

EVAPORATION OF PbO-SiO₂ AND K₂O-PbO-SiO₂ MELTS

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Evaporation of two model glasses, composed of PbO and SiO₂ (molar relation PbO : SiO₂ = 1 : 1) and PbO, K₂O and SiO₂ (9 mol.% PbO, 15.2 mol.% K₂O, 75.8 mol.% SiO₂) was followed by determining of total mass change and change of surface PbO-concentration. Air and carbon dioxide streaming above the melt and saturated by water vapour were applied in order to find their influence on evaporation. Volatilisation losses of the binary and ternary melts increase exponentially in terms of temperature in both dry and moist gases. The time dependence of volatilisation losses was found to be linear in character except ternary melt exposed to high temperatures in dry and moist air. In the latter case the time dependence was parabolic in shape. Concentration of PbO in the surface layer was determined by means of electron microprobe. The concentration value decreases with temperature and time of evaporation. The lowest value of PbO surface concentration was found if evaporation of the ternary melt proceeded in moist atmospheres.

Keywords: Evaporation, Glass melt, PbO

INTRODUCTION

Vaporisation of PbO from silicate melts has been dealt with by many experimental studies most of which were based on determining the loss in weight in terms of parameters affecting the course and results of the process. Significant contributions to the subject matter were provided by experimental investigations aimed at identifying the composition of vapours of volatile components and at determining their partial vapour pressures by means of high-temperature mass spectroscopy [1]. More recently, vaporisation during the melting of glasses in tank furnaces has been studied by mathematical modelling [2 - 3]. Each of these methods contributes to extending the existing knowledge of vaporisation and thus to the possibility of predicting, with a higher degree of precision, the concentration changes in glass as well as in the gaseous phase above the melt that result from volatilisation. Changes in melt component concentration are indicative of the danger of inhomogeneities arising in the glass, whereas the presence of some products of vaporisation may be responsible for increased corrosion of refractories [4]. Knowledge of concentration changes in glass melt and in the gaseous phase is therefore of considerable practical significance. The present paper is concerned with experimental determination of volatilisation losses and concentration changes of two- and three-component lead melts, and is aimed at establishing experimentally to what degree the respective changes can be influenced by temperature and composition of the gaseous phase above the melt. Namely influence of water vapour present in furnace atmosphere was followed, because

some experimental results indicate higher rate of evaporation with increasing water vapour pressure [5 - 7].

EXPERIMENTAL

Samples for determining the volatilisation losses and changes in concentration were prepared by high-temperature exposure under defined conditions in the apparatus shown schematically in figure 1.

Two types of glass melted under laboratory conditions [6,7] were ground (1 - 3 mm) and used as initial materials. Composition of those glasses was determined by chemical analysis after melting and cooling procedure. The binary glass having the composition 21.9 SiO₂, 78.1 PbO (wt.%) contained only one volatile component, PbO, so that it was possible to assess explicitly the relation between concentration changes in the melt and the composition of the gaseous phase. The ternary glass with the composition

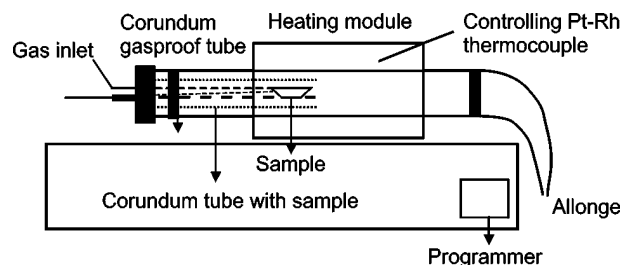


Figure 1. Schematic diagram of apparatus for high-temperature exposure of samples.

62.0 SiO₂, 26.0 PbO, 12.0 K₂O (wt.%) contained in addition to PbO another volatile component, K₂O, whose vaporisation is known to accelerate with increasing water vapour content in the gaseous phase [8]. Experimental data on changes in concentration in the melt of this composition thus allow the differences in the behaviour of these volatile oxides to be assessed. A closer description of the apparatus and of the sample preparation procedure can be found in [5, 6]. The changes in PbO concentration in a surface melt layer following vaporisation were determined by means of the electron microprobe JEOL JSM 25SIII with energy dispersive analyser EDS - NORAN. PbO concentration was determined as the mean PbO content in a surface layer about 1 - 2 mm in thickness.

