ROLE OF WATER VAPOUR
IN VAPORIZATION FROM SILICATE MELTS CONTAINING PbO

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Vaporisation from a multicomponent silicate melt was studied by determining the losses in weight over the temperature range of 1140 -1400 °C in the atmospheres of nitrogen, air and carbon dioxide respectively. The effect of water vapour on vapori-sation from this melt was studied in the gases enriched with water vapour. It was found that the vaporisation losses increase with increasing partial pressure of water vapour and that the differences between vaporisation in the individual atmospheres gradually decrease with increasing partial pressure of water vapour. The vaporisation losses also increased with increasing rate of flow of the gases and particularly with increasing temperature. At the lowest temperature employed (1140 °C) the time dependence of vaporisation losses was approximately linear. However, the vaporisation rate at 1400 °C decreased in terms of time. Water vapour may to a certain extent influence the rates of partial processes taking part in vaporisation.

INTRODUCTION

Vaporisation from silicate melts containing PbO has been dealt with by numerous studies aimed at assessing the effects of the main parameters capable of accelerating or retarding the process [1 - 5]. Also published were simplified physico-chemical models allowing the vaporisation losses to be approximately calculated [6-7]. High-temperature mass spectroscopy was used in determining the composition of gases above the silicate melts and their equilibrium partial pressures [8-9]. Experimental data on vaporisation have so far not allowed a generally acknowledged conception of the controlling process to be established. Some authors consider that vaporisation is controlled by diffusion transport of volatile components in melt [1, 2, 5]. The others think that the process is governed by transport of volatile components in gaseous phase, and still others assume that the part of controlling process is played by chemical reactions taking place at the melt-gas interface and/or in the gaseous phase [11, 12, 15]. In this connection, mention is also made of the role played by water vapour which significantly accelerates vaporisation from melts containing alkali oxides as a result of chemical reactions producing volatile hydroxides with a high vapour pressure [13, 14]. The effect of water vapour on vaporisation from melts containing PbO is assessed in various ways [15 - 17] and thus deserves to be paid attention. Particularly, volatilisation may be affected by increasing content of water vapour in combustion space of glass furnaces due to partial or complete replacing of air with oxygen [18]. The present study is aimed at examining experimentally the effect of water vapour in inert and reactive furnace atmospheres on vaporisation from silicate melts. The experiments were carried out with two types of molten glass, one representing commercial lead glasses while the other was a simple binary system which enabled explicit assessment of the extent to which water vapour may affect vaporisation of PbO.

EXPERIMENTAL PART

Vaporisation from the multicomponent melt (55.30 SiO_2, 26.38 PbO, 1.94 ZnO, 3.05 Na_2O, 11.98 K_2O, 0.30 B_2O_3, 0.017 Fe_2O_3 (wt.%)) and from the binary melt (21.2 SiO_2, 78.8 PbO (wt.%)) was examined by means of the equipment, which was described in detail in [19] and the schematic diagram of which is shown in figure 1. The experimental procedure was also identical with that described in the given study. The experimental equipment allows the losses in weight of the melt to be determined following their high-temperature exposure to flowing pure gases (nitrogen, air, carbon dioxide), or to the gases saturated with water vapour. The experimental temperatures varied over the range of 1140 – 1400 °C for the multicomponent melt, while vaporisation from the two-component one was examined only at 800 ºC. The samples were first melted in a platinum boat 4 × 1 × 1cm in size by ten-minute high-temperature exposure, and then cooled down and weighed. The actual high-temperature exposure always lasted four hours except for the time dependence measurements. Three carrier gas flow rates were used in the course of experimental work (15, 44.3 and 82.8 $dm^3 h^{-1}$). These values correspond to the following gas flow rates at the outlet from the capillary into the furnace space: 0.59, 1.7 and 3.25 m s^{-1}, respectively. The gases were saturated with water vapour in a gas washing frit bottle filled up to one third with distilled water and kept at the respective saturation temperature. The saturation temperatures were over the range of 40

to 95 °C, and the corresponding values of partial water vapour pressure amounted to 7.37 - 84.5 kPa.

RESULTS AND DISCUSSION

The determinations of losses in weight due to vaporisation at identical experimental conditions were repeated 3 to 6 times depending on the dispersion of the values obtained. The vaporisation losses were established by weighing the boat before and after the high-temperature exposure. The standard determination error in terms of weight loss of the sample varied over the range of 0.4 to 6 % where the higher standard error values were obtained for the higher temperatures and at a higher water vapour content in the carrier gases. The experimental results presented here in the form of diagrams and tables are arithmetic means of losses in weight determined under the same conditions. Table 1 presents data on weight losses due to vaporisation from the multicomponent melt at 1140 °C at a flow rate of 3.25 m s^{-1} of dry gases.

