CaCO_3 \qquad (795°C) \tag{13}$$

$$Na_2SO_4 - Na_2SiO_3 \qquad (865°C) \tag{14}$$

To conclude, pure sodium sulphate accelerates glassmaking and fining in two stages – the first stage starts at 500-800°C, where the low melting eutectics form and sulphate avoids agglomeration. The second stage starts when the complete decomposition of sodium sulphate occurs (above 1400°C).

In the case of reduced glasses, it is important to meet the condition of sulphates complete reduction in the glass batch. This reduction is mostly performed by a reaction of the s-g type. Overall, 16.9 g of carbon is required to reduce 100 g of sulphate [17]. The reaction of the carbon in the batch may be described in first step via the set of equations listed below (15 and 16):

$$C + O_2 \rightarrow CO_2 \tag{15}$$

$$C + \tfrac{1}{2}O_2 \rightarrow CO \tag{16}$$

And the so-called Boudouard reaction (17):

$$C + CO_2 \rightarrow 2CO \tag{17}$$

Further investigation in the system $Na_2SO_4 + C + + SiO_2$ brought the conclusion that the mass loss of coal via CO_2 strongly depends on its dispersity. Dispersity plays a role even in the reactivity of sulphate and coal, with the most favourable results when using finely dispersed carbon and coarse sulphate. Furthermore, the flotation of quartz grains has been observed in this system. Even work [22] mentions that when the sulphate/carbon ratio and the chemical oxygen demand of the raw materials and batch are not matched, then the full reduction and even the decomposition of sulphate may not occur. This results in a layer of molten Na_2SO_4 where $CaSO_4$ and Na_2SiO_3 are also dissolved. This layer would just lie atop the silicate melt, because of the mentioned liquation process.

The work [29] investigated the dissolution of sulphur in base glasses. SO_2 gas was bubbled into molten glass and then the samples were evaluated by the XANES analysis. This has proven that sulphate and sulphide coexist in a silicate melt under various conditions. However, no sulphite was found. In conclusion, it is suggested, the sulphite disproportionates to sulphate and sulphide when dissolution occurs in the melt.

The industrial production of reduced glasses uses much less carbon than the stoichiometric reaction would need. The rest of the reducing potential is carried into the batch via raw material containing reducing compo-nents (coke, impurities etc.). Apart from the different reactions of sulphur in the batch, the reducing potential of carbon may influence redox equilibria of other elements, the most important being the Fe^{2+}/Fe^{3+} equilibrium.

Apart from the redox equilibrium in the melt, low basicity leads to a low absorption of SO_3, yielding the SO_4^{2-} ion. This occurs no matter how high the oxidative potential is. However, the fining capacity of such a melt may not be sufficient due to reaction (18):

$$SO_4^{2-} \rightarrow SO_2 + \tfrac{1}{2}O_2 + O^{2-} \tag{18}$$

This equilibrium plus the SO_3 content in glass is the indication of acidification, which is further important for the process of fining. To conclude, the absorption of sulphur gases in melts is dependent on the acidity of melt and on its redox state.

Therefore, melting processes must be judged via the redox potential of glass, determined by the chemical oxygen demand of the raw materials (this varies over a wider range, dependent on their type and purity) and the batch and by monitoring the excess air or oxygen during fuel combustion.

Since also the recycling of the consumer waste glass and the addition of filter dusts into the glass batch makes it harder to estimate the correct concentration of fining agents, it is important to describe the redox state inside the furnace. Nowadays, it is mainly measured by the properties of the final glass, i.e.: colour, spectra, sulphur retention [28] and also by a redox measurement, both laboratory and continuous.

Redox conditions during glass melting may be also changed by moisture content present in a furnace atmosphere, which among other things, results in a higher concentration of OH^- groups in the glass. This reaction may also result in the creation of two different glass layers, oxidized ones (sulphate containing) and reduced ones (sulphide containing). Their interaction generates free SO_2 gas which results in fine seeds present in the final glass [22], [30].

A number of different explanations have been proposed by several authors [22, 30-32]. Sulphates are soluble in water and therefore the moisture has a impact on glass redox. If the batch reacts with water vapour, it has been suggested that instead of reaction (19), it is more likely for the reaction (20) to occur. However, according to [32], NaOH is not formed in soda batch (even moistened), and to activate reaction (20), the NaOH must be purposely introduced into the batch.

$$\begin{aligned}&Na_2S + Na_2SO_4 + 2SiO_2 \rightarrow\\&\rightarrow Na_2O{\cdot}SiO_2 + SO_2 + S\end{aligned} \tag{19}$$

$$Na_2S + H_2O \rightarrow NaOH + H_2S \tag{20}$$

In [30], authors tracked down the most famous mechanism of reaction (21) between sulphate ions and water vapour, where the sulphate ions in the glass melt directly react with water vapour.

$$SO_4^{2-}\,(l) + H_2O\,(g) \rightarrow SO_2\,(l, g) + \frac{1}{2}O_2\,(l, g) + 2OH^-\,(l) \qquad (21)$$

This interaction results in a continual foam that worsens not only the heat transfer process but also the glass fining. The phenomenon of glass foaming, its reasons and results will be discussed in the next chapter.

