

## REDOX EQUILIBRIA OF SULPHUR IN GLASS MELTS

JAROSLAV KLOUŽEK, MIROSLAVA ARKOSIOVÁ, LUBOMÍR NĚMEC

*Laboratory of Inorganic Materials**Joint Workplace of Institute of Inorganic Chemistry ASCR and Institute of Chemical Technology in Prague,  
Technická 5, 166 28 Prague, Czech Republic*

E-mail: klouzekj@vscht.cz

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*The combination of experimental and computational methods used for the study of redox equilibria of sulphur in glass melts makes possible to reveal mechanism and time sequence of redox phenomena taking place during melting process. Both methods were applied for the optimization of sc. reducing sulphate refining realized by the addition of sulphate and reducing agent to the glass batch. The results of experiments supported by the model calculation showed that proper combination of both components at the same time improves homogenization and refining of glass melt and suppresses unwanted bubble nucleation at maximal melting temperatures.*

## INTRODUCTION

Chemical refining performed by several types of refining agents is at present the most frequent way to remove bubbles from glass melts. Among refining agents, sulphates of alkali or alkali-earth metals play an important role being used namely for float and container glass. The sulphate refining however requires high melting temperatures, often above 1500°C. In addition, secondary bubbles formation (reboil) may appear at the melt-solid, i.e. at inhomogeneities, glass electrodes or refractory materials. These disadvantages may be suppressed by sc. reducing sulphate refining facilitated by the addition of reducing agent to the batch. Carbon in the form of graphite or coke is usually used. The use of blast-furnace slag containing up to 1 wt.% of sulphides is also possible.

However, theoretical description of the interaction of reducing agent with sulphate during glass melting process is complicated. Depending on the redox state, several sulphur species including sulphates, sulphites, sulphides, sulphur dioxide and elemental sulphur can exist in the melt.

The aim of this work is to interpret the role of combination of sulphate and reducing agents in glass melting and refining. To study this problem, the experimental methods of evolved gas analysis and direct high temperature observation of bubble behaviour were used to define appropriate chemical reactions and to find the time sequence of corresponding processes. Experimental findings then allow formulation of theoretical model based on the reactions between components, namely reducing agent, sulphate and sulphide and calculation of simultaneous chemical equilibrium of mentioned sulphur components.

## EXPERIMENTAL

The study was carried out on a soda-lime-silica glass of the composition (wt.%): 72.7 SiO<sub>2</sub>, 1.5 Al<sub>2</sub>O<sub>3</sub>, 9.7 CaO, 2.6 MgO, 13.0 Na<sub>2</sub>O, 0.3 K<sub>2</sub>O. Granulated coke of an average particle size 0.5 mm was used as reducing agent. The addition of coke varied between 0 and 0.1 wt.%. The sodium sulphate was dosed to the batch to give the concentration in glass corresponding to 0.20 and 0.25 wt.% SO<sub>3</sub>.

Evolved gas analysis of reaction mixtures was carried out by the gas chromatography. The reaction mixture in the test tube made of silica glass was placed in a laboratory furnace heated at a rate of 5°C/min. Gases evolved from the sample were flushed out to the sampling loops by the stream of air. The loops were repeatedly connected to the stream of carrier gas of the chromatograph. The result of analysis is presented in the form of temperature dependence of evolved amounts of CO<sub>2</sub> and SO<sub>2</sub>.

The residual sulphate content in melted glass samples was determined by the helium extraction followed by gas chromatographic analysis of extracted gases.

The melting of glass batches and the behaviour of bubbles in the melt was observed by a high temperature method. The glass batch was placed in a silica glass observation cell, which was inserted in the observation furnace tempered at 500°C. The sample was then heated to the final temperature 1500°C at the heating rate of 10°C/min. The course of batch melting and refining was evaluated by the measurement of the average bubble growth rate at final temperature by using the image analysis. Heterogeneous nucleation of bubbles was examined by the same observation method. The formation of bubbles on a PtRh wire was observed at the tem-

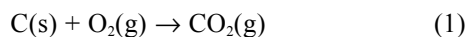
perature increase 2°C/min. The temperature of bubble nucleation was detected by extrapolating the bubble radius to zero.

