

# THE ROLE OF SULFUR IN GLASS MELTING PROCESSES

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*This work is aiming to complete the kinetic data of bubble behavior and nucleation at different redox state controlled by different ratios between carbon and sulphate added to the batch of the soda-lime-silica glass, to elucidate the mechanism of melt foaming at medium temperatures and to provide experimental data showing the effect of sulfur reactions on the sand dissolution. Two generations of bubbles nucleated in the glass melt were indicated by measurements and the bubble growth rates were obtained at temperatures 1300-1500°C to appreciate the bubble fining process and glass foaming. The chemical reaction between water vapour atmosphere and sulfur compounds in glass resulted in bubble nucleation on the glass level and melt foaming. The acceleration of sand dissolution in glasses having lower redox state was observed.*

## INTRODUCTION

The effect of sulfur compounds in glasses were intensively studied both from the point of view of sulfur chemistry in glass melts and their role in the glass melting kinetics [1-9]. The last work of authors was focussed on the study of sulfur reactions in the batch and some kinetic observations of bubble behavior, bubble nucleation and foam formation in the soda-lime-silica glass melt when applying the usual industrial combination of sodium sulfate with carbon as a reducing agent [10-12]. This work sets a goal to classify the role of sulfur compounds in the melting process, to complete the kinetic data of bubble nucleation and behavior at different oxidation-reduction ratios between carbon and sulfate, to elucidate the mechanism of melt foaming at medium to high temperatures and to provide experimental data about sulfur influence on sand dissolution.

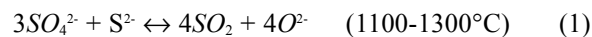
was used providing glass of the following weight composition (wt.%): 74 SiO<sub>2</sub>, 16 Na<sub>2</sub>O and 10 CaO. Sulfate was added to the batch in form of Na<sub>2</sub>SO<sub>4</sub>, purity per analysis. Reducing agent referred as carbon in the paper was dosed in glass batches in form of fine-grounded coke containing 85 % of C. The initial content of SO<sub>3</sub> as sulfate in all glasses was 0.5 % and the redox state of batches involved region between oxidized and medium reduced glasses (the molar ratio C/SO<sub>4</sub><sup>2-</sup> ∈ ⟨0; 9⟩). The iron content in glasses was restricted to iron impurities in raw materials, dry batch components were used to exclude the impact of water vapour. In the typical experiment, the glass batch with given molar ratio of carbon to sulfate was heated from 700°C by the rate of 10°C/min to a given temperature and subsequently kept on the final value 1300, 1400 and 1500°C for necessary time. The atmosphere was air but the atmosphere containing 80 vol. % of water vapour was applied in several experiments.

## EXPERIMENTAL

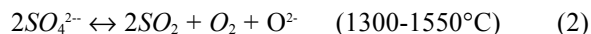
The kinetic observations were applied by direct observations of bubbles and foam at melting temperatures combined with image analysis, by laboratory melts and completed by the analyses of undissolved sand and sulfur presence in glass by the X-ray diffraction and X-ray fluorescence. The soda-lime-silica batch

## RESULTS AND DISCUSSION

The results of EGA analyses presented in literature and last work [10-11] confirmed the important role of several sulfur reactions in the formed glass melt, namely:

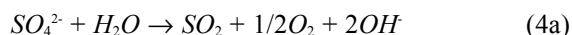


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The courses of cited reactions are responsible for most kinetic effects during glass melting but the detailed mechanism of sulfite presence [7,8] on both fining and sand dissolution, or its impact on bubble nucleation, e.g., are not fully clarified yet.

This work initially tried to use a kinetic measurement based on the assumed reactions between sulfur compounds and water vapour to assess the role of sulfites in the melting process. Water produces OH groups in silicite and borosilicate glasses with relatively strong bond to glass structure and substitution of sulfate ions for OH groups was experimentally proved in previous works [13, 14]. The chemical reaction of water vapour may be potentially expected with all three sulfur compounds:



The already in literature described reaction (4a) between water vapour and sulfates in the melt produced foam on the melt level. In this work, glasses with  $C/SO_4^{2-} \in \langle 0; 9 \rangle$  were contacted with atmosphere containing 80 vol. % of water vapour and the melt level was observed to indicate foam and bubbles on the level in the temperature region (1300) 1400-1500°C after slow controlled heating (10°C/min) of glass batch from 700°C. The partial or full foam formation, as well as bubble nucleation on the glass level were observed in all experiments with  $C/SO_4^{2-} \in \langle 0; 9 \rangle$  and at temperatures

higher than about 1400-1450°C. The bubble nucleation on the melt level was observed in all experiments after applying water vapour and the nucleation intensity grew with temperature. The nucleated and rapidly growing bubbles obviously formed the unstable foam layer at 1500°C. The comparison between the average bubble growth of bubbles present in the melt and bubbles present on the level is presented in Figure 1 for temperatures 1400 and 1500°C.

The considerable diameter growth rates of bubbles on the glass level support the assumption about chemical reaction of sulfur compounds with water vapour on the level. The other mechanisms of the rapid bubble growth were excluded by experiments without water atmosphere or in glasses without any sulfur compounds. The measurements prove the presence of sulfites in the melt as a chemical source of SO<sub>2</sub> at  $C/SO_4^{2-} = 1.5-2$  and most probably in the wide interval of the redox state of glass. The reaction of sulfide ions with water vapour at high  $C/SO_4^{2-}$  ratios cannot be excluded.

The rapid bubble growth on the glass level is most probably initially controlled by the rate of chemical reaction 4a-c and later by the flow of glass containing surface active sulfur species from the melt into the bubble shell jutting over glass level. The surface forces seem to play the decisive role.

### Bubble removal

The values of the diameter growth rate of bubbles in glass at 1500°C against the ratio  $C/SO_4^{2-}$  are plotted as well in Figure 1a. The maximum value at  $C/SO_4^{2-} = 0.5$  indicates the combined effect of reactions (2) and (3) and effect of previous saturation of the melt by SO<sub>2</sub> (reaction 1). At higher values of  $C/SO_4^{2-}$ , the amount of sulfate in the melt decreases [12-13] and the fining

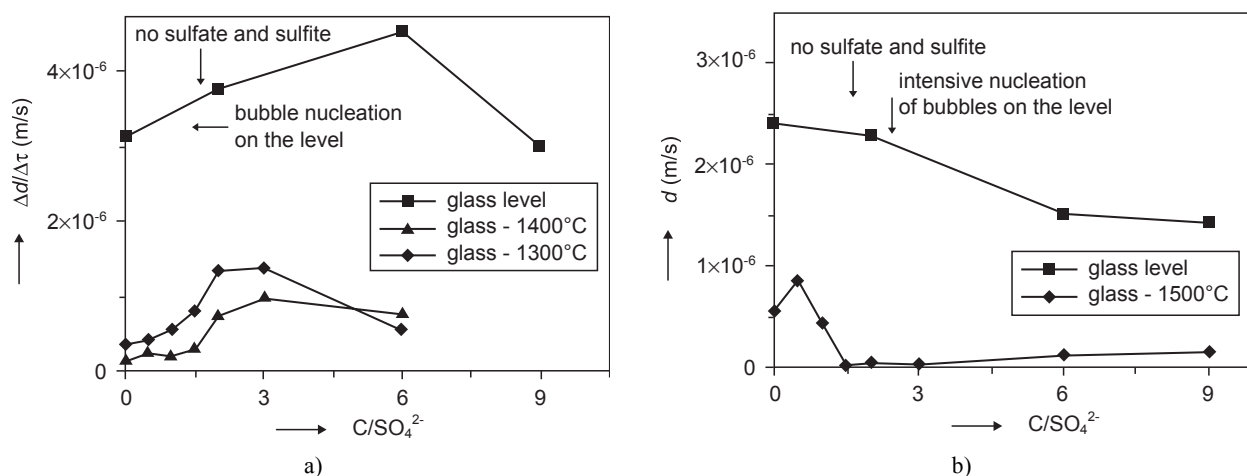


Figure 1. The average bubble growth rates inside of glass and on the glass level at 1300 and 1400°C (a), and 1500°C (b) as a function of the ratio  $C/SO_4^{2-}$ .

