Hans van Limpt,
Ruud Beerkens,
Marco van Kersbergen

TNO Glass Group

**EFFET DE FAIBLES
VARIATIONS
DE COMPOSITION
SUR LES ÉMISSIONS
DE FUMÉES
DES FOURS VERRIERS**

Des changements de composition relativement faibles peuvent avoir des conséquences importantes sur le taux de volatilisation des composants volatils du verre dans les fours de fusion.
Des tests ont été menés afin de mesurer l'impact de changements mineurs dans le mélange vitrifiable sur les taux d'envolement de composants volatils et des émissions de poussières dans des atmosphères simulées de fours. Les résultats de ces tests en laboratoire ont été utilisés pour développer et améliorer un modèle applicable dans les fours de fusion de l'industrie verrière. Les relations de transfert de masse pour le mouvement des composants volatils dans les turbulences de fumées ont été utilisées pour adapter les modèles de volatilisation valables dans les laboratoires aux applications en fours verriers industriels.
Dans cet article, l'impact du soufre et des chlorures sur les taux de volatilisation du sodium et du potassium provenant des fontes de silicate multi-composants lors de productions de verre industriel sera démontré.

Effect of small glass composition changes on flue gas emissions of glass furnaces

Relatively small changes in glass composition might have drastic consequences on the evaporation rates of volatile glass components in glass melting furnaces. Transpiration evaporation tests have been applied to measure the impact of minor glass composition changes on the evaporation rates of volatile glass components in simulated furnace atmospheres. The results of these laboratory evaporation tests were used to develop and optimize an universally applicable evaporation model to estimate evaporation rates and dust emissions for industrial glass melt furnaces. Mass transfer relations for the transport of volatile glass melt species into the turbulent gas phase were used to upscale the evaporation models valid for the lab tests to applications for industrial glass furnaces. In this paper, the impact of sulfur and chlorides on the evaporation rates of sodium and potassium from multi-component silicate melts for industrial glass production will be demonstrated.

INTRODUCTION AND OBJECTIVE

Most glass furnaces apply fossil fuel firing to transfer heat directly from the combustion processes above the melting batch and glass melt. Evaporation processes and subsequent condensation processes during the cooling of the flue gases are major causes of pollutant emissions from glass furnaces [1].
Since 2000, Beerkens and van Limpt [2-5] applied evaporation models to calculate and estimate the evaporation rates of volatile species (e.g. Na, K, B, S and Cl) in industrial glass furnaces. This paper describes the influence of minor components in the melt, like sulfur and chlorides, on the evaporation of sodium and potassium from alkali-lime-silicate melts.

THEORY

In industrial fossil fuel fired glass furnaces, components like Na, K,

S and Cl are released from melting alkali-lime-silicate batches and from the surface of the glass melt. A significant part of the emitted sulfur and chloride components are released from the melting batch [6-8]. In this paper we only focus on evaporation processes from glass melts.

EVAPORATION OF SODIUM AND POTASSIUM SPECIES

The water vapor concentration or partial vapor pressure of water in the atmosphere mainly determines the sodium vaporization rate. At dry oxidized conditions, the sodium vaporization is negligible. The formation of sodium hydroxide vapor by reaction of sodium oxide at the glass melt surface with water vapor [5, 9-13] is the most important example of evaporation during the melting of soda- (lime)-silicate glasses. The vapor pressure of NaOH is proportional to $(aNa_2O \cdot pH_2O)^{\frac{1}{2}}$ at equilibrium conditions. Here aNa_2O is the chemical activity of Na_2O in the melt and pH_2O the partial water vapor pressure in the furnace atmosphere. The equilibrium constant $KNaOH$ of this chemical reaction is only temperature dependent.

Furthermore, the evaporation of elementary Na from the melt is proportional to $pO_2^{\frac{1}{4}}$ [14] as a result of the reduction of Na_2O at the melt surface. Na_2O at the surface of the melt might be reduced also by reducing gases in the atmosphere like CO [3]. K_2O in the melt will evaporate as KOH [9] or at reducing conditions as elementary potassium.

