

THE REDOX DISTRIBUTION AT THE INTERFACE OF GLASS MELTS WITH DIFFERENT OXIDATION STATE

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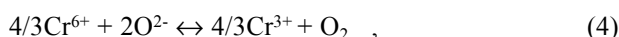
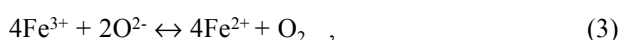
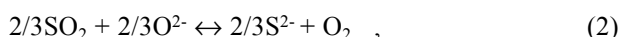
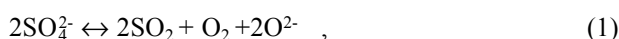
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A simplified computational model of refining gas transfer through the quiescent plane interface between oxidized and reduced glass melts containing sulfur compounds as refining agents is presented. The results of calculations show no oversaturation of glasses by gases, namely by SO₂, in the vicinity of the interface. This was confirmed by laboratory experiments that did not detect any bubble nucleation in the interface region. However, if the glasses were quickly mixed by stirring, a considerable amount of bubbles evolved in the melt. In addition, high glass oversaturation by SO₂ was calculated from redox equilibria for instantaneously mixed glasses.

INTRODUCTION

Changing the glass color in an industrial melting furnace, frequently applied under increased demand of glass cullet recycling, is a sensitive technological task. Possible occurrence of foam of sulfur dioxide and an elevated level of bubble defects resulting from a rapid mixing of glasses with different oxidation state evoked an interest in a theoretical study of this problem. The process involves the transport of oxidation-reduction species by diffusion and convection, and chemical reactions that occur as the glasses get into contact. The aim of this work is to model two extreme cases of glass mixing, i.e. mixing by diffusion and instantaneous mixing. Soda-lime-silica glasses with different redox state were used for the verification of the model. Both glasses contained sulfate and sulfide anions, as well as multivalent chromium and iron oxides. Thus, the following oxidation-reduction reactions occur at their interface:



THEORETICAL PART

In semi infinite quiescent glasses that are in contact at a planar interface, only diffusion and chemical

reaction occur. If the diffusion of redox ions is neglected, the mass balance of oxygen and sulfur dioxide can be described by:

$$\frac{\partial c_{\text{O}_2}}{\partial \tau} = D_{\text{O}_2} \frac{\partial^2 c_{\text{O}_2}}{\partial x^2} + \left(\frac{\partial c_{\text{O}_2}}{\partial \tau} \right)_{\text{CH}} \quad (5)$$

$$\frac{\partial c_{\text{SO}_2}}{\partial \tau} = D_{\text{SO}_2} \frac{\partial^2 c_{\text{SO}_2}}{\partial x^2} + \left(\frac{\partial c_{\text{SO}_2}}{\partial \tau} \right)_{\text{CH}} \quad (6)$$

where c_i is the concentration of i -th component, x is the distance (m), τ is time (s), D_i is diffusion coefficient ($\text{m}^2 \text{s}^{-1}$) of i -th component. Subscript CH indicates the change of component concentration due to the chemical reaction. Using the stoichiometry of reactions (1 - 4), the equations (5) and (6) become:

$$\frac{\partial c_{\text{O}_2}}{\partial \tau} = D_{\text{O}_2} \frac{\partial^2 c_{\text{O}_2}}{\partial x^2} + \frac{3}{2} \frac{\partial c_{\text{S}^{2-}}}{\partial \tau} - \frac{1}{2} \frac{\partial c_{\text{SO}_4^{2-}}}{\partial \tau} - \frac{1}{4} \frac{\partial c_{\text{Fe}^{2+}}}{\partial \tau} + \frac{3}{4} \frac{\partial c_{\text{Cr}^{3+}}}{\partial \tau} \quad (7)$$

$$\frac{\partial c_{\text{SO}_2}}{\partial \tau} = D_{\text{SO}_2} \frac{\partial^2 c_{\text{SO}_2}}{\partial x^2} - \frac{\partial c_{\text{S}^{2-}}}{\partial \tau} - \frac{\partial c_{\text{SO}_4^{2-}}}{\partial \tau} \quad (8)$$

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with initial and boundary conditions

$$\begin{aligned} \tau = 0, \quad x < 0, \quad c_i = c_i(\text{ox}) \quad \tau > 0, \quad x \rightarrow -\infty, \quad c_i = c_i(\text{ox}) \\ x \geq 0, \quad c_i = c_i(\text{red}) \quad \tau > 0, \quad x \rightarrow \infty, \quad c_i = c_i(\text{red}) \end{aligned}$$

where $c_i(\text{ox})$ and $c_i(\text{red})$ are the initial concentration of redox species in oxidized and reduced glass (see table 1). The set of differential equations (7 - 8) was solved numerically by the procedure developed by Glass Service Ltd.