Flow rate of gases streaming above the melt was observed by flowmeter with accuracy 0.5% and the gases were saturated with water vapour in a washing frit bottle filled up with distilled water kept at the respective saturation temperature. The flow rate and the water vapour pressure applied are within the range of values found in industry furnaces.

RESULTS AND DISCUSSION

The data on weight losses due to volatilisation in terms of temperature are summarised for the binary glass melt in figures 2 and 3 and for the ternary glass

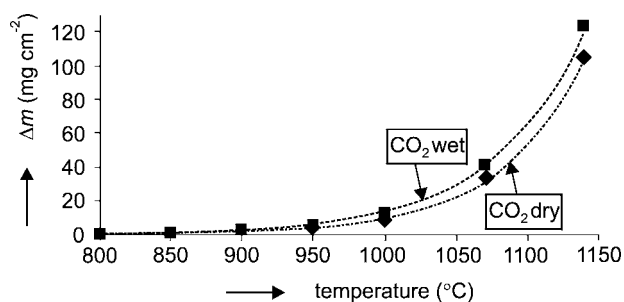


Figure 2. Temperature dependence of weight losses due to vaporisation in dry and wet CO₂ from PbO-SiO₂ binary melt. Time 240 minutes, flow rate 82.8 dm³/h, p_{H₂O} = 31.15 kPa.

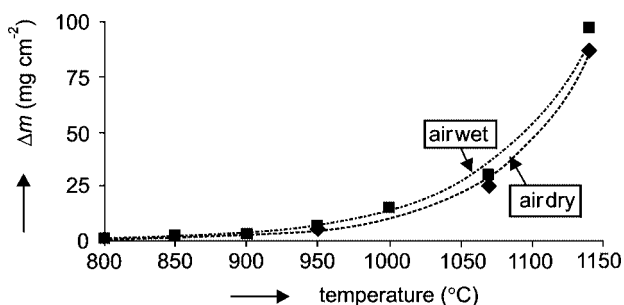


Figure 3. Temperature dependence of weight losses due to vaporisation in dry and wet air from PbO-SiO₂ binary melt. Time 240 minutes, flow rate 82.8 dm³/h, p_{H₂O} = 31.15 kPa.

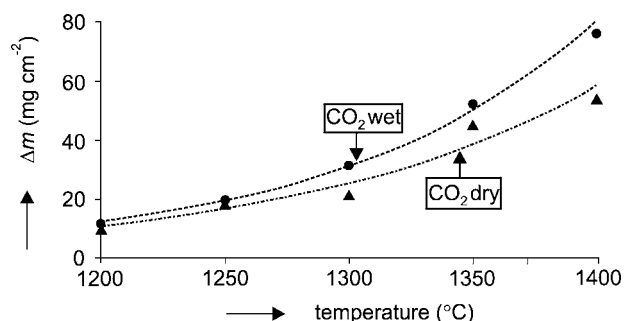


Figure 4. Temperature dependence of weight losses due to vaporisation from K₂O-PbO-SiO₂ ternary melt in dry and wet CO₂.

Time 240 minutes, flow rate 82.8 dm³/h, p_{H₂O} = 31.15 kPa.

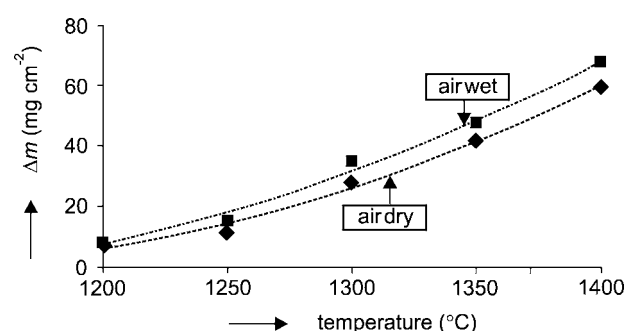


Figure 5. Temperature dependence of weight losses due to vaporisation from K₂O-PbO-SiO₂ ternary melt in dry and wet CO₂. Time 240 minutes, flow rate 82.8 dm³/h, p_{H₂O} = 31.15 kPa.

melt in figures 4 and 5. The losses in weight of the binary melt increased exponentially with increasing temperature. This applied to vaporisation in both dry and moist atmospheres. Volatilisation losses were found to be a little higher in wet gases in comparison with dry gases.