IMPACT OF SULFATES IN THE GLASS MELT ON THE EVAPORATION OF SODIUM SPECIES

Sulfur oxides in the combustion space are known to increase the volatilization of sodium compounds [15]. The impact of sodium sulfate (Na_2SO_4) addition to the batch or melt, on evaporation of sodium or potassium species from an industrial float glass has been investigated by Gebhardt [6]. The emission of particulate matter (dust) increases linearly with the amount of Na_2SO_4 in the batch. Matousek [7] also found higher evaporation losses for sodium with increasing sulfate content in the melt.
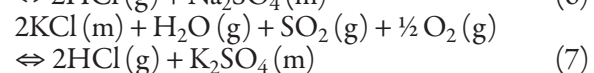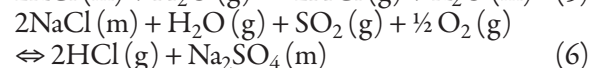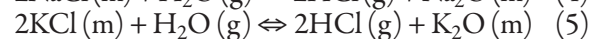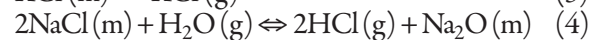
Conradt and Scholze [9] used laboratory evaporation experiments to investigate the impact of sulfate content in the glass (melt) on the sodium evaporation rates from soda-lime-silicate glass melts ($SiO_2 : Na_2O : CaO = 74 : 16 : 10$ mass- %). In glass melts with sulfur concentrations (expressed as SO_3 concentration), between 0.07 and 0.97 mass- %, higher sodium releases have been measured compared to SO_3 free glass melts with the same sodium content. It was concluded that for industrial practice-relevant SO_2 vapor pressures (< 500 Pa) from sulfate containing soda-lime-silicate melts, the increased sodium release (compared to sulfur free melts) was mainly a result of evaporation reaction 1.

$$Na_2SO_4 \, (m) \Leftrightarrow Na_2SO_4 \, (g) \qquad (1)$$
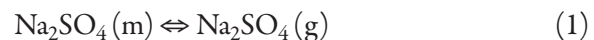
EVAPORATION OF CHLORIDE SPECIES

In commercially produced soda-lime-silicate glass melts, such as container glass melts and float glass melts, chlorides are present due to contaminations or impurities of the applied raw materials or recycled glass cullet. For an industrial amber glass furnace it was shown [8] that about 40 % of the evaporated chloride species were released from the blank melt and 60 % volatilizes from the melting batch. At high, not specified temperatures, NaCl is assumed to be the major volatile chloride species (reaction 2). Below 1000 °C, chloride species may evaporate under influence of water vapor and SO_2 (reactions 4 and 6). The possible evaporation reactions of chlorides from a melt are given by equations 2 to 7.

In industrially prepared glass melts, chlorides are sometimes deliberately applied as flux or fining agent. Emerging NaCl or KCl vapor bubbles in the case of 'chloride' fining also influence the mixing of the melt and have probably impact on the release of species like NaCl, KCl or HCl or even NaOH and KOH (suppressing depletion of sodium and potassium at the surface). The impact of the presence of chlorides in the melt on the evaporation of different glass components from the glass melt surface as well as chloride fining will be discussed in a next paragraph.

$$NaCl \, (m) \Leftrightarrow NaCl \, (g) \qquad (2)$$
$$KCl \, (m) \Leftrightarrow KCl \, (g) \qquad (3)$$
$$2NaCl \, (m) + H_2O \, (g) \Leftrightarrow 2HCl \, (g) + Na_2O \, (m) \qquad (4)$$
$$2KCl \, (m) + H_2O \, (g) \Leftrightarrow 2HCl \, (g) + K_2O \, (m) \qquad (5)$$
$$2NaCl \, (m) + H_2O \, (g) + SO_2 \, (g) + \tfrac{1}{2} O_2 \, (g)$$
$$\Leftrightarrow 2HCl \, (g) + Na_2SO_4 \, (m) \qquad (6)$$
$$2KCl \, (m) + H_2O \, (g) + SO_2 \, (g) + \tfrac{1}{2} O_2 \, (g)$$
$$\Leftrightarrow 2HCl \, (g) + K_2SO_4 \, (m) \qquad (7)$$