Table 1. The initial concentration of redox species (mol m⁻³) at temperature 1200 °C.

	oxidized glass	reduced glass
c_{O_2}	0.08	1×10^{-8}
c_{SO_2}	0.27	3.64
$c_{\text{SO}_4^{2-}}$	80.0	0.38
$c_{\text{S}^{2-}}$	4×10^{-11}	12.2
$c_{\text{Fe}^{2+}}$	12.0	81.0
$c_{\text{Fe}^{3+}}$	80.0	11.0
$c_{\text{Cr}^{3+}}$	10.0	11.8
$c_{\text{Cr}^{6+}}$	1.76	1×10^{-5}

Input data

Table 1 summarizes initial concentrations of redox species introduced in reactions (1–4) for two glasses, one oxidized (float glass) and the other reduced (amber glass). The temperature dependencies of equilibrium constants of reactions (2–4) presented in table 2 were obtained experimentally by equilibrating the glass melt containing single polyvalent element with the defined atmosphere at constant temperature, followed by chemical analysis of redox species in quenched samples [1]. The procedure was completed by the measurement of the internal oxygen partial pressure [2]. Values of the sulphate equilibrium constant were calculated by using the experimental values of equilibrium partial pressures of oxygen and sulfur dioxide in soda-lime-silica melt [3]. Other experimental data including solubility and diffusion coefficients of sulfur dioxide were taken from [4].

Table 2. The temperature dependence of equilibrium constants of reactions (1-4) having the form $K_i = \exp(A_i - B_i/T)$, T in Kelvins.

	A_i	B_i (K)
$K_{\text{SO}_4^{2-}}^{(T)}$	6.280	29946
$K_{\text{S}^{2-}}^{(T)}$	35.353	78031
$K_{\text{Fe}}^{(T)}$	18.397	42469
$K_{\text{Cr}}^{(T)}$	11.716	17558

In instantaneously mixed glasses specified above, the resulting oxidation-reduction equilibrium can be described as

$$K_{\text{SO}_4}^{(T)} = \frac{(\bar{c}_{\text{SO}_2} + 2x_1 - 2/3x_2)^2 \left(\bar{c}_{\text{O}_2} + \sum_{i=1}^4 x_i \right)}{(c_{\text{SO}_4}^{\circ} - 2x_1)^2} \quad (9)$$

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

$$K_{\text{Fe}}^{(T)} = \frac{(\bar{c}_{\text{Fe}^{2+}} + 4x_3)^4 \left(\bar{c}_{\text{O}_2} + \sum_{i=1}^4 x_i \right)}{(c_{\text{Fe}^{3+}}^{\circ} - 4x_3)^4} \quad (11)$$

$$K_{\text{Cr}}^{(T)} = \frac{(\bar{c}_{\text{Cr}^{3+}} + 4/3x_4)^{4/3} \left(\bar{c}_{\text{O}_2} + \sum_{i=1}^4 x_i \right)}{(\bar{c}_{\text{Cr}^{6+}} - 4/3x_4)^{4/3}} \quad (12)$$

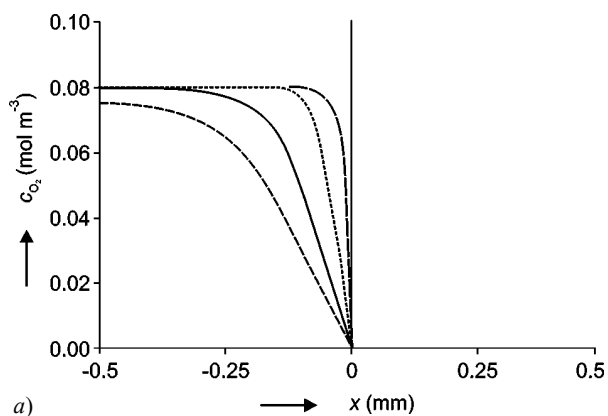
where $K_i^{(T)}$ are the temperature dependent equilibrium constants, \bar{c}_i is the initial concentration of i -th components after mixing and x_i is the change of reaction extent. Standard state of oxygen ions (see reactions (1 - 4) was taken to be their concentration at the temperature and pressure of the melt. For other components, the standard state of concentration equal to 1 mol m⁻³ was used.