The values established do not show any great differences but agree with those published earlier on a certain retarding effect of carbon dioxide and on an indistinct accelerating effect of oxygen on vaporisation losses [12, 13]. This provides evidence for the effect of chemical composition of the gaseous atmosphere on vaporisation from this type of melt, which is probably associated with chemical and physical interactions at the melt-gas interface or in its proximity in the gaseous phase. The diagram, which shows the course of vaporisation in moist gases (figure 2), supports this assumption. In the presence of water vapour, the losses in weight increase with increasing partial pressure of water vapour. However, the differences between the individual gases decrease with increasing partial pressure of H_2O. At a partial water vapour pressure of 84.5 kPa the water vapour naturally prevails in the gas mixtures and differences in the weight losses between various gasses are already minimal.

It is therefore possible to conclude that with increasing partial pressure of water vapour the influence of water vapour gradually prevails independently of the type of carrier gas. Explanation of the role of water vapour can be provided on the basis of several assumptions depending on which of the partial processes taking part in vaporisation takes over the role of the controlling process. If diffusion transports in melt were the controlling process, the effect of water vapour would be associated with its ability to accelerate the process, probably by reducing viscosity of the melt. A similar effect of water vapour in the gaseous phase appears to be less probable because viscosity of gases as a rule somewhat increases with increasing water vapour content. However, acceleration of vaporisation resulting from chemical changes caused by reactions of water vapour with components of the melt cannot be ruled out. In such a case the role of the controlling process would be taken over by a chemical reaction, the principle of which is difficult to define without

Table 1. Losses in weight due to vaporisation from the multicomponent melt in dry gases

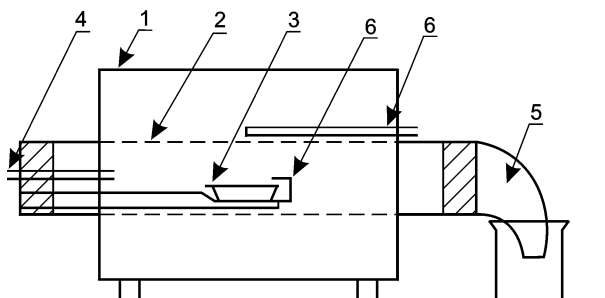| gas	loss in weight (mg cm^{-2})
air	10.8
CO_2	8.0
Nitrogen	9.9

Figure 1. Apparatus for thermal exposure of glass samples (1-heating module, 2-inner sintered alumina tube, 3-sintered alumina boat, 4-gas inlet, 5-gas outlet, 6-thermocouples).

additional experimental data. Such a reaction may result in formation of compounds with a higher partial pressure compared to the original volatile components; i.e. the intensified vaporisation would be associated with its different chemism. Credibility of such assumptions can be assessed to a certain degree when taking into account the additional experimental results, which were restricted to comparing vaporisation in dry and wet atmospheres of CO_2.

Figure 3 shows the dependence of losses in weight on the rates of flow of dry and moist carbon dioxide at various temperatures. The diagram shows that the weight losses due to vaporisation increase with the flow rates of gases. These finding allows to conclude that vaporisation depends on the transport of volatile components in gaseous phase. The dependence on temperature indicates that the rate of the process increases substantially with temperature.

Figures 4 and 5 show plots of temperature dependence of weight losses due to vaporisation in dry and moist CO_2 (partial pressure of water vapour 19.9 kPa) for three different rates of flow. In both atmospheres the vaporisation losses increase roughly exponentially with temperature, which can be interpreted so that he controlling process has the character of an activated one. Also this proves that the accelerating effect of water vapour becomes more distinct with increasing temperature.