## RESULTS AND DISCUSSION

### Evolved gas analysis

The first set of experiments involves the study of the mechanism, temperature range and time sequence of the interaction between the sulphate and the reducing agent. Figure 1 shows the results of analysis of gases evolved from the mixture containing sulphate (0.20 wt.% SO<sub>3</sub>), granulated coke (0.05 wt.%) and glass cullet. Other raw materials were not used as the CO<sub>2</sub> formed by the decomposition of carbonates may overlap gas peaks evolved during studied interaction.

The first maximum of evolved CO<sub>2</sub> at the temperature of 350°C corresponds with the oxidation of carbon by air oxygen.



The second CO<sub>2</sub> maximum between 600 and 900°C indicates the reaction between the reducing agent and the sulphate.

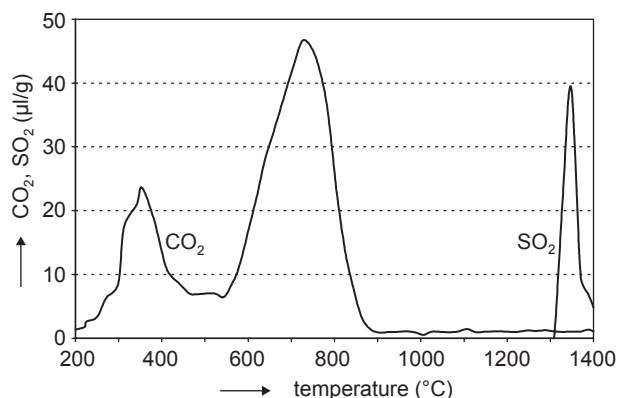
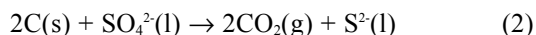


Figure 1. Evolved gas analysis of the mixture coke-sulphate-cullet.

As no other CO<sub>2</sub> maxima were detected, it can be supposed that the carbon oxidation by the sulphate is complete, i.e. no carbon dissolved in the melt exists at higher temperatures. In addition, the temperature range of the reaction indicates that in the reaction (2) enters only the sulphate present in the batch, but not the sulphate present in the glass cullet. A comparison of the reaction stoichiometry and the amount of dosed sulphate suggests that the sulphate conversion is only about 20%. This value shows that majority of the added carbon is oxidized by the air and does not react with the sulphate.

Most studies of oxidation of carbon at temperatures below 1000°C take into account so-called Boudouard reaction occurring in the glass batch [1-3]:

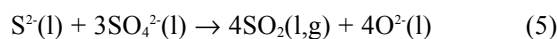


The reduction of sulphate is then facilitated by the reaction with carbon monoxide:



The gas chromatographic system used in this study is however unable to detect evolved carbon monoxide and confirm the last mechanism. Nevertheless, the most important result of mentioned reactions is the formation of sulphide ions.

The evolution of SO<sub>2</sub> detected above 1300°C demonstrates the reaction of remaining sulphate with sulphides originated by the reaction (2) or (4):



### Batch melting tests

Figure 2 shows an example of high temperature images of the melting tests recorded after 60 minutes dwell at the temperature of 1500°C. Average values of the growth rate of bubble diameter ( $\Delta d/\Delta \tau$ ) presented in the figure 3 were measured in glass melts prepared from batches with the addition of sulphate (0.20 and 0.25 wt.% SO<sub>3</sub>) and with different amount of coke. The melt containing only 0.20 wt.% SO<sub>3</sub> exhibits the relatively low value of  $\Delta d/\Delta \tau = 7.6 \times 10^{-7}$  m/s. The addition of coke