EXPERIMENTAL

Transpiration evaporation experiments were used to measure the evaporation rates of different glass melt compositions. The experimental set-up and procedure is described extensively by van Limpt [2]. A platinum/rhodium boat filled with glass is placed in the tube furnace. At the desired set-point temperature the tube is flushed with a controlled gas flow. During an evaporation experiment, the temperature and gas composition (pO_2, pH_2O, pN_2) are fixed. The evaporation rates of the volatile species are measured as a function of time by sampling the gases with a platinum/rhodium sampling probe. From the measured evaporation rates, the known mass transfer relations and the evaporation reaction, saturation vapor pressures and chemical activities of volatile glass compounds can be derived [2]. The measured chemical activities are compared with results of thermodynamic modeling.

THERMODYNAMIC MODELS

To calculate saturation pressures of a volatile gaseous species i (pi^*), the chemical activity aj of a volatile glass compound j is required. The thermodynamic Associated Species Model, described by Steiner [16] and Van Limpt [2] is applied to predict the chemical activities of volatile glass compounds like aNa_2O and aK_2O. This model is validated for multi-component alkali-silicate glass melts [2].

RESULTS

In this chapter, the results of laboratory transpiration experiments with alkali-lime-silicate melts are presented. The impact of SO_3 and chlorides on the evaporation of sodium and potassium species are discussed in the next chapters.

EFFECT OF SO3 IN GLASS ON SODIUM EVAPORATION

The impact of sulfur in the glass (mainly present as sulfate in oxidized glass melts [17]) on the evaporation of sodium species from the surface of alkali silicate melts has

been investigated with our transpiration set-up for two float glass melt compositions shown in Table 1. Evaporation experiments for float glass melts with sulfur or without sulfur, exposed to dry as well as a humid atmosphere are performed. The evaporation rates of sodium species and sulfur species have been measured.

Van Limpt [2] showed the results of transpiration evaporation tests with a float glass composition containing sulfur (in this oxidized molten glass the sulfur is mainly in the sulfate state), exposed to a dry atmosphere (O_2/N_2 gas mixture, $pO_2 = 0.11$ bar) at T = 1460 °C. The measured molar ratio of the evaporated alkali compounds and evaporated sulfur: $(QNa + QK)/QS \approx 2$. Thus, Na_2SO_4 and K_2SO_4 are probably the main volatile species. From the measured total sodium evaporation rate and the assumption that all sodium evaporates as Na_2SO_4 in a dry atmosphere, the chemical activity of Na_2SO_4 (aNa_2SO_4) in the surface layer of the melt has been calculated on a value of 0.06 for T = 1460 °C and an initial SO_3 concentration of 0.25 mass- %.

Component	Float glass without SO$_3$ (wt-%)	Float glass with SO$_3$ (wt-%)
SiO$_2$	73	72
Na$_2$O	14	14
K$_2$O	0.2	0.2
SO$_3$	0	0.25
Cl	0	0

Table 1: Measured average chemical composition (XRF) of different float glass compositions with and without SO$_3$. The compositions have been measured for glass samples obtained from transpiration evaporation tests. The table only contains the components SiO$_2$, Na$_2$O, K$_2$O, SO$_3$ and Cl

Additional to the previously described experiments, carried out under dry conditions, transpiration experiments with float glass melts have been performed in an oxidized and humidified atmosphere ($pH_2O \approx 0.33$ bar). Under these conditions the expected major volatile sodium species are NaOH and Na_2SO_4.

Figure 1 shows the measured total sodium evaporation rates from float glass melts with initially 0.25 mass- % SO_3 and without sulfur in the glass. Compared to glass melts without sulfur, the total sodium evaporation rates from the same glass melt compositions, but with sulfur are about 20 to 50 % higher in the temperature range between 1400 and 1500 °C. SO_2 fining already took place before the evaporation experiments during the preparation of the glass samples.

The results of the evaporation tests are used to demonstrate that:
a) sodium depletion at the surface of the melt and
b) extra NaOH evaporation as a result of the reaction

between Na_2SO_4 in the melt and water vapor in the atmosphere, do not explain the increased sodium evaporation rates from melts containing SO_3.

