

INTERACTIONS OF GASES AND VAPOURS WITH GLASS MELTS

PART 2 - SULPHATE LAYER PRECIPITATION
AND VAPOUR INTERACTIONS

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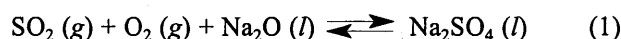
The governing equations and the initial and boundary conditions of interactions between gas (vapour) phase and a glass melt are presented for the following processes: precipitation of the sulphate layer on the glass level and its interaction with the melt, volatilization of a glass component from the melt without chemical reaction and with chemical reaction on the phase boundary or in the gas phase (reactive evaporation). In addition, the special cases of the physical and chemical evaporation are presented.

INTRODUCTION

Interactions of gases and vapours with glass melt involve a wide class of phenomena, influencing both glass properties and glass melting process. When trying to describe the interactions quantitatively, the main processes should be defined, their ordering and the controlling processes, as well as the respective chemisms should be defined. As for gas (vapour) - glass melt interactions, the consecutive transport in liquid phase, boundary reaction and transport in gas phase (or on the contrary) are assumed. The transport in liquid seemed to be the main controlling phenomenon, however, both surface reaction and transport in gas phase appear to play an important role in real technological conditions. That is why the general treating of interactions and model simplifications - using experimental studies - are needed to find and to describe the particular cases. In the first part of this work [1], the general case has been described, having considered the control function of all three steps of interaction process, involving the respective chemical reaction. The interactions of physically and chemically soluble technological gases with glass melts and oxidation-reduction equilibria of gases in the melt were theoretically treated to present the appropriate cases of gas - glass melt interactions. The goal of this part is to describe the precipitation of sulphate layer on glass level and its interaction with both atmosphere and glass melt, as well as to present the relations, governing the general case of the volatile component evaporation from a glass melt with or without chemical reaction. The potentially possible special cases of evaporation are presented, too.

THE PRECIPITATION AND INTERACTION OF
THE SULPHATE LAYER ON THE GLASS LEVEL

The sulphate layer can precipitate on the glass level at high concentrations of SO₂ and O₂ in atmosphere and at low temperatures [2]. The same phenomenon may occur on bubble surfaces [3, 4]. The cause of this behaviour consists in chemical dissolution of SO₂ + O₂ mixture in the basic glass melt (see paragraph 4 in [1]), and in the limited solubility of arisen sulphate in the glass. The process is controlled by the chemical reaction [2]:



The precipitated sodium sulphate can form layer or pools on the glass level, and interacts with both gas and liquid phase (layer growth or disappearing). The acceptable explanation for the hydrodynamic behaviour of the layer assumes the precipitated sulphate is drifted by the glass melt and the glass convection close to the inter-phase boundary glass melt - sulphate layer is very restricted (rigid phase boundary owing to the presence of the surface active sodium sulphate). The mass transfer of SO₂ between glass melt and layer is considered the controlling mechanism of layer interaction with glass while the chemical reaction (1) controls the layer formation or decomposition from the gas side. The simplified outline of the mentioned behaviour is presented in figure 1.

The rate of the layer formation or decomposition from the glass side is given by [2]:

$$\left(\frac{dx}{d\tau}\right)_{x=0} = \frac{M_{\text{Na}_2\text{SO}_4}^2}{M_{\text{SO}_2} \rho_{\text{Na}_2\text{SO}_4}} D_{\text{SO}_2}^l \left(\frac{\partial c_{\text{SO}_2}^l}{\partial x}\right)_{x=0} \quad (2)$$

Where M_{SO_2} and $M_{\text{Na}_2\text{SO}_4}$ are the appropriate molecular masses and $\rho_{\text{Na}_2\text{SO}_4}$ is the sodium sulphate density.

If only one oxidation-reduction reaction in the glass melt is considered, namely the reaction of sulphate ions (see equations (31) and (35a) in Part 1 [1]), the transport of three components in the static glass melt close to the layer is described by equations (35a) and (59 - 60) in Part 1 [1].