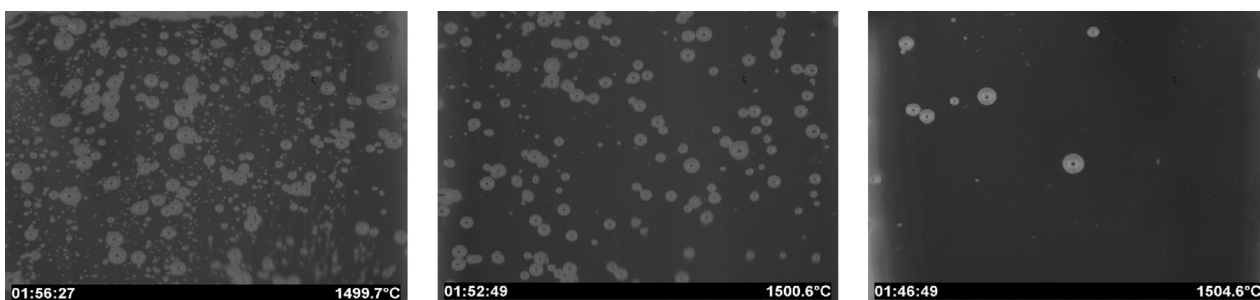


Figure 2. The course of the melting process, 0.20 wt.% SO<sub>3</sub> and 0, 0.01 and 0.05 wt.% coke.

brings considerable increase of the refining efficiency, when the bubble growth values exceed  $1.5 \times 10^{-6}$  m/s. The dependence of the average bubble growth rate on the addition of reducing agent exhibits typical maximum, here at the coke level of 0.02 wt.%. The decrease of  $\Delta d/\Delta \tau$  at higher additions of coke content in the batch corresponds with the decrease of residual sulphate content in glass presented in the figure 4. As can be seen, the addition of 0.05 wt.% of coke results in the content of sulphate 0.105 wt.%. Despite this considerable decrease of the sulphate content, the value of  $\Delta d/\Delta \tau = 1.46 \times 10^{-6}$  m/s indicates the high refining efficiency of the melt.

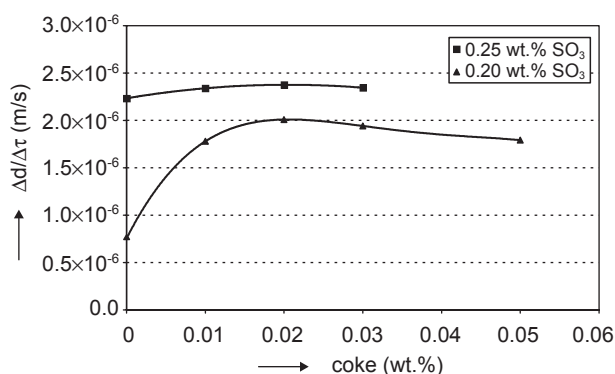


Figure 3. Figure 3. The average bubble growth rate vs. coke addition to the batch.

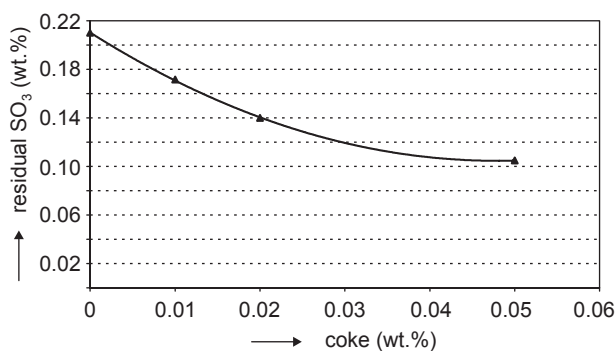


Figure 4. The residual SO<sub>3</sub> in the melt vs. coke addition to the batch.

Elevated sulphate content 0.25 wt.% results in very high bubble growth rates ( $\Delta d/\Delta \tau > 2 \times 10^{-6}$  m/s, figure 3) and the addition of reducing agent has almost no effect on the refining efficiency.

### Reboil and behaviour of nucleated bubbles

Important information about the interaction reducing agent - sulphate yields the observation of bubble nucleation and the behaviour of nucleated bubbles (figure 5). In oxidized, sulphate-containing glasses, a linear correlation between the nucleation temperature and remaining sulphate content is observed (figure 6). At higher addition of reducing agent resulting in the formation of sulphides in glass, the bubble nucleation occurs at temperatures below 1450°C.