The time dependence of the vaporisation loss is important for assessing the kinetics and mechanism of vaporisation. This dependence is shown in figure 6 for two temperatures (1140 and 1400 °C) and for carbon dioxide dry and moist (partial water vapour pressure 19.9 kPa). The rate of gas flow was 3.25 m s^{-1} and the
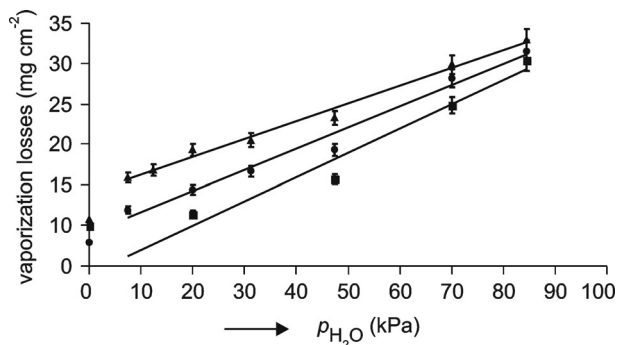
Figure 2. Losses due to vaporisation from multicomponent melt vs. partial pressure of water vapour in various carriers gases at 1140 °C at a gas flow rate of 3.25 m s⁻¹.
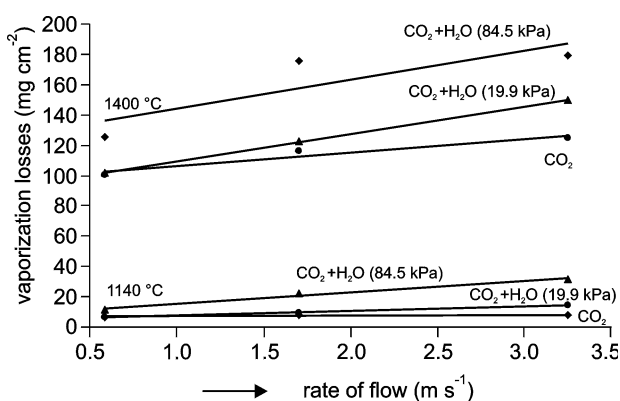

Figure 3. Vaporisation losses vs. rate of flow of dry and moist CO_2 at 1140 °C and 1400 °C respectively (time 4 hours).
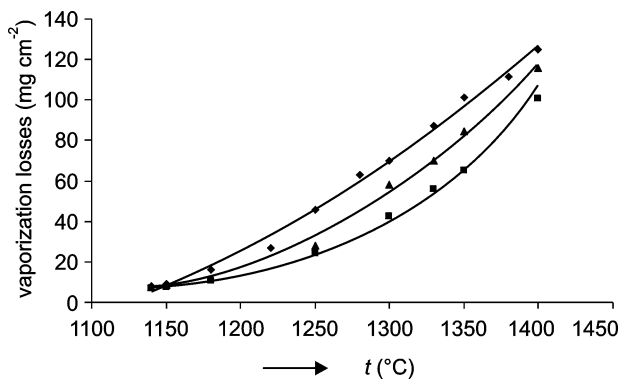

Figure 4. Vaporisation losses vs. temperature in dry CO_2 atmosphere at various flow rates for the time of exposure of 4 hours.
◆ - 3.25 m s⁻¹, ▲ - 1.7 m s⁻¹, ■ - 0.59 m s⁻¹

Figure 5. Vaporisation losses vs. temperature in moist CO_2 atmosphere (pH₂O = 19.9 kPa) at various rates of flow for the time of exposure of 4 hours.
◆ - 3.25 m s⁻¹, ■ - 1.7 m s⁻¹, ▲ - 0.59 m s⁻¹

Figure 6. Vaporisation losses vs. time at 1140 °C and 1400 °C respectively in dry CO_2 and moist CO_2 (p$_{H2O}$ = 19.9 kPa) at the same rate of flow (3.25 m s⁻¹) for the time of exposure of 4 hours.