Analogous conclusions can be derived from the temperature dependence of losses in weight due to vaporisation from the ternary melt (figures 4 and 5). The differences between losses due to vaporisation in dry and wet gases are more distinct as with the binary melt, namely in case of wet carbon dioxide. The ternary melt appears to be more sensitive with respect to water vapour, which can be explained by simultaneous evaporation of K₂O and PbO. Water vapour enhances namely evaporation of K₂O by the chemical reaction K₂O (glass) + H₂O(g) → KOH(g) taking place on the melt surface [9]. The reaction product exhibits higher equilibrium pressure than K₂O, which results in more rapid evaporation. Also an acceleration of diffusion of volatile components (PbO, K₂O) in the melt due to interaction of the melt with water vapour can speed up evaporation.

The time dependence of loss in weight due to vaporisation from the binary melt (figure 6) is linear in character, which is indicative of time-independent

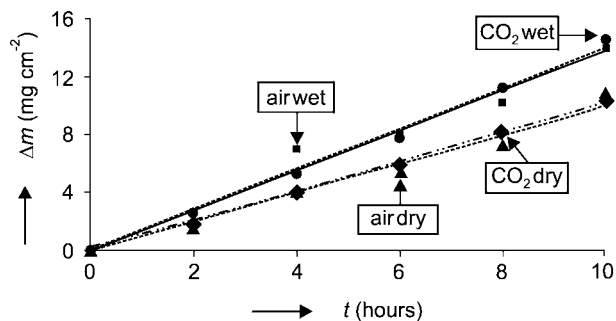


Figure 6. Time dependence of loss in weight due to vaporisation from the PbO-SiO₂ binary melt.

Gas flow rate 82.8 dm³/h, exposure temperature 950°C, in the atmosphere of dry and moist CO₂ and in that of dry and moist air, $p_{\text{H}_2\text{O}} = 31.15$ kPa.

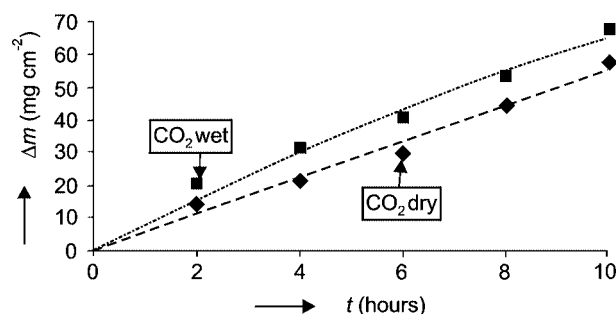


Figure 7. Time dependence of losses in weight during vaporisation from the K₂O-PbO-SiO₂ glass melt. Gas rate of flow 82.8 dm³/h, exposure temperature 1300°C; in dry a moist CO₂ respectively, $p_{\text{H}_2\text{O}} = 31.15$ kPa.

vaporisation rate. These data are in agreement with [10]. The losses in weight for dry gases show very small differences so that the interlaced linear dependencies are almost identical. In moist gases the vaporisation is accelerated, almost identically in carbon dioxide and in air. Again, practically the same straight line can fit the dependencies of volatilisation losses in wet gases.

Figure 7 shows that the time dependence of losses in weight due to vaporisation from the ternary melt in the atmosphere of dry and moist carbon dioxide is almost linear, similarly to vaporisation from the binary melt. A small tendency to parabolic shape was observed in case of wet CO₂. In contrast to this, the time dependence of vaporisation from the ternary melt in dry and moist air apparently has parabolic shape; i.e. in this case the vaporisation rate decreases in terms of time (figure 8).

The comparison of the results in figures 7 and 8 shows almost identical vaporisation in the short times followed (up to 4 hours). Then, a decrease of evaporation in the air atmosphere was indicated and the parabolic shape of the time dependence was observed. The blocking effect of air was observed only in case of ternary melt and could be assigned to diminishing of

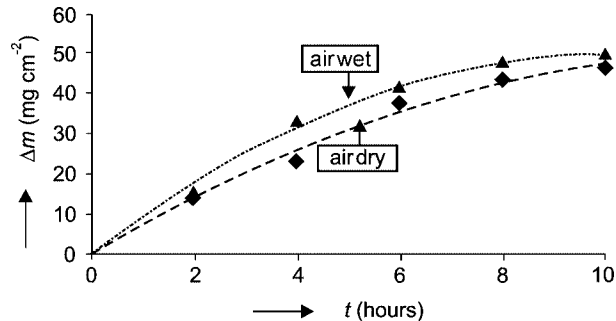


Figure 8. Time dependence of weight loss during vaporisation from the K₂O-PbO-SiO₂ ternary melt.