From the measured evaporation rates shown Figure 1, the chemical activities of Na_2SO_4 are obtained. The chemical activities of Na_2SO_4 in a glass melt exposed to a humid atmosphere ($pH_2O = 0.33$ bar), seem to be at least 2 times higher ($0.13 < aNa_2SO_4 < 0.20$) than the aNa_2SO_4 values derived at dry evaporation conditions ($aNa_2SO_4 \approx 0.06$).
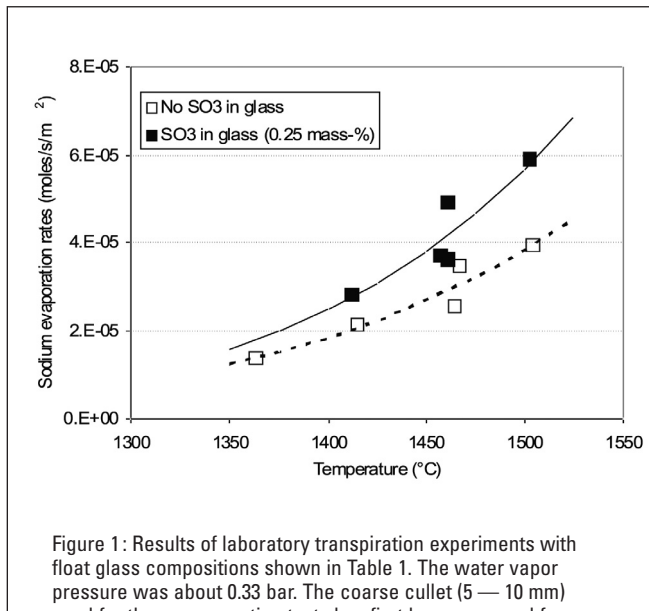

Figure 1: Results of laboratory transpiration experiments with float glass compositions shown in Table 1. The water vapor pressure was about 0.33 bar. The coarse cullet (5 — 10 mm) used for these evaporation tests has first been prepared from pure raw materials that are melted above the fining temperature. During the evaporation tests no fining (gas bubble evolution) has been observed

Based on the results of transpiration experiments for float glass melts (with and without sulphate addition) at 1460 ± 5 °C, the chemical activities of Na_2O at the surface of the melt were derived from the measured NaOH evaporation rates. From the melt containing sulfate, it is assumed that NaOH and Na_2SO_4 are the only volatile sodium species and that all the measured sulfur release evaporates as Na_2SO_4. Furthermore, the thermodynamic Associated Species Model has been used to calculate the chemical activity of Na_2O for the bulk composition of the melt. All the derived chemical activities for Na_2O are about similar: $1.4 \cdot 10^{-8} \pm 0.2 \cdot 10^{-8}$. Therefore, sodium depletion at the surface of the melt cannot explain the differences in sodium evaporation between melts with and without sulfur.

If one would assume that all sodium evaporates as NaOH (no Na_2SO_4 evaporation), the calculated virtual activity values for aNa_2O in glass compositions with SO_3 are much higher: $2.9 \cdot 10^{-8} < aNa_2O < 4.6 \cdot 10^{-8}$, which correspond with Na2O surface concentrations between 16 and 19 mass- %. SEMEDX pro-

file measurements in float glass samples containing sulfur, after transpiration experiments however, do not show these high concentrations near the surface of the melt.

For soda-lime-silicate glass melts with sulfur in the melt, NaOH and Na_2SO_4 are the main evaporating sodium species in humid and oxidized atmospheres. The evaporation rate of Na_2SO_4 is proportional to the chemical activity of Na_2SO_4 at the surface of the melt. But, the surface layer becomes Na_2SO_4 depleted.

The effect of water vapor in the atmosphere on the extra release of sodium species from the melt is still not completely understood. Because of the lower maximum SO_3 concentration in a humid atmosphere, sulfur species have to be released from the melt when being exposed to a humid atmosphere. The formation of SO_2 bubbles and the formation of a dynamic, continuously refreshed foam layer at the surface of the melt may also promote the evaporation rates of volatile glass components.