RESULTS AND DISCUSSION

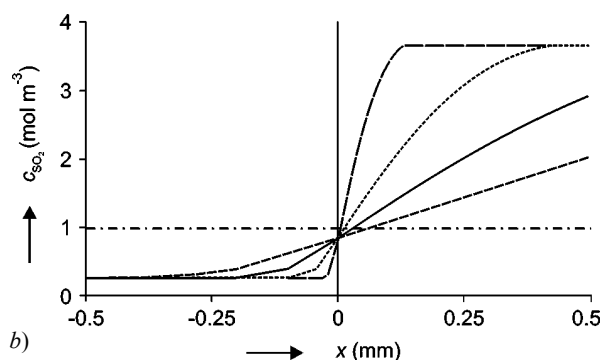
Diffusion mixing

Figures 1 and 2 present the calculated evolution of concentration profiles of oxygen, sulfur dioxide, and sulfate and sulfide ions at temperatures 1200 and 1400 °C. The interface of glasses is located at $x = 0$, oxidized glass at $x < 0$, and reduced glass at $x > 0$. At lower temperatures (1200 °C) oxygen diffuses from the oxidized to the reduced glass (figure 1a) and reacts with the sulfide ions at the interface (figure 1d). Sulfur dioxide from this reaction is transported to the oxidized glass (figure 1b) where it reacts with oxygen to form sulfate ions. Sulfate ions exhibit a concentration maximum in this region (figure 1c). Note that no concentration maximum of SO₂ develops close to the interface, even when sulfur dioxide concentration in amber glass is higher than its solubility. This oversaturation is not high enough to generate foaming.

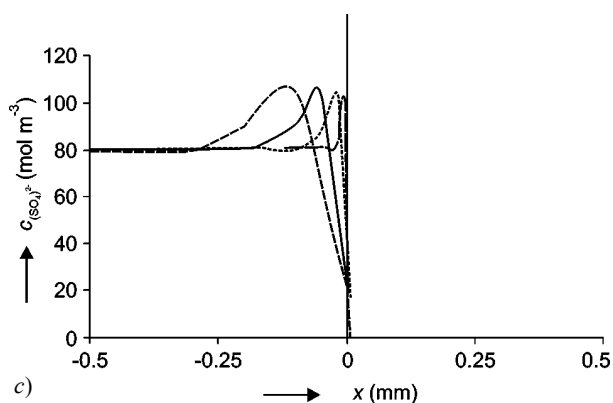
An almost identical situation exists at temperature 1400 °C. Oxygen reacts quantitatively with sulfide ions (figure 2a). Sulfur dioxide produced by this reaction (figure 2b) forms sulfate ions in amber glass (figure 2c), i.e. the glass interface is moving into the amber glass.



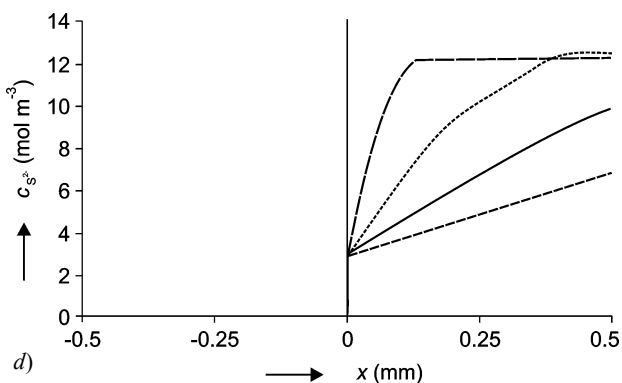
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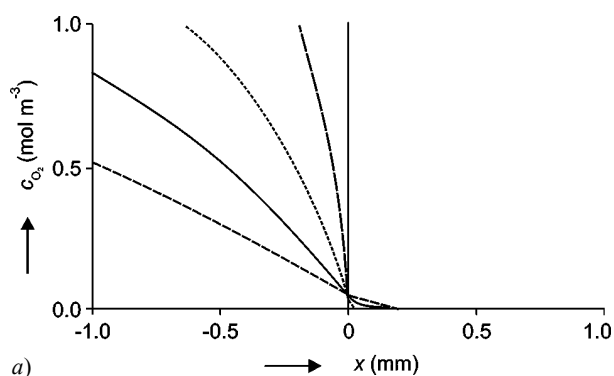
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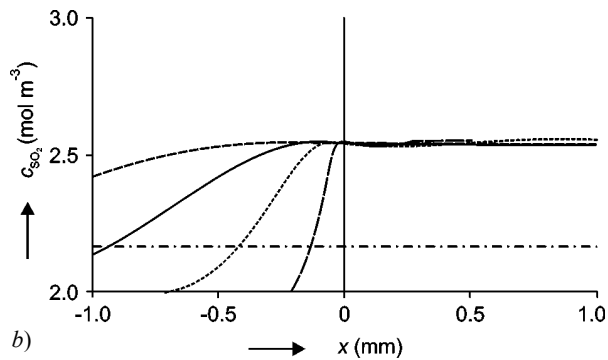
c)