Gas rate of flow 82.8 dm³/h., exposure temperature 1300°C; in dry and moist air respectively, $p_{\text{H}_2\text{O}} = 31.15$ kPa.

diffusion flux in the melt in presence of oxygen. Oxygen could be responsible for a shift of equilibrium of the dissociation reactions e.g. $\text{PbO} = \text{Pb}^{2+} + \text{O}^{2-}$ in the melt which results in lower concentration of Pb ions capable to move easier than the PbO molecules. Further experiments are necessary to verify this assumption and to obtain a plausible explanation of this phenomenon.

Results presented so far confirm influence of water vapour on evaporation of both melts examined i.e. both the binary and ternary melt. Thus, increased rate of evaporation observed in case of ternary melt in wet atmospheres was caused not only by higher evaporation of potassium oxide, but in a certain extent also by more intensive vaporisation of PbO. From the dependence of PbO vaporisation on water vapour content in furnace atmosphere in case of the binary melt it follows, that also some processes taking part in PbO vaporisation are accelerated by water vapour namely at higher temperatures. It is difficult without additional experiments to identify the processes unambiguously. While influence of water vapour on evaporation of alkali oxides is usually explained by evaporation of alkali hydroxides with higher equilibrium pressure, it is difficult to draw analogous conclusion in case of lead oxide. Lead oxide does not produce with water any stable compound displaying remarkably higher equilibrium pressure compared to PbO. Taking into account a simplified model of evaporation [11], water vapour could accelerate a transport process i.e. diffusion in the melt and/or diffusion in the gaseous phase. It can be expected that water vapour dissolved in binary melt can diminish viscosity of the binary melt and consequently accelerate diffusion process in the melt. Also an acceleration of diffusion in the gaseous phase should be taken in to account as a possible reason for enhancing evaporation in the atmosphere containing water vapour. In ternary melt, water vapour is responsible for rapid depletion of surface layer by K₂O and in such a way for increasing of viscosity with time of evaporation. Consequently, diffusion flux of the volatile components towards melt surface is decreasing with time, which diminishes the rate of the volatilisation

process in case of ternary melt in a longer period of time. This can be applied to evaporation of ternary glass in air, while in case of CO₂ atmosphere only very small depression of rate of volatilisation was observed. Experimental measurement of an influence of CO₂ on viscosity of the ternary melt and on possible change in viscosity of the gaseous phase could help enlighten the difference in volatilisation.

The influence of water on viscosity of binary and ternary melts was confirmed experimentally by viscosity measurements of melts in situ (after melting from raw materials) and after saturating the melts by water (see table 1). The melts were saturated by water vapour by temperatures of 900 °C (binary melt) and of 1300 °C (ternary melt) for the time of 60 minutes.

Table 1. Viscosity of binary and ternary melts in original state and after saturation by water vapour.

	temperature (°C)	log η (dPas)	
		original	saturated
binary melt	900	1.23	1.20
ternary melt	1300	2.92	2.99

The increase of viscosity of the ternary melt saturated by water vapour supports the idea of a slow decrease of diffusion flux in the melt and consequently diminishing of evaporation rate with time. In case of binary melt viscosity is decreasing with time accelerating evaporation in presence of water vapour. This does not exclude acceleration effect of water vapour on diffusion in gaseous phase and consequently on PbO evaporation.

Following tables summarise results of PbO concentration values measured in the surface layer of the sample after volatilisation. Table 2 shows the temperature dependence of PbO surface concentration in the binary melt. The values are decreasing with temperature of evaporation both in dry and wet gases. In agreement with the figures 2 and 3 only very small difference was found between concentrations after volatilisation in dry and water vapour containing gases.

Table 2. PbO concentrations (wt.%) in surface layer of the binary melt in terms of temperature in various atmospheres (gas flow rate 82.8 dm³/h, time of exposure 240 minutes, partial water vapour pressure in moist gases 31.15 kPa).

temperature (°C)	CO ₂	CO _{2wet}	air	air _{wet}
original conc.	79.0	79.0	79.0	79.0
800	79.0	78.0	78.7	77.9
1000	75.6	74.8	74.5	73.5

Table 3 represents the temperature dependence of PbO surface concentration in case of ternary melt evaporation. The decrease of PbO concentration with temperature is very distinct and appears to be much more pronounced than for the binary melts. This is in agreement with the difference in weight loss data in dry and wet gases (see figures 4 and 5).