effect shifts from  $\text{SO}_2 + \text{O}_2$  to only  $\text{SO}_2$ . The analogical dependences acquired at temperatures 1300 and 1400°C show that the effect of  $\text{SO}_2$  increases with growing ratio  $\text{C}/\text{SO}_4^{2-}$  up to about  $\text{C}/\text{SO}_4^{2-} = 3$  (Figure 1b). The reason for this behavior is most probably increasing amount of sulfite ions in glass and previous saturation of the melt by  $\text{SO}_2$ . The increase in values of the bubble growth rates in reduced glasses ( $\text{C}/\text{SO}_4^{2-}$  was 6 and 9) at 1500°C and their decrease at 1300 and 1400°C may be brought about by the glass chemical inhomogeneity.

### Glass foaming

The evaluation of foam observations during experiments at 1300 and 1400°C is plotted in Figure 2. The height of the peak of  $\text{SO}_2$  coming from EGA measurements, the maximal foam height and volume, and the time of melt foaming coincide with maximal values of bubble growth rates at both temperatures.

The observations provided a picture of foaming initiated not only on the glass level, but also in the whole volume of glass. Among relevant quantities of that phenomenon - the number of nucleation sites  $N$ , the size of already present small bubbles  $a_0$ , the bubble growth rate and the number of repeated nucleations  $n$  - the bubble growth rate seems the most significant to fill the volume of melt by tightly packed bubbles in a relatively short time. The theoretical dependence between the time necessary for nucleated or grown equal bubbles to fill tightly the given volume of glass (under conditions corresponding to experiments), and the mentioned first three quantities is presented in Figure 3. The bubble growth rate appears the most significant quantity.

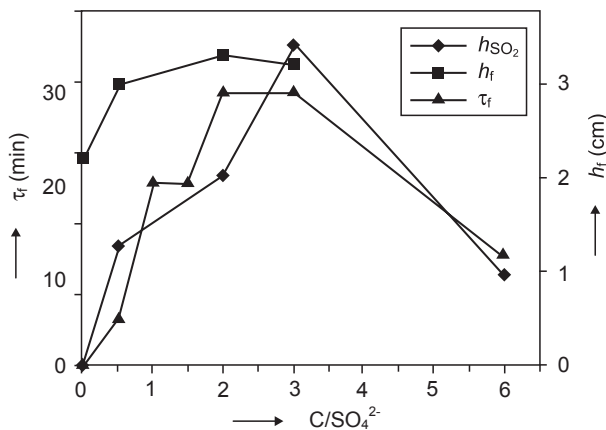


Figure 2. The dependence of the height of the  $\text{SO}_2$  peak,  $h_{\text{SO}_2}$  (EGA measurement), the maximal height and volume of foam -  $h_f$ , and time of foaming,  $\tau_f$  (high temperature observations) on the  $\text{C}/\text{SO}_4^{2-}$  ratio at the temperature 1300°C.

If atmosphere reacts with sulfur species in glass, the intensive bubble nucleation and the very high bubble growth rate on the level set conditions for foam formation (see Figure 1). The theoretical time necessary to cover the glass level by the continuous bubble layer should be then only hundreds of seconds according to Figure 3, which fact was confirmed by foam observations in experiments.

Considering the results in literature [9] and obtained by foaming observations in this and previous works [11, 12], three mechanisms of melt foaming in glass melts containing sulfur compounds may be assumed:

1. The volume of rising bubbles attaining the glass level is higher than the volume of decayed foam. The bubbles accumulate on the glass level in layers. The decisive processes for foam formation are the high initial bubble number and rapid bubble growth in glass, as well as bubble rapid rising to the glass level (glass at refining temperatures).
2. The volume of glass characterized by the intensive bubble nucleation, relatively rapid bubble growth and low bubble rising velocities forms the foam in the glass volume (glass containing sulfate with reducing agent at medium temperatures). The decisive processes are bubble nucleation and growth.
3. Some components of glass react with atmosphere under gas development, increase the volume of bubbles present on the glass level and nucleate there new bubbles. The decisive processes are the bubble nucleation.