Completely different behaviour of nucleated bubbles can be observed in the course of temperature decrease. Bubbles in oxidized, sulphate containing glasses are dissolved quickly, bubbles in reduced amber glasses do not dissolve in the melt. This situation is quantified in table 1, which shows measured values of bubble growth and dissolution rates. Glass containing pure sulphate has highest dissolution rate when temperature decreases. Small addition of carbon increases bubble growth rate when temperature increases and

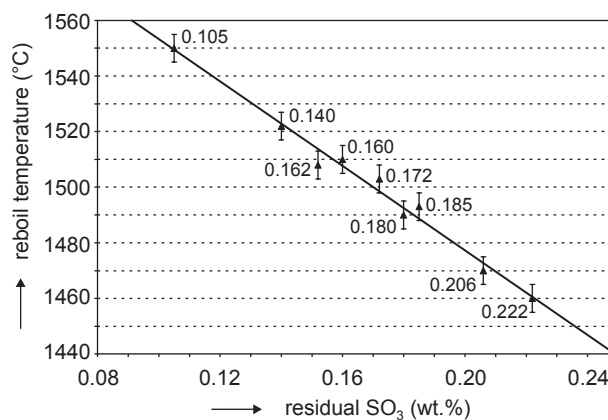


Figure 6. The temperature of bubble nucleation vs. residual sulphate content.

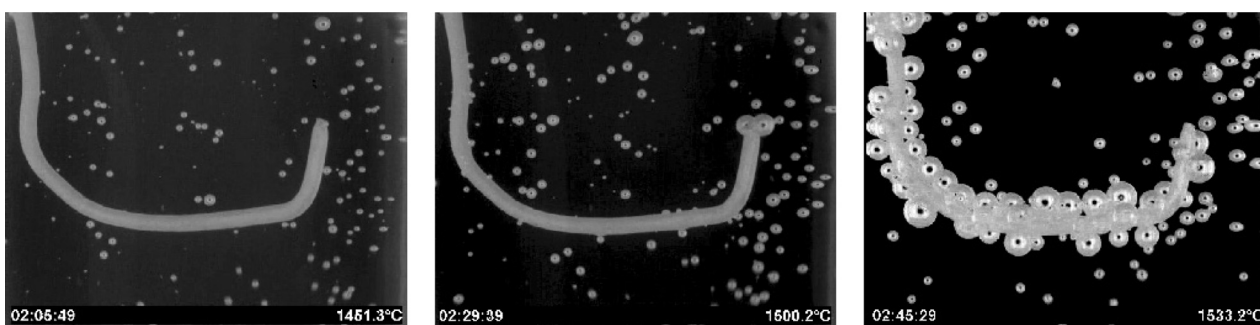


Figure 5. The observation of bubble nucleation in the melt.

decreases the bubble dissolution rate at descending temperature owing to lower residual sulphate content. Bubble growth in amber glass indicates a high level of saturation by SO<sub>2</sub>, consequently medium rates of the bubble growth rate at rising temperature were obtained and no bubble dissolution at descending temperature was observed (table 1, line 3).

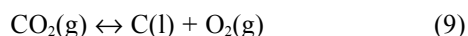
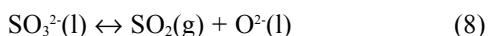
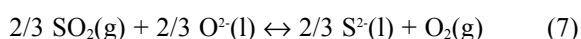
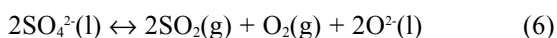
#### Summary of the experiments

Presented experimental findings make possible to suggest the mechanism and time sequence of important phenomena taking place during the whole melting process. Evolved gas analysis has shown that the chemical reaction between both components takes place within the temperature interval 600-900°C. The most important acceleration factor of melting and refining process is the formation of sulphide, which reacts with residual sulphate at temperatures above 1300°C. Formation of sulphur dioxide resulting from this reaction, brings about intensive bubble nucleation and stirring and foaming of the melt. Probable phenomenon is the formation of sulphites, reported by similar studies [3, 4].

At refining temperatures, the growth rate of bubbles depends on the carbon/sulphate ratio, i.e. on melt saturation by both refining gases. Behaviour of bubbles nucleated at high melting temperatures differs according to the redox state of glass. In oxidized glasses, bubbles are formed by the mixture SO<sub>2</sub> and O<sub>2</sub>, which is easily soluble in the melt when the temperature is decreases. Reduced glasses produce pure SO<sub>2</sub> bubbles insoluble at the temperature decrease.