Table 3. Concentration of PbO (wt.%) in the surface layer of the ternary melt in terms of temperature in various atmospheres (gas flow rate 82.8 dm³/h, time of exposure 240 minutes, partial water vapour pressure in moist gases 31.15 kPa).

temperature (°C)	CO ₂	CO _{2wet}	air	air _{wet}
original conc.	26.0	26.0	26.0	26.0
1200	24.2	24.4	24.8	24.3
1400	13.7	11.9	18.5	16.2

Table 4 demonstrates the time dependence of PbO concentration in the surface layer of the binary melt after volatilisation. The concentration values decrease with time indicating a small effect of diffusion in the melt on the overall rate of evaporation. Similar tendency in PbO concentration in terms of time was found in case of the ternary melt (see table 5). The shift of PbO concentration with time to the lower values is much more pronounced in this case. Surface layer of the ternary melt is more depleted by PbO than the surface layer of the binary melt. This is in agreement with the assumption of the decreasing PbO diffusion flux in the melt with time during the ternary melt vaporisation.

Table 4. Concentration of PbO (wt.%) in surface layer of the binary melt in terms of time in various atmospheres (gas flow rate 82.8 dm³/h, temperature 950°C, partial water vapour pressure in moist gases 31.15 kPa).

t (hours)	CO ₂	CO _{2wet}	air	air _{wet}
0	79.0	79.0	79.0	79.0
4	77.2	76.6	77.8	74.8
10	75.4	74.1	76.6	76.4

Table 5. PbO concentration (wt.%) in surface layer of the ternary melt in terms of time following volatilisation in various atmospheres (gas flow rate 82.8 dm³/h, temperature 1300°C, partial water vapour pressure in moist gases 31.15 kPa).

t (hours)	CO ₂	CO _{2wet}	air	air _{wet}
0	26.0	26.0	26.0	26.0
2	21.9	19.6	21.3	22.6
10	20.5	17.6	19.4	19.1

CONCLUSION

Examination of vaporisation from PbO-SiO₂ and from ternary K₂O - PbO - SiO₂ melts showed that the losses in weight due to volatilisation increase exponentially in terms of temperature in both dry and moist gases (air, CO₂).

The time dependence of losses in weight due to vaporisation from the binary melt at 950 °C is linear in character both for dry and wet gases. Results of vaporisation from the ternary glass melt at 1300 °C showed almost linear time dependence in atmospheres of dry and moist CO₂; if the vaporisation took place in dry or moist air, the time dependence was parabolic in shape.

Determination of PbO concentration in the surface layer of glass melt by means of the electron microprobe gives evidence for a decrease of these values in terms of increasing temperature of vaporisation from both the binary and the ternary melt. The PbO concentration decrease was much more pronounced in case of ternary melt. Water vapour affects the decrease of the original PbO concentration only in a small extent.

Concentration of PbO in the surface layer of the binary melt slightly decreases in terms of time of volatilisation in particular in moist gases. The concentration decrease with time was again more pronounced in case of ternary melt evaporation.

Evaporation from the ternary melt is significantly more accelerated by water vapour than vaporisation of the binary melt.

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VYPAŘOVÁNÍ TAVENIN PbO-SiO₂ A K₂O-PbO-SiO₂

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Vypařování dvou modelových skel, složených z PbO a SiO₂ (binární sklo, molární poměr PbO:SiO₂ = 1:1) a PbO, K₂O a SiO₂ (ternární sklo, 9 mol.% PbO, 15,2 mol.% K₂O, 75,8 mol.% SiO₂) bylo sledováno stanovením celkové změny hmotnosti a změny koncentrace PbO v povrchové vrstvě. Vliv složení plyné atmosféry na vypařování byl sledován tak, že vzduch, nebo oxid uhličitý v suchém stavu, resp. syčené vodní parou proudily nad taveninami. Ztráty těkáním binární a ternární taveniny rostou exponenciálně s teplotou při vypařování v suchých i vlhkých plynech. Časová závislost ztrát vypařováním je lineární s výjimkou ztrát ternární taveniny při vypařování v suchém a vlhkém vzduchu. V tomto případě měla časová závislost parabolický tvar.

Koncentrace PbO v povrchové vrstvě taveniny byla stanovena pomocí elektronové mikrosondy. Hodnota této koncentrace klesá s teplotou a časem vypařování výrazněji při vypařování z ternární taveniny ve vlhké atmosféře. Vodní pára významně akceleruje vypařování ternární taveniny a méně urychluje vypařování z taveniny binární.