vaporisation time 4 hours. At 1140 °C the time dependence has linear character which corresponds to a constant vaporisation rate and thus to steady character of the controlling process. The difference in vaporisatio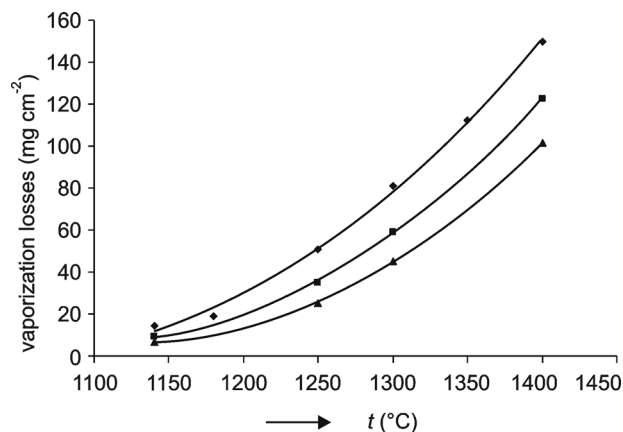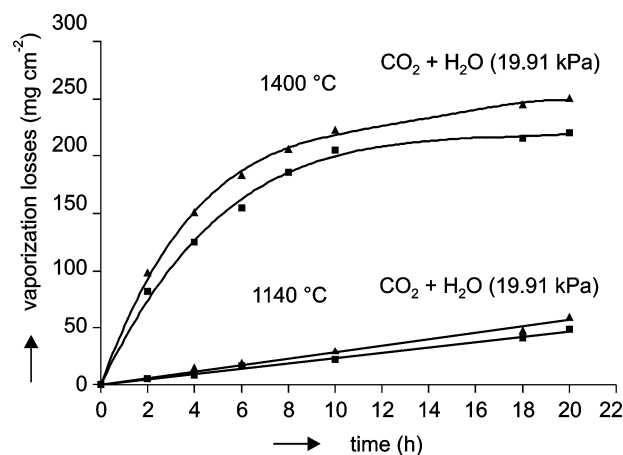n between dry and moist carbon dioxide is very small so that the vaporisation process is probably controlled by steady-state diffusion in gaseous atmosphere, as also indicated by the dependence on the rate of flow of gases. At 1400 °C, the time dependence has parabolic course for both dry and moist CO_2. The difference in vaporisation losses in dry and moist CO_2 is larger at higher temperatures. It may be assumed that at this higher temperature the controlling process is not steady and that its rate gradually decreases in terms of time.

In the case of the multicomponent melt, extensive vaporisation of several volatile components (alkali oxides, boric oxide, zinc oxide, lead oxide) can be expected to take place over the temperature range of 1140 – 1400 °C. On determining the losses in weight due to vaporisation, lead oxide will take a decisive part

Table 2. Losses in weight due to vaporisation from PbO-SiO_2 binary melt

gas	loss in weight (mg cm^2)
CO_2	0.87
$CO_2 + H_2O$	2.25

owing to its weight and high content in the melt. The method employed did not allow the shares of the other oxides to be determined. This fact represents a drawback of the method and may also play a certain part particularly in the interpretation of data on vaporisation in atmospheres with a higher content of water vapour. For this reason the effect of water vapour on vaporisation from the PbO - SiO_2 binary melt was examined, where at the relatively low temperature (800 °C) the total vaporisation loss can be assumed to be caused by vaporisation of PbO alone. Table 2 shows a comparison of vaporisation from this melt in atmospheres of dry and moist CO_2. From this comparison it follows that under identical external conditions (rates of flow of the gases 3.25 m s^{-1}, time 4 h, temperature 800°C) the vaporisation loss in dry CO_2 was substantially lower than in moist CO_2 (p_{H_2O} = 70.1 kPa).

CONCLUSION

The present study of vaporisation from a multicomponent silicate melt containing PbO deals with the effect of water vapour content in air, nitrogen and carbon dioxide respectively, on losses in weight due to vaporisation. It was found that the vaporisation losses increase with increasing partial pressure of water vapour in the gases. The differences in vaporisation losses in the different atmospheres decrease gradually with increasing partial pressure of water vapour. The vaporisation losses likewise increase with increasing rate of flow of the gases. The vaporisation is most extensively accelerated by temperature whose increase leads to an exponential growth of losses in weight. At 1140 °C the vaporisation rate is approximately constant whereas at 1400°C it decreases in terms of time. Acceleration of vaporisation by water vapour was also observed in the case of the binary PbO-SiO_2 melt where the losses in weight resulted solely from vaporisation of PbO alone.

Acknowledgement

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ÚLOHA VODNÍ PÁRY PŘI VYPAŘOVÁNÍ SILIKÁTOVÝCH TAVENIN S OBSAHEM PbO

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Vypařování multikomponentní silikátové taveniny bylo sledováno stanovením hmotnostních úbytků v teplotním rozmezí 1140-1400 °C v atmosféře dusíku, vzduchu a oxidu uhličitého. Účinek vodní páry na vypařování této taveniny byl studován v těchto plynech, obohacených vodní parou. Bylo prokázáno, že ztráty vypařováním rostou se vzrůstajícím parciálním tlakem vodní páry a že rozdíly mezi vypařováním v různých atmosférách se s rostoucím parciálním tlakem vodní páry postupně snižují. Ztráty vypařování rostou dále s rychlostí proudění plynů a zejména s teplotou. Za nejnižší sledované teploty (1140 °C) je závislost ztrát vypařováním na čase přibližně lineární. Rychlost vypařování při teplotě 1400 °C naproti tomu s časem klesá. Vodní pára může v jisté míře ovlivnit rychlost dílčích dějů, které se podílejí na procesu vypařování.