The following initial and boundary conditions are valid:

$$\begin{aligned} \tau = 0; \quad x < 0; \quad c_{\text{SO}_2}^l = c_{\text{oSO}_2}^l; \quad c_{\text{O}_2}^l = c_{\text{oO}_2}^l; \quad c_{\text{SO}_4}^l = c_{\text{oSO}_4}^l; \\ \text{equation (35a) in Part 1 is valid} \\ \tau > 0; \quad x < 0; \quad c_{\text{SO}_2}^l = c_{\text{oSO}_2}^l; \quad c_{\text{O}_2}^l = c_{\text{oO}_2}^l; \quad c_{\text{SO}_4}^l = c_{\text{oSO}_4}^l; \\ \text{equation (35a) in Part 1 is valid} \\ \text{for all } \tau; x = 0; \quad c_{\text{SO}_2}^l = c_{\text{sSO}_2}^l; \quad c_{\text{O}_2}^l = c_{\text{sO}_2}^l; \quad c_{\text{SO}_4}^l = c_{\text{sSO}_4}^l; \\ \text{and equation (35a) in Part 1 is valid.} \end{aligned} \quad (3)$$

Where c_{si}^l is the concentration of the i -th component in the glass melt saturated by the sodium sulphate.

The formation and decomposition of the sulphate layer from the gas side, controlled by equation (1), is given by [2]:

$$\left(\frac{dx}{d\tau}\right)_{x=\delta} = \frac{k_{\text{SO}_4}^l}{\rho_z} (RT)^{2/3} \left\{ \left[c_{\text{SO}_2}^g (c_{\text{O}_2}^g)^{1/2} \right]_{x=\delta} - c_{\text{sSO}_2}^g (c_{\text{sO}_2}^g)^{1/2} \right\} \quad (4)$$

Where $k_{\text{SO}_4}^l$ is the rate constant of the sulphate layer formation, ρ_z is the density of the stoichiometric mixture $\text{SO}_2 + \text{O}_2$ (2:1), $c_{\text{sSO}_4}^g$ and $c_{\text{sO}_2}^g$ are the gas phase concentrations of SO_2 and O_2 in equilibrium with sulphate layer or with glass saturated by sodium sulphate, respectively.

The transport of SO_2 and O_2 in gas phase is described by equations (36 - 37) in Part 1 [1] under the initial and boundary conditions:

$$\begin{aligned} \tau = 0; \quad x > \delta; \quad c_{\text{SO}_2}^g = c_{\text{oSO}_2}^g; \quad c_{\text{O}_2}^g = c_{\text{oO}_2}^g \\ \tau > 0; \quad x \gg \delta; \quad c_{\text{SO}_2}^g = c_{\text{oSO}_2}^g; \quad c_{\text{O}_2}^g = c_{\text{oO}_2}^g \\ \text{for all } \tau; x = \delta; \quad \text{equation (35a) in [1] is valid where} \\ c_{\text{O}_2}^g = c_{\text{si}}^g \text{ and } c_{\text{SO}_2}^g = c_{\text{si}}^g / \kappa_i \end{aligned} \quad (5)$$

The rate of sulphate layer growth or dissolution gives the difference:

$$\frac{d\delta}{d\tau} = \left(\frac{dx}{d\tau}\right)_{x=\delta} - \left(\frac{dx}{d\tau}\right)_{x=0} \quad (6)$$

If the transport of SO_2 and O_2 in gas phase is fast enough, equations (36 - 37) in [1] are omitted and the following boundary conditions are valid in the gas phase:

$$\begin{aligned} \text{for all } \tau; x > \delta; \quad c_{\text{SO}_2}^g = c_{\text{oSO}_2}^g; \quad c_{\text{O}_2}^g = c_{\text{oO}_2}^g \\ x = \delta; \quad \text{equation (35a) in [1] is valid where} \\ c_{\text{O}_2}^g = c_{\text{si}}^g \text{ and } c_{\text{SO}_2}^g = c_{\text{si}}^g / \kappa_i \end{aligned} \quad (7)$$

In later stages of layer existence (layer is thick), the simultaneous control by Na_2O transport through both melts is probable.