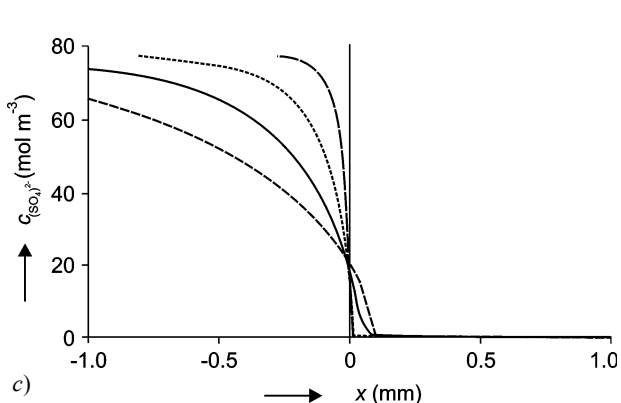
d)



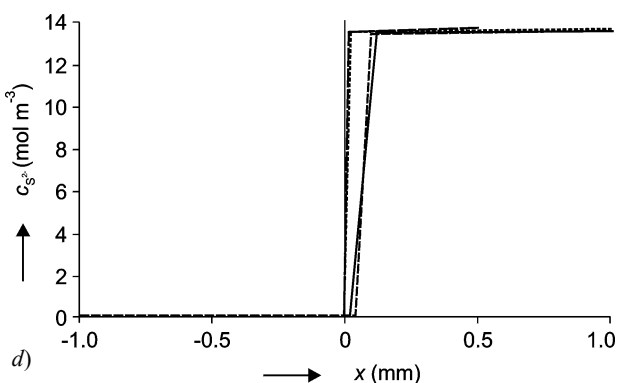
a)



b)



c)



d)

Figure 1. The concentration profiles of redox species at the float-amber glass interface at 1200 °C.

a) oxygen, b) sulfur dioxide, c) sulfate ions, d) sulfide ions.
 — $\tau = 100$ s, \cdots $\tau = 1000$ s, --- $\tau = 5000$ s, --- $\tau = 20000$ s, - - - - SO_2 solubility

Figure 2. The concentration profiles of redox species at the interface float-amber glass interface at 1400 °C.

a) oxygen, b) sulfur dioxide, c) sulfate ions, d) sulfide ions.
 — $\tau = 100$ s, \cdots $\tau = 1000$ s, --- $\tau = 5000$ s, --- $\tau = 20000$ s, - - - - SO_2 solubility

The amber glass is again oxidized without oversaturating by SO₂.

The modeled process was verified by laboratory experiments. A layer of amber glass melt in the silica glass observation cell was cautiously covered by float glass. The melt interface was video-recorded, and no bubble formation was observed.

Instantaneous mixing

To estimate the effect of instantaneous mixing of glasses on foaming, redox equilibria in mixed glasses were simulated using equations (9–12). Figure 3 shows the temperature dependence of calculated equilibrium concentrations of redox species.

According to figure 3b, sulfur dioxide concentration in glass is about ten times higher compared with its solubility at temperature interval 1200 – 1400 °C. Manual mixing of both glasses in an observation cell experimentally proved the result of calculation. An intensive bubble nucleation and glass foaming were observed [5].