In conclusion, the behaviour of sulphur added via sodium sulphate is influenced by redox conditions in a glass melt. The redox is given mainly by the composition of the batch, primarily by the addition of reducing agents, further by impurities and by the composition and impurity of the added cullets. Sulphate in a glass melt reacts in redox reactions or is gathered on the surface of melt, where on the one hand it helps to fight sand agglomeration, while on the other hand it slows chemical reactions in the batch. Dissolution of sulphate in a melt strongly decreases with the acidity of the glass, because thermal decomposition of sulphate occurs too. In the case of acidic melts, its content in glass is very low.

However, thermal decomposition is essential for the fining of oxidized glasses. The existence of reducing impurities leads to the reduction of sulphates, whereas the most important reduction is to SO_2 and further to sulphide (650-1000°C). The evolution of SO_2 enhances the melt stirring and so its homogenization and dissolution of sand particles. The simultaneous existence of S^{2-} and SO_4^{2-} leads to the oxidation of sulphides and this reaction leads to yet another evolution of SO_2 gas (1100-1300°C). In general, the evolved gases help the fining process, however they also lead to bubble nucleation especially on the surface of the solid parts in the batch. Further, the microconvection does enhance the dissolution of sand seeds but also it slows down the fining (secondary bubbles) and may cause a severe melt foaming in the later stages of melting.

The melting process is influenced not only by the presence of different oxidational states of sulphur but also by the dissolution of its compounds in the melts. Sulphates are relatively well soluble, especially in basic melts (from tenths up to several percent). Even sulphides are well soluble, however the solubility of tetravalent sulphur is low, practically its physical solubility is up to hundreds of a percent. In conclusion, the solubility of sulphur with the melt basicity demonstrates a characteristic V-curve.

Summarizing the sulphate fining action, two mechanisms of fining via SO_2 are described. In the case of oxidised melts, it is the thermal decomposition of sulphates. The process is intensive; however it demands high temperatures (1450°C and more). In reduced melts, sulphides with remaining sulphates generate the fining gas. The intensity of this process is significant during lower temperatures (<1300°C) and is typical especially for amber glasses.

A significant reaction of sulphate with water vapour in glass melts produces gaseous SO_2 and O_2 while OH groups are also formed in the glass. The presence of water vapour in the atmosphere during melting may lead to intensive and fast foaming.

Colours produced by fining agents in glasses

Colours produced by sulphur present in glass melts

It has been well known for a long time that the addition of various carbon sources in glass technology may lead to yellowish – reddish tints in the resulting glass. At first, the dissolved carbon particles were assumed to be responsible for this colour, however this opinion was proved wrong. Nowadays it is well accepted that in the order to obtain an amber colour in glass the presence of sulphur and iron is needed. As for the responsible chromophore, it was discussed for a long time whether polysulphides and or compounds of sulphides with iron, cause reddish colours in strongly basic glasses. However, the results of spectroscopy and analytical measurements proved that the chromophore is carried by tetrahedral Fe^{3+} surrounded by three ions of oxygen and one ion of S^{2-}. Sulphur in this chromophore may be bound only to Fe^{3+} or to bridging Si^{4+}. The excess of charge is compensated by Na^+ or Ca^{2+} respectively.
The greatly desired amber colour of glass may be obtained in alkali glasses containing sulphur and iron under reducing conditions. However, too great a reducing melt may decrease the intensity of the amber colour due to lack of a Fe^{3+} ion in melt.

Amber glasses absorb well through UV, violet and blue spectra, however the absorption of yellow, red and IR is almost non-existent. To obtain the best intensity of amber, alkali glasses are used, in preference to potassium over sodium. However, the glasses must not contain, PbO, ZnO, and CdO since these metals tend to form strong complexes with sulphur [33].

An amber glass is susceptible to reboil. Therefore, one of the most important things is to keep the SO_3 (SO_2 and O_2 respectively) content in the glass melt as low as possible [34]. If SO_3 is present, the amber chromophore is destroyed, as reaction (22) suggests. The mechanism of reboil will be discussed in the further chapters of this review.

$$2Fe^{3+} - 3S^{2-} + 6SO_3 + 3/2\,O_2 \leftrightarrow Fe_2O_3 + 9SO_2 \qquad (22)$$

Arsenic oxide, Antimony oxide and Cerium oxide

According to [35], an increase in the concentration of arsenic oxide added to the soda-lime-silica batch, results in greenish glass. Otherwise, no such research, which would claim arsenic oxide was the glass colourant, was found.