#### MODEL CALCULATIONS

The theoretical model based on experimental findings considers simultaneous equilibrium of components entering appropriate chemical reactions:



The calculation of simultaneous equilibrium is based on solving the set of equations (10) – (13). The quantities  $c_i$  are molar concentrations of components at the initial (reference) temperature,  $x_i$  are changes of the reactions extent and  $T$  is absolute temperature.

The temperature dependences of equilibrium constants of sulphate and sulphide reactions were measured experimentally. The values of sulphite and carbon equilibria were estimated from literature data [3, 6].

$$K_{\text{SO}_4^{2-}} = \frac{\left(\bar{c}_{\text{SO}_2} + 2x_1 - \frac{2}{3}x_2 + x_3\right)^2 \left(\bar{c}_{\text{O}_2} + \sum_{i=1}^4 x_i\right)}{\left(\bar{c}_{\text{SO}_4^{2-}} - 2x_1\right)^2} = \exp(41.508 - 81606/T) \quad (10)$$

$$K_{\text{S}^{2-}} = \frac{\left(\bar{c}_{\text{S}^{2-}} + \frac{2}{3}x_2\right)^{2/3} \left(\bar{c}_{\text{O}_2} + \sum_{i=1}^4 x_i\right)}{\left(\bar{c}_{\text{SO}_2} + 2x_1 - \frac{2}{3}x_2 + x_3\right)^{2/3}} = \exp(35.353 - 78031/T) \quad (11)$$

$$K_{\text{SO}_3^{2-}} = \frac{\left(\bar{c}_{\text{SO}_2} + 2x_1 - \frac{2}{3}x_2 + x_3\right)}{\left(\bar{c}_{\text{SO}_3^{2-}} - x_3\right)} = \exp(3.504 - 7864/T) \quad (12)$$

$$K_c = \frac{(\bar{c}_c + x_4) \left(\bar{c}_{\text{O}_2} + \sum_{i=1}^4 x_i\right)}{\left(\bar{c}_{\text{CO}_2} - x_4\right)} = \exp(-21206/T) \quad (13)$$

The computation procedure consists of three steps simulating the course of the interactions according to the scenario mentioned. In the first step only the reaction between carbon and sulphate takes place and carbon is completely consumed. Produced sulphides react in the second step at the temperature of 1300°C with the remaining sulphate, usually to saturate or oversaturate the melt with sulphur dioxide. In this step, the formation of sulphites could be considered too. The final step is the simulation of the melt heating to maximal temperatures.

Table 1. The growth or dissolution rates of nucleated bubbles (m/s).

Sulphate and coke in the batch	Increasing temperature 2°C/min	Decreasing temperature 10°C/min
0.20 wt.% SO <sub>3</sub>	1.11 × 10 <sup>-6</sup>	-1.22 × 10 <sup>-6</sup>
0.20 wt.% SO <sub>3</sub> ; 0.01 wt.% C	1.35 × 10 <sup>-6</sup>	-1.00 × 10 <sup>-6</sup>
0.20 wt.% SO <sub>3</sub> ; 0.10 wt.% C	2.90 × 10 <sup>-7</sup>	1.00 × 10 <sup>-7</sup>

Figures 7-12 present the results of calculation. The dependence of the concentration of the individual sulphur redox species on carbon/sulphate molar ratio is shown in the figure 7. Here the presence of sulphite is considered, as well as melt saturation by the SO<sub>2</sub>. The decrease of sulphate concentration followed by the

decrease of the redox state of glass is obvious. The saturation of the melt by SO<sub>2</sub> takes place at very low carbon content. The carbon/sulphate ratio equal to 0.5 results in the state when sulphates disappear from the melt and sulphide starts to be the dominating sulphur component. The areas of calculated existence of sulphate

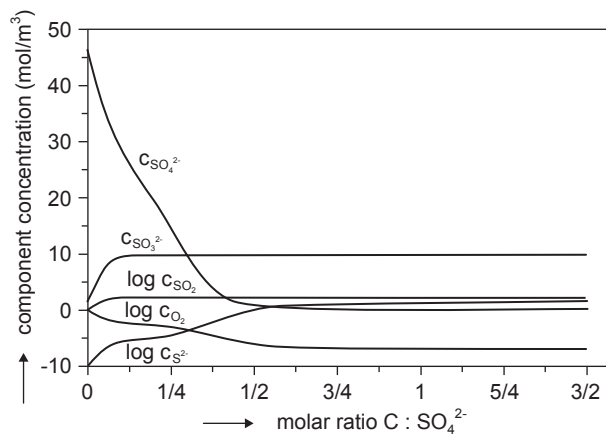


Figure 7. The sulphur species concentration vs. molar ratio C/SO<sub>4</sub><sup>2-</sup>, 1300°C. Total sulphur concentration 0.167 wt.% SO<sub>3</sub>.