VOLATILIZATION OF GLASS COMPONENTS FROM A MELT WITHOUT CHEMICAL REACTION

If the volatile glass component is designated by the subscript A , the appropriate governing reactions of the general case are (all three steps share the control):

$$\frac{\partial c_A^l}{\partial \tau} = D_A^l \nabla^2 c_A^l - v^l \nabla c_A^l \quad (8)$$

$$\frac{\partial c_A^g}{\partial \tau} = D_A^g \nabla^2 c_A^g - v^g \nabla c_A^g \quad (9)$$

The initial and boundary conditions are given by:

$$\begin{aligned} \tau = 0; \quad x < 0; \quad c_A^l = c_{\text{oA}}^l \\ \quad \quad \quad x > 0; \quad c_A^g = c_{\text{oA}}^g \\ \tau > 0; \quad x \rightarrow -\infty; \quad c_A^l = c_{\text{oA}}^l \\ \quad \quad \quad x \rightarrow \infty; \quad c_A^g = c_{\text{oA}}^g \\ \text{for all } \tau; x = 0; \quad \frac{\partial c_A^l}{\partial \tau} = k_A (c_A^l - c_A^g / \kappa_A) \end{aligned} \quad (10)$$

Where k_A is the rate constant of the surface reaction and κ_A is the equilibrium factor between concentration of the component A in the melt and gas.

Special cases:

1. The surface reaction is fast enough [5], equations (8 - 9) are valid. The initial and boundary conditions for $\tau \geq 0$ and $x = 0$ are:

$$c_A^l = c_A^g \kappa_A \quad (11)$$

2. If the surface reaction is controlling, the following equation will be valid for all τ and $x = 0$:

$$\left(\frac{\partial c_A}{\partial \tau}\right)_{x=0} = k_A (c_{\text{oA}}^l - c_{\text{oA}}^g / \kappa_A) \quad (12)$$

3. The transport in gas phase is controlling, equation (9) is valid with the initial and boundary conditions:

$$\begin{aligned} \tau \geq 0; \quad x < 0; \quad c_A^l &= c_{0A}^l \\ \tau = 0; \quad x > 0; \quad c_A^g &= c_{0A}^g \\ \text{for all } \tau; x = 0; \quad c_A^g &= c_{0A}^g / \kappa_A \end{aligned} \quad (13)$$

4. The transport in liquid phase is controlling [6], equation (8) is valid with the initial and boundary conditions:

$$\begin{aligned} \tau = 0; \quad x < 0; \quad c_A^l &= c_{0A}^l \\ \tau \geq 0; \quad x > 0; \quad c_A^g &= c_{0A}^g \\ \text{for all } \tau; x = 0; \quad c_A^g &= c_{0A}^g \kappa_A \end{aligned} \quad (14)$$

5. The transport in gas phase and surface reaction are controlling, equation (9) is valid with the initial and boundary conditions:

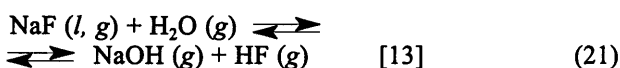
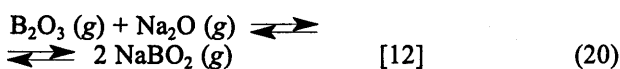
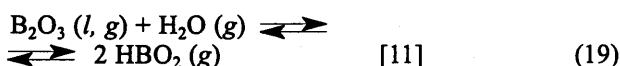
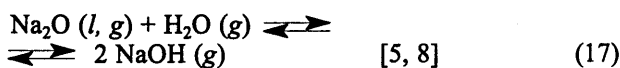
$$\begin{aligned} \tau \geq 0; \quad x < 0; \quad c_A^l &= c_{0A}^l \\ \tau = 0; \quad x > 0; \quad c_A^g &= c_{0A}^g \\ \text{for all } \tau; x = 0; \quad \frac{\partial c_A^l}{\partial \tau} &= k_A(c_{0A}^l - \kappa_A c_A^g) \end{aligned} \quad (15)$$