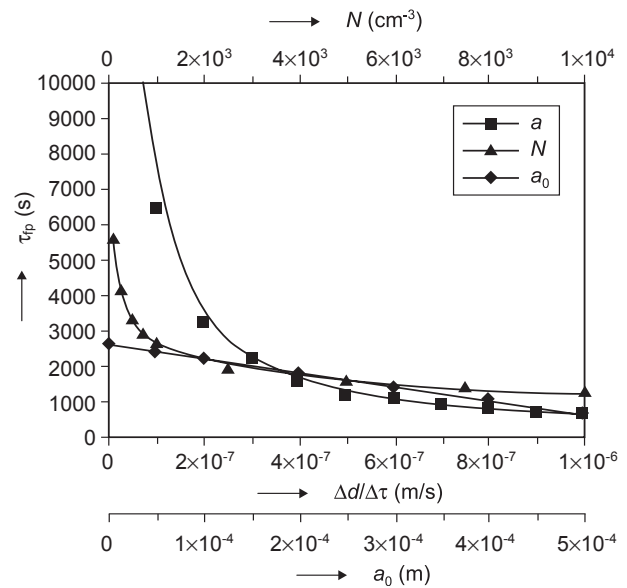


Figure 3. The theoretical time of full packing of the given volume of glass by equal bubbles as a function of number of nucleation sites, the initial bubble radius and the bubble radius growth rate. Arbitrary temperature.

ation on the level and transport of reacting components from glass into bubble shells jutting over the glass level. The mentioned mechanism may be significant for glasses produced by oxyfuel melting.

### Bubble nucleation

Two generations of nucleated bubbles were observed in glass melt when applying the melt observation. The first bubble generation comes from the melt supersaturation and sulfite decomposition (Reaction (3)) at medium temperatures and was observed for  $C/SO_4^{2-} > 1$ , in coincidence with the increasing bubble growth rates at these temperatures. The second generation occurs at temperatures higher than about 1450°C and corresponds to the spontaneous decomposition of sulfates.

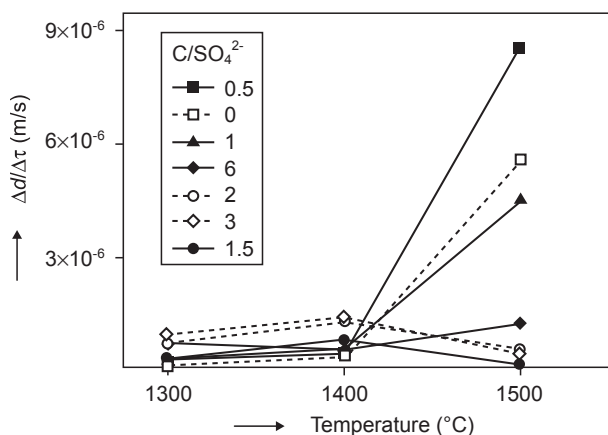


Figure 4. The temperature dependence of the bubble growth rate, indicating the bubble nucleation at higher bubble growth rates.

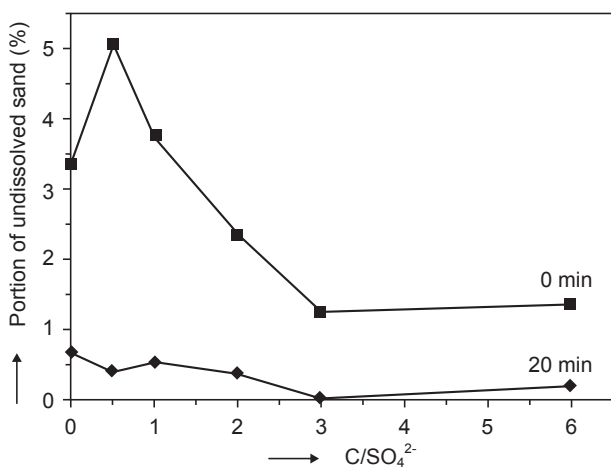


Figure 5. The dependence between the portion of undissolved sand and the ratio  $C/SO_4^{2-}$  at the temperature 1300°C.

The nucleation at high temperatures was observed at  $C/SO_4^{2-} \leq 1$ . Figure 4 presents the temperature dependence of bubble growth rates which shows a steep increase in the bubble growth rate joined with  $SO_2 + O_2$  bubble nucleation at 1500°C and for  $C/SO_4^{2-} \leq 1$ , and also shows relatively high bubble growth rates at temperatures 1300 and 1400°C joined with nucleation of  $SO_2$  bubbles at  $C/SO_4^{2-} > 1$ .