Figure 4 compares both mixing rates with respect to sulfur dioxide concentration in glass melt. Diffusive

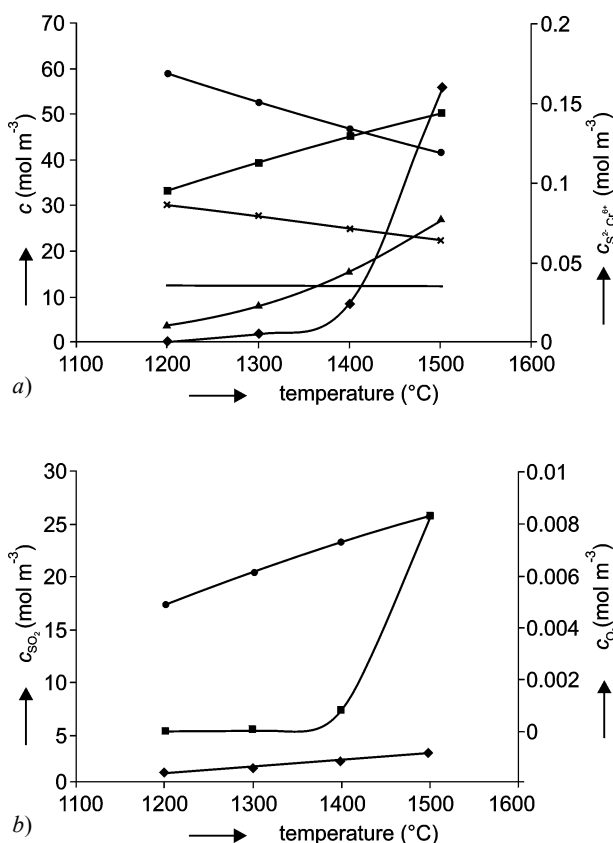


Figure 3. The temperature dependence of redox species concentrations when the glasses are instantaneously mixed.

a) \times - SO₄²⁻, \blacksquare - Fe³⁺, \blacklozenge - Cr⁶⁺, \bullet - Fe²⁺, — - Cr³⁺, \blacktriangle - S²⁻
 b) \bullet - SO₂, \blacklozenge - SO₂ solubility, \blacksquare - O₂.

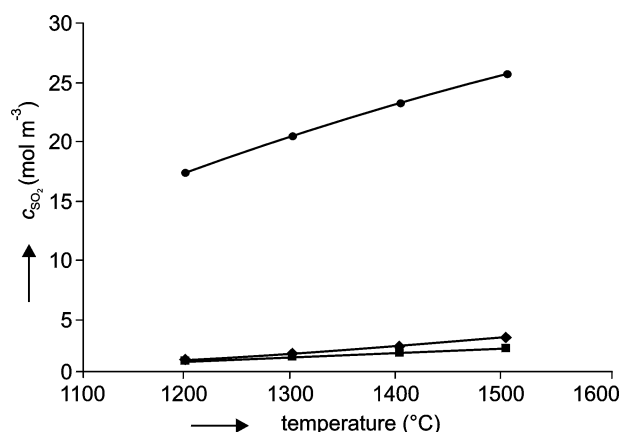


Figure 4. The comparison of diffusion and instantaneous mixing of glasses.

\bullet - instantaneous mixing, \blacklozenge - SO₂ solubility, \blacksquare - mixing by diffusion

mixing proceeds without oversaturation, as the SO₂ concentration on the boundary does not exceed gas solubility. When glasses are quickly stirred, the mixture becomes over saturated with sulfur dioxide, resulting in potentially intensive glass foaming.

CONCLUSION

Two extreme cases of mixing glasses with different oxidation-reduction states can be applied to real conditions of the color transition in a glass melting furnace. Mixing ability of the melting space as well as the difference of initial redox states of appropriate glasses appear to be the main factors of glass oversaturation by SO₂ and possible subsequent bubble nucleation and glass foaming.

Acknowledgement

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Submitted in English by the authors.

**OXIDAČNĚ REDUKČNÍ ROVNOVÁHA
NA ROZHRAŇÍ SKEL
S ODLIŠNÝM OXIDAČNÍM STAVEM**

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Článek uvádí výpočetní model transportu čedičích plynů nehybným rovinným rozhraním mezi skly s odlišným oxidačním stavem obsahující sloučeniny síry. Výpočty ukázaly, že skla nejsou v blízkosti rozhraní přesycena oxidem siřičitým. Tento výsledek byl potvrzen laboratorními experimenty, které neprokázaly nukleaci bublin v oblasti rozhraní obou skel. Pokud však byla tavenina rychle mechanicky promíchána, objevilo se velké množství bublin vlivem přesycení taveniny oxidem siřičitým. Toto přesycení bylo také odhadnuto výpočtem oxidačně redukční rovnováhy intenzivně míchaných skel.