6. The transport in liquid phase and surface reaction are controlling [6, 7, 8], equation (8) is valid with the initial and boundary conditions:

$$\begin{aligned} \tau = 0; \quad x < 0; \quad c_A^l &= c_{0A}^l \\ \tau \geq 0; \quad x > 0; \quad c_A^g &= c_{0A}^g \\ \text{for all } \tau; x = 0; \quad \frac{\partial c_A^l}{\partial \tau} &= k_A(c_A^l - \kappa_A c_{0A}^g) \end{aligned} \quad (16)$$

VOLATILIZATION OF A GLASS COMPONENT WITH CHEMICAL REACTION ON THE GLASS SURFACE OR IN THE GAS PHASE

Several volatilization processes are obviously bound with chemical reaction leading to process acceleration. As an example, following reactions may be mentioned:



The presented reactions enable to estimate the significant role of vaporization chemisms for the entire vaporization process. Unfortunately, the chemical data about the vaporization of components from a glass melt are scarce and not unambiguous [14]. Nevertheless, the acceptable idea of chemical vaporization is the following process: the volatile component evaporizes from the melt (therefore an equilibrium exists between the liquid and gas form of the component on the phase boundary), and the gas form reacts partially or completely with another component in gas phase. The second reacting component is either coming from the glass (reaction (20)) or it was originally present in the gas phase (reactions (17 - 19) and (21)).

As an example of "reactive evaporation", the evaporation of Na_2O from the melt and its reaction with water vapour will be treated (reaction (17)). The concentration of molecular water in the glass melt will be considered negligible (reaction (24) in [1]), as well as the NaOH solubility in the melt. The transport equations of reacting components will therefore involve the transport of Na_2O through the glass, the chemical reaction in the gas phase and the respective chemical equilibrium of three reacting components in the gas phase.

The governing equations are:

$$\frac{\partial c_{\text{Na}_2\text{O}}^l}{\partial \tau} = D_{\text{Na}_2\text{O}}^l \nabla^2 c_{\text{Na}_2\text{O}}^l - v^l \nabla c_{\text{Na}_2\text{O}}^l \quad (22)$$

$$\frac{\partial c_{\text{Na}_2\text{O}}^g}{\partial \tau} = D_{\text{Na}_2\text{O}}^g \nabla^2 c_{\text{Na}_2\text{O}}^g - v^g \nabla c_{\text{Na}_2\text{O}}^g + \left(\frac{\partial c_{\text{Na}_2\text{O}}^g}{\partial \tau} \right)_{\text{ch}} \quad (23)$$

$$\frac{\partial c_{\text{H}_2\text{O}}^g}{\partial \tau} = D_{\text{H}_2\text{O}}^g \nabla^2 c_{\text{H}_2\text{O}}^g - v^g \nabla c_{\text{H}_2\text{O}}^g + \left(\frac{\partial c_{\text{H}_2\text{O}}^g}{\partial \tau} \right)_{\text{ch}} \quad (24)$$

$$\frac{\partial c_{\text{NaOH}}^g}{\partial \tau} = D_{\text{NaOH}}^g \nabla^2 c_{\text{NaOH}}^g - v^g \nabla c_{\text{NaOH}}^g + \left(\frac{\partial c_{\text{NaOH}}^g}{\partial \tau} \right)_{\text{ch}} \quad (25)$$

The values of $(\partial c_i / \partial \tau)_{\text{ch}}$ are bound by the stoichiometry of reaction (17):

$$\left(\frac{\partial c_{\text{Na}_2\text{O}}^g}{\partial \tau} \right)_{\text{ch}} = \left(\frac{\partial c_{\text{H}_2\text{O}}^g}{\partial \tau} \right)_{\text{ch}} = -\frac{1}{2} \left(\frac{\partial c_{\text{NaOH}}^g}{\partial \tau} \right)_{\text{ch}} \quad (26)$$