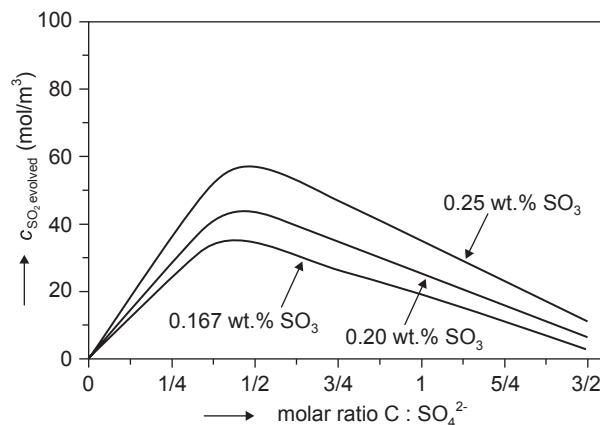


Figure 10. The evolved amount of SO<sub>2</sub> vs. molar ratio C/SO<sub>4</sub><sup>2-</sup>, 1300°C.

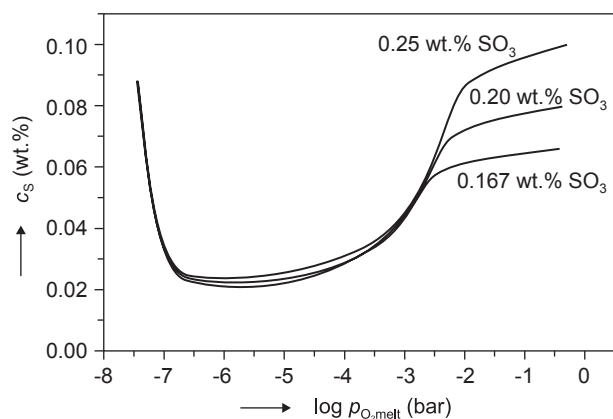


Figure 8. The total sulphur concentration vs. redox state of glass (log p<sub>O<sub>2</sub></sub>), 1300°C.

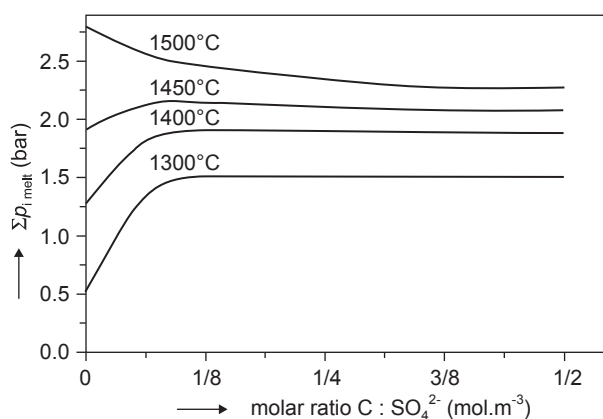


Figure 11. The refining potential (p<sub>O<sub>2</sub></sub> + p<sub>SO<sub>2</sub></sub>) vs. molar ratio C/SO<sub>4</sub><sup>2-</sup>. Glass melt contains sulphites.

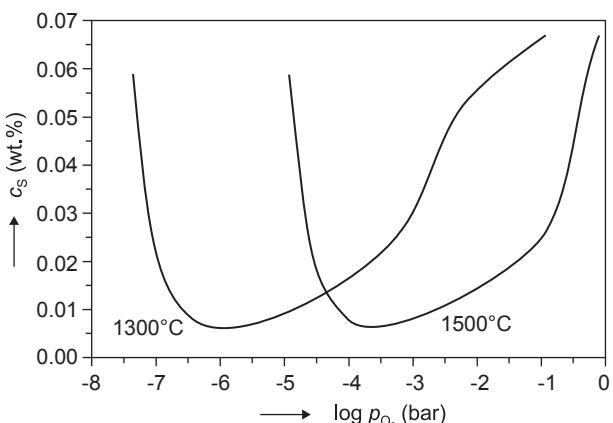


Figure 9. The total sulphur concentration vs. redox state of glass (log p<sub>O<sub>2</sub></sub>), 0.20 wt.% SO<sub>3</sub>.