### Sand dissolution

The potential effect of the observed glass micro and macroconvection on the sand dissolution due to evolution of gases and nucleation of bubbles was assumed but quantitative data should be provided. The effect should be particularly significant at lower and medium temperatures where the number potential nucleation sites on undissolved sand particles is high. Figure 5 brings the decrease in the portion of undissolved sand when increasing the ratio  $C/SO_4^{2-}$  in glass samples just reaching temperature 1300°C and after keeping the melt for 20 min at this temperature. Further experiments are however needed to appreciate the role of sulfur compounds more precisely.

### CONCLUSION

The kinetic measurements involving reaction of sulphur compounds in glass with the atmosphere containing high portion of water vapour proved sulfite presence in reduced glass and indicated its role for the melting process. Among reactions of sulphur compounds in batch and glass during melting, the reactions between sulfide and sulfate and the decomposition of sulfate and sulfite are the most significant phenomena for the glass melting and fining process. The consequence of the reactions is the both physical and chemical saturation of the melt by gases and their release in later stages. The intensive glass melt foaming occurred in the bulk glass at medium temperatures. New generation of bubbles  $SO_2 + O_2$  was observed at high temperatures and  $C/SO_4^{2-}$  less than 1 and nucleation of  $SO_2$  bubbles at medium temperatures and  $C/SO_4^{2-}$  higher than 1. The decrease in the fraction of undissolved sand with increasing  $C/SO_4^{2-}$  ratio was observed.

### Acknowledgement

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#### References

1. Jebsen-Marwedel H.: *Glastechn.Ber.* 17, 325 (1939).
2. Fincham C. J. B., Richardson F. D.: *Proc. Royal Soc. London* 223A, 40 (1954).
3. Holmquist S.: *J. Am. Ceram. Soc.* 49, 467 (1966).
4. Conroy A. R., Manring W. H., Bauer W. C.: *Glass Ind.* 47, 84, 110, 133 (1966).
5. Manring W. H., Billings D. D., Conroy A. R., Bauer W. C.: *Glass Ind.* 48, 374, 378 (1967).
6. Muller-Simon H.: *Glastechn.Ber.GlassSci.Technol.* 71, 157 (1998).
7. Beerkens R.: *Physics and Chemistry of Glasses* 43, 189 (2002).
8. Beerkens R.: *J. Am. Ceram. Soc.* 86, 1893 (2003).
9. Beerkens R., Van der Schaaf J.: *J. Am. Ceram. Soc.* 89, 24 (2006).
10. Kloužek J., Arkosiová M., Němec L.: *Ceramics-Silikáty* 50, 134 (2006).
11. Kloužek J., Arkosiová M., Němec L., Cincibusová P.: *Glass Technol.: Eur. J. Glass Sci. Technol. A* 48, 176 (2007).
12. Arkosiová M., Kloužek J., Němec L.: *International Workshop "Sulfur in glasses and melts"*, March 1-2, 2007, Hannover (Germany).
14. Cable M., Rasul C. G.: *J. Am. Ceram. Soc.* 50, 528 (1967).
15. Hanke K.P.: *Glastechn.Ber.* 50, 144 (1977).

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#### ÚLOHA SÍRY V TAVICÍM PROCESU SKEL

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Cílem práce je doplnit kinetická data chování a nukleace bublin v závislosti na redox stavu skla řízeném hodnotou poměru mezi uhlíkem a síranem ve vsázce sodno-vápenato-křemičitého skla, vyjasnit mechanismus tvorby pěny při středních tavicích teplotách a poskytnout experimentální data vlivu reakcí síry na rychlost rozpouštění pískových zrn. Měření provedená při teplotách 1300-1500°C indikovala dvě generace bublin, u kterých byly stanoveny k hodnocení procesů čerení a pění hodnoty středních rychlostí růstu. Chemické reakce mezi vodní párou v atmosféře a sloučeninami síry ve skle mají za výsledek nukleaci bublin a tvorbu pěny na hladině skloviny. Ve sklech s nízkým redox stavem bylo pozorováno urychlení procesu rozpouštění pískových zrn.