Taking into account equation (26), equations (23 - 25) can be arranged as follows:

$$\frac{\partial c_{\text{Na}_2\text{O}}^g}{\partial \tau} - \frac{\partial c_{\text{H}_2\text{O}}^g}{\partial \tau} = D^g(\text{Na}_2\text{O}) - D^g(\text{H}_2\text{O}) \quad (27)$$

$$2 \frac{\partial c_{\text{Na}_2\text{O}}^g}{\partial \tau} - \frac{\partial c_{\text{NaOH}}^g}{\partial \tau} = 2D^g(\text{Na}_2\text{O}) + D^g(\text{NaOH}) \quad (28) \quad \frac{\partial c_{\text{H}_2\text{O}}^g}{\partial \tau} = D^g(\text{H}_2\text{O}) \quad (33)$$

Where:

$$D^g(i) = D_i^g \nabla^2 c_i^g - v \nabla c_i^g \quad (29) \quad \frac{\partial c_{\text{NaOH}}^g}{\partial \tau} = D^g(\text{NaOH}) \quad (34)$$

If the chemical reaction (17) is fast enough, the equilibrium sets all over the gas phase:

$$K_{\text{Na}_2\text{O}} = \frac{[c_{\text{NaOH}}^g]^2}{c_{\text{Na}_2\text{O}}^g c_{\text{H}_2\text{O}}^g} \quad (30)$$

And $c_{\text{Na}_2\text{O}}^g = c_{\text{Na}_2\text{O}}^l / K_{\text{Na}_2\text{O}}$.

If reaction (17) is slow and reversible (the Na_2O component does not react completely), the following kinetic relation can be written:

$$\left(\frac{\partial c_{\text{Na}_2\text{O}}^g}{\partial \tau} \right)_{\text{ch}} = -k_{\text{Na}_2\text{O}} (c_{\text{Na}_2\text{O}}^g - c_{\text{Na}_2\text{O}^{\text{eq}}}^g) (c_{\text{H}_2\text{O}}^g - c_{\text{H}_2\text{O}^{\text{eq}}}^g) \quad (31)$$

Where $k_{\text{Na}_2\text{O}}$ is the rate constant of equation (17) and $c_{\text{Na}_2\text{O}^{\text{eq}}}^g$ as well as $c_{\text{H}_2\text{O}^{\text{eq}}}^g$ are the appropriate equilibrium values under given temperature (calculated from equation (30)).

Thus, if the process is controlled by mass transport in both phases and chemical reaction (17) is fast enough, equations (22), (27 - 28) and (30) should be solved to get the concentration distributions of Na_2O (l), Na_2O (g), H_2O (g) and NaOH (g).

If, on the contrary, reaction (17) is slow enough, the concentration distribution of the mentioned components is obtainable by solution of equations (22), (27 - 28) and equation (23) with equation (31).

The initial and boundary conditions for both treated cases are:

$$\begin{aligned} \tau = 0; \quad x < 0; \quad c_{\text{Na}_2\text{O}}^l &= c_{\text{Na}_2\text{O}}^l & \text{equation (30) is valid} \\ \tau = 0; \quad x > 0; \quad c_{\text{Na}_2\text{O}}^g &= c_{\text{Na}_2\text{O}}^g & \\ \tau > 0; \quad x \rightarrow -\infty; \quad c_{\text{Na}_2\text{O}}^l &= c_{\text{Na}_2\text{O}}^l & \\ \tau > 0; \quad x \rightarrow \infty; \quad c_{\text{Na}_2\text{O}}^g &= c_{\text{Na}_2\text{O}}^g & \text{equation (30) is valid} \end{aligned}$$

for all $\tau; x = 0$:

- fast chemical reaction, equation (30) is valid
- slow chemical reaction, equation (31) is valid.

$$(32)$$

Special cases:

1. The reaction (17) realizes almost completely, i.e. the concentration of Na_2O in the gas phase will be negligible. Then reaction (17) will be significant only on the phase boundary.