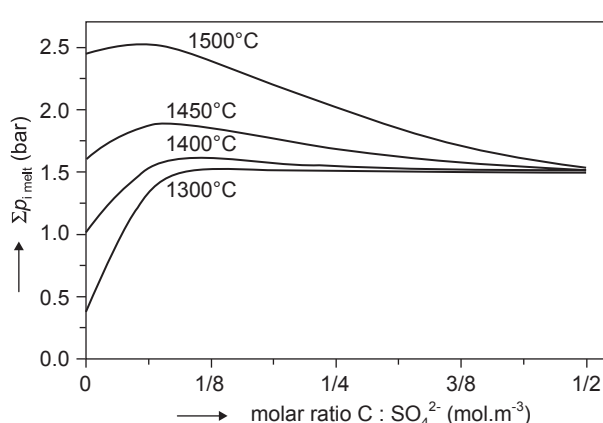


Figure 12. The refining potential (p<sub>O<sub>2</sub></sub> + p<sub>SO<sub>2</sub></sub>) vs. molar ratio C/SO<sub>4</sub><sup>2-</sup>. Glass melt without sulphites.

and sulphide then result in very well known dependence of sulphur solubility on redox state of glass (figure 8) [6]. In addition, the shift of the minimum to higher redox values with increasing temperature (figure 9) corresponds to results of other experimental studies [7-9]. Figure 10 presents the calculated amount of sulphur dioxide evolved from the melt at 1300°C as a function of molar ratio carbon/sulphate. The refining efficiency of the melt (bubble growth rate) can be derived from calculated values of sulphur dioxide and oxygen concentrations in the melt. Figures 11 and 12 summarize these quantities in the form of dependence between internal partial pressures of both gases and the carbon/sulphate ratio. Internal partial pressures were calculated by using previously measured values of gas solubilities [10]. The saturation of the melt by the SO<sub>2</sub> was assumed as soon as the specific amount of released SO<sub>2</sub> exceeded its solubility in the melt. Figure 12, representing the case when the sulphite existence was not considered, shows a qualitative agreement with experimental observation (figure 3), exhibiting a slight maximum of refining rate at small carbon additions.

## CONCLUSION

Redox chemistry of sulphur species in glass melts during the interaction of reducing agent with the sulphate was studied by the combination of experimental and computational methods. The reaction between the reducing agent and sulphate, taking place in the temperature interval 600-900°C, results in the formation of sulphide, which subsequently reacts with residual sulphate at temperatures above 1300°C. The results of experiments supported by the model calculations showed that appropriate combination of reducing agent and sulphate at the same time improves homogenization and refining of glass melt and inhibits undesired bubbles nucleation at maximal melting temperatures.

## Acknowledgement

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## OXIDAČNĚ-REDUKČNÍ ROVNOVÁHY SÍRY VE SKELNÝCH TAVENINÁCH

JAROSLAV KLOUŽEK, MIROSLAVA ARKOSIOVÁ,  
LUBOMÍR NĚMEC

*Laboratoř anorganických materiálů,  
Společné pracoviště ÚACH AVČR a VŠCHT Praha,  
Technická 5, 166 28 Praha 6*

Ke studiu oxidačně-redukčních rovnováh síry ve skelných taveninách byla použita kombinace experimentálních a výpočetních postupů umožňující nalézt mechanismus a časovou souslednost dějů v průběhu tavicího procesu. Uvedené postupy byly prakticky aplikovány pro optimalizaci tzv. redukčního síranového čerání realizovaného společným přídavkem síranu a redukovadla do vsázky. Výsledky experimentů spolu s modelovými výpočty ukázaly, že při vhodné kombinaci obou komponent lze urychlit homogenizační a čerací proces a současně potlačit nežádoucí nukleaci bublin při maximálních teplotách.