Antimony oxide on the other hand is in combination with antimony sulphide well used as a glass colourant and is known as “antimony ruby”. The creation of complex $Sb_2O_3.Sb_2S_3$ occurs, when glass is reheated up to 700°C after casting.

As for the cerium oxide, its usage is in the centre of interest for the creation of yellow glasses, e.g. the automobile’s yellow bulbs [36]. In combination with titanium oxide, it provides a desirable yellow colour of glass without creating a need for a strongly reduced glass, which is required when the production of yellow glass is provided via sulphides (e.g. CdS).

Cerium oxide, without titanium oxide, added in concentrations lower than a 5 wt. %, even results in just a slightly yellow glass or even a colourless glass. However, glass containing cerium and arsenic oxides, even in low concentrations turn brown when exposed to the sun’s radiation. In connection with the mentioned facts, cerium oxide may be used for the decolourization of glasses, but in the spite of the mentioned solarization of glasses neither arsenic nor antimony oxide must be present [33].

The presence of cerium, antimony or arsenic oxide in a glass that already contains a colouring polyvalent ion may change the resulting colour of such a glass. These oxides have reducing power that follows the order: Sb>As>Sn>Cu>Ce. Therefore, the usage of these compounds should be considered individually, according to the present colouring oxide and its reaction to the oxidizing effect of the selected fining agent [37].

CONCLUSION

In this paper, we have provided the comprehensive review on fining agents and four main issues connected with their usage in glass technology. In our focus was the detailed description of sodium sulphate usage, though we have mentioned other fining agents from groups of halides and oxides. In our second part of this review, we will mainly focus on possible mathematical modelling of glass fining, bubbles nucleation and fining and finally the foams in glasses will enclose this major review.

Acknowledgements

This work has been supported by the Student’s research grant project of the internal grant agency of the University of Chemical Technology, Prague, “Factors of continual glass melting process, kinetics and space utilization” and Financial support from Specific University Research (MSMT No. 20-SVV/2016).

REFERENCES

1. Hrma P., Marcial J., Swearingen K. J., Henager S. H., Schweiger M. J., TeGrotenhuis N. E. (2011): Conversion of batch to molten glass, II: Dissolution of quartz particles. *Journal of Non-Crystalline Solids*, *357*, 820–828. doi: 10.1016/j.jnoncrysol.2010.11.096
2. Kröger C., Eligehausen H. (1959): Über das Wärmeleitvermogen des einschmelzenden Glasgemenges. *Glastechnische Berichte, 32*, 362-373.
3. Bunting J. A., Bieler B. H. (1969): Batch free time versus crucible volume in glass. *American Ceramic Society Bulletin, 48*, 781–785.
4. Vierneusel U., Goerk H., Schuller K. H. (1981): Suppression of segregation on crucible melts. *Glastechnische Berichte, 54*, 332-337.
5. Němec L. (1977): Refining in the glassmelting process. *Journal of the American Ceramic Society, 60*, 436–440. doi: 10.1111/j.1151-2916.1977.tb15528.x
6. Němec L. (1979): Intensification of Glass Melting by Bubbling – Part 3: Utilization of Molten Glass Stirring in the Technologic Scale. *Sklář a Keramik, 29*, 144–150.
7. Schweiger M.J., Hrma P., Humrickhouse C. J., Marcial J., Riley B. J., TeGrotenhuis N. E. (2010): Cluster formation of silica particles in glass batches during melting. *Journal of Non-Crystalline Solids ,356*, 1359–1367. doi: 10.1016/j.jnoncrysol.2010.04.009
8. Hlaváč J. (1983). *The technology of glass and ceramics*. Elsevier scientific Publication company.
9. Taylor T. D., Rowan K. C. (1983): Melting Reactions of Soda-Lime-Silicate Glasses Containing Sodium Sulfate. *Journal of the American Ceramic Society, 66*, 227-228. doi: 10.1111/j.1151-2916.1983.tb11015.x
10. Hong K. S., Speyer R. F. (1993): Thermal Analysis of Reactions in Soda-Lime Silicate Glass Batches Containing Melting Accelerants: I, One- and Two- Component Systems. *Journal of the American Ceramic Society, 76*, 598–604. doi: 10.1111/j.1151-2916.1993.tb03648.x
11. Lee S. W., Speyer R. F., Hong K. S., Condrate A., Hapanowicz R. P. (1992): Characterization of gas components and deposits in bubbles in silicate glasses prepared with sodium sulphate. *Journal of Materials Science, 27*, 4961–4966. doi: 10.1007/BF01105261
12. Němec L., Kloužek J. (2003): Modelling of glass refining kinetics Part 1. Single bubbles. *Ceramics – Silikaty, 47*, 81–87.
13. Kloužek J., Arkosiová M., Němec L., Cincibusová P. (2007): The role of sulphur compounds in glass melting. *Glass Technology - European Journal of Glass Science and Technology, 48*, 176–182.
14. Arkosiová M., Kloužek J., Němec L. (2008): The Role of Sulfur in Glass Melting Process. *Ceramics – Silikaty, 52*, 155–159.
15. Hrma P., Bartoň J., Tolt T. L. (1986): Interaction Between Solid, Liquid and Gas During Glass Batch Melting. *Journal of Non-Crystalline Solids, 84*, 370-380. doi: 10.1016/0022-3093(86)90799-4
16. Verheijen O. S. (2003). *Thermal and chemical behavior of glass forming batches.* Thesis, Technical university Eindhoven., ISBN 90-386-2555-3.
17. Minko N. I., Morozova I. I., Binaliev I. M. (2015): Interaction in Sodium Sulfate – Carbon Mixtures as a Function of Their Dispersity. *Glass and Ceramics, 72*, 159–165. doi:10.1007/s10717-015-9746-y
18. Němec L. (2008). Čeření skel, in Berka I. (Ed.): *Tavení*