If the mass transport in both phases controls this process, reaction (22) (the transport of Na_2O in the liquid phase) and reactions:

are valid. The initial and boundary conditions on the phase boundary are:

for all $\tau; x = 0$:

- reaction (17) is fast enough: equation (30) is valid on the phase boundary to calculate the values of $(c_{\text{H}_2\text{O}}^g)_{x=0}$ and $(c_{\text{NaOH}}^g)_{x=0}$; for the concentration of $c_{\text{Na}_2\text{O}}^l$, we have: $c_{\text{Na}_2\text{O}}^l = c_{\text{Na}_2\text{O}}^g K_{\text{Na}_2\text{O}} \rightarrow 0$
- reaction (17) is slow: (35)

$$\left(\frac{\partial c_{\text{Na}_2\text{O}}^g}{\partial \tau} \right)_{x=0} = -k_{\text{Na}_2\text{O}} c_{\text{Na}_2\text{O}}^g c_{\text{H}_2\text{O}}^g \quad (36)$$

2. The transport in gas phase is fast.

Equation (22) is valid and the following initial and boundary conditions on the phase boundary:

- reaction (17) is fast enough: equation (30) is valid with $c_{\text{NaOH}}^g = c_{\text{NaOH}}^g$ and $c_{\text{H}_2\text{O}}^g = c_{\text{H}_2\text{O}}^g$; therefore as well $(c_{\text{Na}_2\text{O}}^g)_{x=0}$ will be constant (see equation (30)).
- reaction (17) is slow (mixed control): equation (31) or (36) (reaction is almost completed) is valid with $c_{\text{H}_2\text{O}}^g = c_{\text{H}_2\text{O}}^g$ [15].

3. The transport in liquid phase is fast.

Equations (27) and (28) are valid as well as equation (30) if reaction (17) is fast enough. For the case of slow reaction (17) (mixed control), equations (27) and (28) as well as equation (31) with equation (23) should be solved. The initial and boundary conditions on the phase boundary are:

- reaction (17) is fast enough, equation (30) is valid with $c_{\text{Na}_2\text{O}}^l = c_{\text{Na}_2\text{O}}^l$
- reaction (17) is slow, equation (31) is valid with $c_{\text{Na}_2\text{O}}^g = c_{\text{Na}_2\text{O}}^l / K_{\text{Na}_2\text{O}}$.

The evaporation of fluorides from the glass melt is influenced by the water vapour concentration in the gas phase, by the gas phase hydrodynamics and by glass convection in the liquid driven by surface tension fluctuations [16, 17]. The probable chemism of evaporation is given by reaction (21).

The governing equations are:

$$\frac{\partial c_{\text{NaF}}^l}{\partial \tau} = D^l(\text{NaF}) \quad (37)$$

$$\frac{\partial c_{\text{NaF}}^g}{\partial \tau} = D^g(\text{NaF}) + \left(\frac{\partial c_{\text{NaF}}^g}{\partial \tau} \right)_{\text{ch}} \quad (38)$$

$$\frac{\partial c_{\text{H}_2\text{O}}^g}{\partial \tau} = D^g(\text{H}_2\text{O}) + \left(\frac{\partial c_{\text{H}_2\text{O}}^g}{\partial \tau} \right)_{\text{ch}} \quad (39)$$

$$\frac{\partial c_{\text{NaOH}}^g}{\partial \tau} = D^g(\text{NaOH}) + \left(\frac{\partial c_{\text{NaOH}}^g}{\partial \tau} \right)_{\text{ch}} \quad (40)$$

$$\frac{\partial c_{\text{HF}}^g}{\partial \tau} = D^g(\text{HF}) + \left(\frac{\partial c_{\text{HF}}^g}{\partial \tau} \right)_{\text{ch}} \quad (41)$$

The reaction stoichiometry gives:

$$\left(\frac{\partial c_{\text{NaF}}^g}{\partial \tau} \right)_{\text{ch}} = \left(\frac{\partial c_{\text{H}_2\text{O}}^g}{\partial \tau} \right)_{\text{ch}} = - \left(\frac{\partial c_{\text{NaOH}}^g}{\partial \tau} \right)_{\text{ch}} = - \left(\frac{\partial c_{\text{HF}}^g}{\partial \tau} \right)_{\text{ch}} \quad (42)$$