SODIUM AND POTASSIUM EVAPORATION FROM INDUSTRIAL GLASS MELT COMPOSITIONS CONTAINING CHLORIDES AND SULFUR

For a multi-component alkali-lime-silicate melt containing Na_2O, K_2O, sulfur and chlorine ($Na_2O \approx$ 10 mass- %, $K_2O \approx 5$ mass- %, $SO_3 \approx 0.1$ mass- %, Cl ≈ 0.1 mass- %), the evaporation rates of sodium- and potassium-species are about 40 to 60 % higher at 1500 °C compared to melts without sulfur and chlorine, but with the same basic composition concerning the other components. Linear correlations were found between the chloride evaporation rates and sulfur release rates when changing the sulfur contents in the melt or when changing the water vapor pressure in the atmosphere. This observation may be a result of the effect of sulfur on the occurrence of stronger convection in the melt. This leads to higher release rates of compounds such as Na_2SO_4, KCl and NaCl. The for-
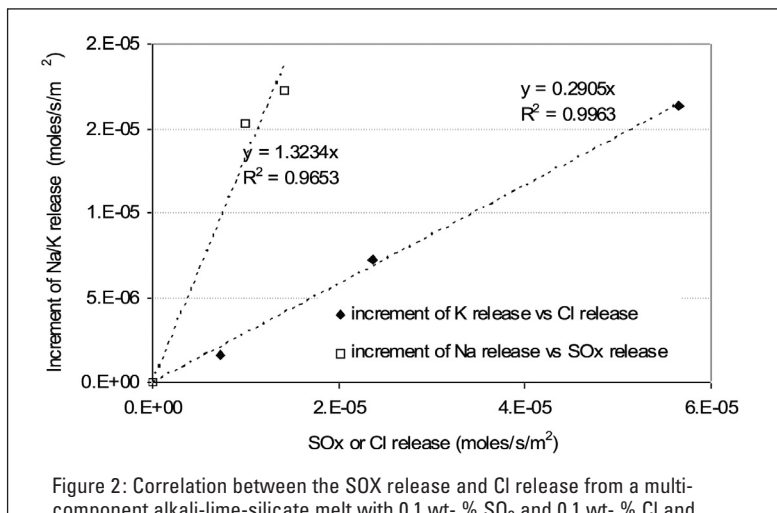
Figure 2: Correlation between the SOX release and Cl release from a multi-component alkali-lime-silicate melt with 0.1 wt- % SO$_3$ and 0.1 wt- % Cl and the measured increase in total Na- en K-release of this melt compared to the evaporation rates from an almost identical melt without SO$_3$ and without Cl

mation of SO$_2$ bubbles and the formation of a foam layer at the surface of the melt, might not only effect sulfur evaporation but will influence the release rates of chloride compounds as well.

From the observed linear correlation between the measured potassium evaporation rates and chloride evaporation rates (see figure 2) it was concluded that from these melts chlorides mainly evaporate as KCl rather than NaCl.

For alkali-lime-silicate melts, chlorides and sulfates promote the release of alkali species. The main evaporation species from soda-lime-silicate float glass melts and multi-component alkali-limesilicate melts with chlorides are: NaOH, KOH, Na$_2$SO$_4$, KCl and at reducing conditions Na and K.

CONCLUSIONS

For alkali-lime-silicate melts, chlorides and sulfates promote the release of alkali species, by formation of Na$_2$SO$_4$, NaCl, KCl or possibly K$_2$SO$_4$ vapors. In a static

melt, the evaporation rates of these species are limited by the relatively slow diffusion transport from the bulk to the surface of the melt. Depletion of sulfur and chloride species at the glass melt surface becomes more significant as the evaporation process proceeds. However, temperature gradients, local differences in surface tension and bubbles in the melt can strongly affect the (local) convection in the melt. Depletion at the surface will (partly) be eliminated and the evaporation rates of these minor species increase.

The formation of SO$_2$ bubbles and the formation of a dynamic, continuously refreshed foam layer at the surface of the melt may also promote the evaporation rates of volatile glass components.