skla, ČSS. pp. 48–91.

19. Shelby J.E., (2005). *Introduction to Glass Science and Technology.* 2nd ed. Royal Society of Chemistry.
20. Vargin V. V., Osadchaya G. A. (1960): Cerium dioxide as a fining agent and decolorizer for glass. *Glass and Ceramics, 17*, 78–82. doi:10.1007/BF00692388
21. Corning, (1936). Method of fining borosilicate glasses. US 2035318.
22. Minko N. I., Binaliev I. M. (2013): Role of Sodium Sulfate in Glass Technology. *Glass and Ceramics, 69*, 361–365. doi: 10.1007/s10717-013-9479-8
23. Ooura M., Hanada T. (1998): Compositional dependence of solubility of sulphate in silicate glasses. *Glass Technology, 39*, 68–72.
24. Holmquist S. (1966): Oxygen ion activity and the solubility of sulfur trioxide in sodium silicate melts. *Journal of the American Ceramic Society, 49*, 467–473. doi:10.1111/ j.1151-2916.1966.tb13301.x
25. Manabe S., Kitamura K. (1986): Effect of sodium sulfate and temperature on the fining of float glass. *Journal of Non-Crystalline Solids, 80*, 630–636. doi: 10.1016/0022-3093 (86)90456-4
26. Vernerová M. (2011): *Oxidation-reduction reactions in the glass melts and during glass melting.* Thesis, UCT Prague.
27. Beerkens R. G. C. (2009): Fining of Glass Melts: What We Know About Fining Processes Today. *69th Conference on glass problems*, 13–28.
28. Beerkens R. G. C, Kahl K. (2002): Redox and sulfur chemistry of soda lime silica glass melts. *Physics and chemistry of glasses, 43*, 189–198.
29. Backnaes L., Stelling J., Behrens H., Goettlicher J., Mangold S., Verheijen O., Beerkens R. G. C., Deubener J. (2008): Dissolution mechanisms of tetravalent sulphur in silicate melts. Evidences from sulphur K edge XANES studies on glasses. *Journal of the American Ceramic Society, 91*, 721–727. doi: 10.1111/j.1551-2916.2007.02044.x
30. Vernerová M., Kloužek J., Němec L. (2015): Reaction of soda–lime–silica glass melt with water vapour at melting temperatures. *Journal of Non-Crystalline Solids, 416*, 21–30. doi:10.1016/j.jnoncrysol.2015.02.020
31. Stelling J., Behrens H., Wilke M., Göttlicher J., Chalmin-Aljanabi E. (2011): Interaction between sulphide and H_2O in silicate melts. *Geochimica et Cosmochimica Acta, 75*, 3542-3557. doi: 10.1016/j.gca.2011.03.030
32. Pankova N. A., Markov S. I. (1994): Silicate formation in the wet batch. *Glass and Ceramics, 51*, 2–4. doi:10.1007/ BF00682528
33. Fanderlik I., (1978). *Barvení skla.* SNTL.
34. Myers D., Ross P. (2006): Amber glass - 40 years of lessons learned. *66th Conference on glass problems*, 129–139.
35. Firth E. M., Dokin F. W., Turner C. (1926): XV. The function of arsenic in soda-lime-silica glass. Part II. *Journal of the society of the glass technology, XI*, 190–213.
36. Trusova E. E., Bobkova N. M., Gurin V. S., Gorbachuk N. I. (2007): Formation of coloring complexes in glass colored with cerium and titanium oxides. *Glass and Ceramics, 64*, 346–348. doi: 10.1007/s10717-007-0086-4
37. Stalhandske Ch. (2000): The impact of refining agents on glass colour. *Glasteknisk tidskrift, 55*, 65–71.