The arrangement of equations (38 - 42) gives:

$$\frac{\partial c_{\text{NaF}}^g}{\partial \tau} - \frac{\partial c_{\text{H}_2\text{O}}^g}{\partial \tau} = D^g(\text{NaF}) - D^g(\text{H}_2\text{O}) \quad (43)$$

$$\frac{\partial c_{\text{NaOH}}^g}{\partial \tau} - \frac{\partial c_{\text{HF}}^g}{\partial \tau} = - D^g(\text{NaOH}) - D^g(\text{HF}) \quad (44)$$

$$\begin{aligned} \frac{\partial c_{\text{NaF}}^g}{\partial \tau} + \frac{\partial c_{\text{H}_2\text{O}}^g}{\partial \tau} + \frac{\partial c_{\text{NaOH}}^g}{\partial \tau} + \frac{\partial c_{\text{HF}}^g}{\partial \tau} &= \\ = D^g(\text{NaF}) + D^g(\text{H}_2\text{O}) + D^g(\text{NaOH}) + D^g(\text{HF}) &\quad (45) \end{aligned}$$

If the reaction is fast enough, the equilibrium sets:

$$K_{\text{NaF}} = \frac{c_{\text{NaOH}}^g c_{\text{HF}}^g}{c_{\text{NaF}}^g c_{\text{H}_2\text{O}}^g} \quad (46)$$

Where $c_{\text{NaF}}^g = c_{\text{NaF}}^l / K_{\text{NaF}}$.

For the slow chemical reaction, we have:

$$\left(\frac{\partial c_{\text{NaF}}^g}{\partial \tau} \right)_{\text{ch}} = - k_{\text{NaF}} (c_{\text{NaF}}^g - c_{\text{NaF}}^g) (c_{\text{H}_2\text{O}}^g - c_{\text{H}_2\text{O}}^g) \quad (47)$$

Thus, for rapid reaction (21), the set of equations (37), (43 - 45) and equation (46) is solved, while in the case of slow chemical reaction equations (37), (43 - 45) and equation (38) with (47) give the concentration profiles of reacting components in both phases.

The initial and boundary conditions are:

$$\begin{aligned} \tau = 0; \quad x < 0; \quad c_{\text{NaF}}^l &= c_{\text{oNaF}}^l \\ x > 0; \quad c_{\text{NaF}}^g &= c_{\text{bi}}^g, \quad \text{equation (46) is valid} \\ \tau > 0; \quad x \rightarrow -\infty; c_{\text{NaF}}^l &= c_{\text{oNaF}}^l \\ x \rightarrow \infty; \quad c_{\text{NaF}}^g &= c_{\text{bi}}^g, \quad \text{equation (46) is valid} \end{aligned}$$

for all $\tau: x = 0$:

- reaction (21) is fast enough, equation (46) is valid
- reaction (21) is slow, equation (47) is valid (48)

If the glass convection, driven by fluctuations of surface tension, is effective enough, the evaporation is controlled by the transport in gas phase only [16, 17]. The governing equations are (43 - 45) and (46) in the case of rapid chemical reaction or (43 - 45) and (38) with (47) for slow chemical reaction. If the equilibrium is shifted to the reaction products ($c_{\text{NaF}}^g \rightarrow 0$), then the volatilization, controlled by the transport in gas phase, will be described by the set of equations (39 - 41) with $(\partial c_i / \partial \tau)_{\text{ch}} = 0$ and the initial and boundary conditions on the phase boundary are:

- reaction (21) is fast enough, equation (46) is valid with $c_{\text{NaF}}^g = c_{\text{oNaF}}^l / K_{\text{NaF}}$
- reaction (21) is slow:

$$\left(\frac{\partial c_{\text{NaF}}^g}{\partial \tau} \right)_{x=0} = - k_{\text{NaF}} c_{\text{oNaF}}^l / K_{\text{NaF}} (c_{\text{H}_2\text{O}}^g - c_{\text{H}_2\text{O}}^g) \quad (49)$$