From the investigations, it appeared that the main evaporation species from soda-lime-silicate float glass melts and multi-component alkali-lime-silicate melts are: NaOH, KOH, Na$_2$SO$_4$, KCl and at reducing conditions Na and K. ■

RÉFÉRENCES

[1] R.G.C. Beerkens, 'Deposits and condensation from flue gases in glass furnaces', Thesis Technical University Eindhoven (1986)

[2] J.A.C. van Limpt, 'Modeling of evaporation processes in glass melting furnaces', PhD thesis University of Eindhoven, ISBN : 978-90-386-1147-1 (2007)

[3] R.G.C. Beerkens, J.A.C. van Limpt, 'Evaporation in industrial glass melt furnaces', Journal of Glass Science and Technology 74 (2001), 9, p. 245-257

[4] R.G.C. Beerkens, 'Modelling the Kinetics of Volatilization from Glass Melts', J. Am. Ceram. Soc., 84 (2001), 9, p. 1952-1960

[5] H. van Limpt, R. Beerkens, O. Verheijen, 'Models and experiments for sodium evaporation from sodium containing silicate melts', J. Am. Ceram. Soc., 89 (2006), 11, p. 3446-3455

[6] F. Gebhardt, 'Emissionen von Glasschmelzwannen und deren Minderung durch schmelztechnische Ma nahmen', Glastech. Ber., 59 (1986), 12, p. 344-349

[7] J. Matousek, 'Evaporation of silicate glasses containing Na2SO4', Riv. Stn. Sper. Vetro, 9 (1979), 5, p. 159-163

[8] R. Conradt, 'Zur Chlorverdampfung bei der Glasschmelze', Glastech. Ber., 59 (1985), 4, N20

[9] R. Conradt, H. Scholze, 'Zur Verdampfung aus Glasschmelzen', Glastech. Ber., 59 (1986), 2, p. 34-52

[10] D.M. Sanders, W.C. Haller, 'Effect of water vapor on sodium vaporization from two silica based glasses', J. Am. Ceram. Soc., 60 (1977), p. 138-141

[11] H.A. Schaeffer, D.M. Sanders, 'Verdampfungsvorgänge an einem Na2O-CaO-SiO2-Glas, Dampfdruckund Konzentrationsprofilmessungen', Glastech. Ber., 49 (1976), 5, p. 95-102

[12] D.M. Sanders, H.A. Schaeffer, 'Reactive Vaporization of Soda-Lime-Silica Glass Melts', J. Am. Ceram. Soc., 59 (1976), 3-4, p. 96-101

[13] K.P. Hanke, H. Scholze, 'Einfluss der Ofenatmosphäre auf die Verdampfung aus Glasschmelzen', Glastech. Ber., 50 (1977), p. 271-275

[14] D.M. Sanders, W.K. Haller, 'Influence of pO2 on vaporization of sodium-disilicate at 1345 °C', J. Am. Ceram. Soc., 62 (1979), 7-8, p. 424-425

[15] R. Brückner, Zur Kinetik des Stoffaustausches an der Grenzflächen zwischen Silikatglas- und Salzschmelzen und des Stofftransportes in Silikatglasschmelzen unter besonderer Berücksichtigung des Verhaltens von Na2SO4 und seinen Zersetzungsprodukten. Teil I: Grenzflächenenergetische Ausgleichsprozesse bei Stoffaustauschvorgängen'Glastech. Ber., 34 (1961), 9, p. 438-455, Teil II ,'Der Substanzaustausch zwischen Silikatglas- und Salzschmelzen'Glastech. Ber., 34 (1961), 11, p. 515-528, Teil III,'Thermische und chemische Zersetzung von Na2SO4 und der Substanzaustausch zwischen Silikatglasschmelzen und SO2-haltigen Atmosphären', Glastech. Ber., 35 (1962), 2, p. 93-105

[16] A. Steiner, 'Foam glass production from vitrified municipal waste fly ashes', PhD-thesis University of Eindhoven (2006)

[17] P. Laimböck, 'Foaming of glass melts'Thesis Eindhoven University of Technology, The Netherlands (1998)

Nomenclature

a chemical activity in melt [-]
K equilibrium constant [Pa$^{(q \cdot m)}$]
p partial vapor pressure [Pa]
Q molar flux density [mole·m^{-2}·s^{-1}]
T absolute temperature [K or °C]

Subscripts and superscripts

* saturated gaseous atmosphere
g gas phase
i component i in gas phase
j (evaporating) component in melt
m melt phase