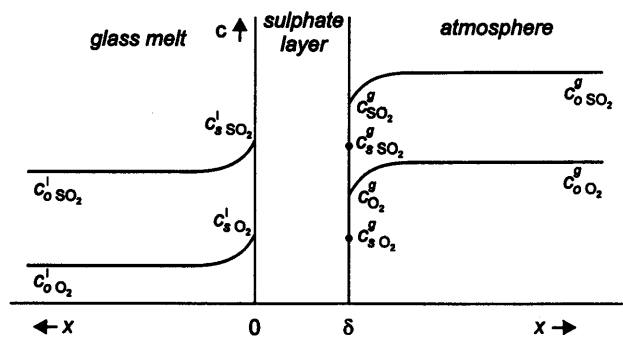


Figure 1. The schematic picture of concentration distribution of SO₂ and O₂ close to sulphate layer.

CONCLUSION

The algorithms for numerical solution of the equations, presented in both part of this work, are generally at disposal and the qualitative descriptions of the treated gas (vapour) - glass melt interactions are mostly known from laboratory measurements. However, two problems arise when trying to describe the particular phenomenon: availability of the appropriate equilibrium data (equilibrium constants, gas solubilities in glasses and equilibrium partial pressures of volatile compo-

nents), of the kinetic data (rate constants of desorption or absorption, rate constants of chemical reactions), of the transport data (diffusion coefficients of transported components), and knowledge of the truthful chemism of some processes of reactive evaporation. These facts are challenge to the development and application of the appropriate experimental methods as are measurement of gas solubilities and diffusivities in glass melts, equilibration of glass melts with reacting gases or gas mixtures and vapours, and establishing analytical methods for component determination both in liquid and gas phase.

Another important task appears to be revealing relations between glass composition and some physical constants, as are diffusion coefficients of transported components and equilibrium or rate constants of chemical reactions. This activity has a special significance for the volatilisation process. The dependence between glass composition and glass properties causes the governing equations of component volatilization describe only idealized, potentially possible cases. That is why this theoretical study cannot replace the fundamental experimental research of these processes. Nevertheless, the proposed equations can be subsequently used to describe the general non-steady state case, working under real conditions and being characterized by the changes of control mechanisms with time.

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INTERAKCE PLYNŮ A PAR SE SKELNÝMI TAVENINAMI

ČÁST 2.

INTERAKCE VYLOUČENÉ SÍRANOVÉ VRSTVY A INTERAKCE PAR

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Jako příklad interakce plynné fáze se skelnou taveninou je uvedena tvorba síranové vrstvy na hladině skloviny při dostatečně vysokém parciálním tlaku SO_2 a O_2 v atmosféře a za přítomnosti alkalických oxidů v tavenině. Analogicky s chováním vrstvy vyloučené na povrchu bublin jsou tvorba nebo rozklad vrstvy ze strany plynné fáze řízeny chemickou reakcí. Ze strany skelné fáze může vrstva rovněž růst nebo se rozpouštět ve sklovině; tento proces je řízen transportem v kapalně fázi. Ve druhé části práce jsou uvedeny základní řídicí rovnice pro odpařování těkavé složky ze skloviny v obecném případě. Vedle obecných rovnic jsou zmíněny rovněž vztahy popisující chování ve speciálních případech, tj. odpařování řízené transportem v kapalně nebo plynné fázi, odpařování řízené povrchovou interakcí a smíšené případy řízení, tj. současné řízení transportem v kapalně fázi a povrchovou reakcí nebo povrchovou reakcí a transportem v plynné fázi. Poslední část práce se zabývá mechanismem odpařování těkavé složky za působení chemické reakce (reaktivní odpařování). Je rovněž uveden obecný případ i případy speciální, zahrnující mj. řízení transportem jen v jedné z fází a smíšenou kontrolou transportu v jedné fázi a chemickou reakcí (jak povrchovou, tak v plynné fázi). V reálném případě může docházet ke změně řídicího děje s časem a k podstatnějším změnám vlastností taveniny v povrchové vrstvě. Proto jsou uvedené vztahy popísem idealizovaným, někdy vztaženým k určité fázi odpařování. U všech případů jsou uvedeny počáteční a okrajové podmínky řešení.