Chemistry of Evaporation from Silicate Melts

Josef Matoušek
Institute of Chemical Technology Prague, Department of Glass and Ceramics, Technická 5,
16628 Prague 6, Czech Republic.

The origin of the dust emissions of glass melting furnaces is associated with number of chemical reactions passing through the melting of the components of the batch and consequently during the formation of the volatile compounds and their interaction with the reactive components of gaseous phase. Chemical reactions also take place during the cooling and condensation of waste gases of the glass melting furnaces. At the stage of glass melt formation the glass raw-materials with higher vapour tension volatile at relatively low temperatures. Alkaline oxides, borates and lead oxide are easy to evaporate from the silicate melts. Alkaline oxides evaporate incongruently with dissociation, while borates evaporate congruently in a monomolecular form or in the form of a dimer. Lead oxide evaporates in the form of simple molecules or in a poly-molecular form. If volatile component reacts with some of the reactive compounds present in gaseous phase, its evaporation can be accelerated. Water vapour significantly accelerates volatilisation of alkali oxides and boron oxide. Reactions with sulphur dioxide, particularly in the presence of water vapour, accelerate volatilisation of alkaline oxides. Carbon monoxide and oxygen modify the chemical equilibrium of dissociative reactions and in this way influence evaporation of alkaline oxides, PbO and others components of silicate melts. Sodium sulphate is the main component of the condensate of the waste gases by the melting of soda lime glasses, while PbO and $PbSO_4$ are the main solid components found in waste gases coming from melting of lead glasses. Alkaline borates are usual products of evaporation of glasses containing boric oxide. The application of the methods and knowledge of the high temperature chemistry can contribute significantly to obtain more detailed information about the nature of chemical changes accompanying evaporation of volatile components from silicate melts.

1. Introduction

Evaporation of volatile components from silicate melts is the main source of dust emissions from glass furnaces. For illustration, in dust emissions from tank furnaces for melting flat glass, more than 95% is sodium sulphate which is generated by condensation of products of sodium oxide vaporisation [1]. Glass furnaces for melting other kinds of glass produce numerous other dust particles, generated by condensation of volatile compounds of boron, potassium, lead, selenium, fluorine, phosphor and other elements. Current knowledge of the vaporisation process includes the effect of main technological factors on vaporisation, and basic ideas on elementary sub-processes which make up this process. According to the so far published theories [2, 3, 4], the process of vaporisation includes transportation sub-processes in the melt and in the gaseous phase, and chemical reactions. The aim of this paper is to summarise basic data on evaporation during the stage when the glass melt is being formed, and on vaporisation of molten silicates in relation to chemical reactions which accompany this process.

2. Types of chemical reactions

1. Formation reactions - reactions in the batch and melt which lead to the formation of volatile compounds.
2. Evaporation reactions - decomposition or polymerising reactions which take place during the transition of the volatile compounds from the melt to gaseous phase.

3. Interface reactions - chemical reactions between some components of liquid and gaseous phases. These chemical reactions form a basis of the so-called reactive evaporation.
4. Gaseous reactions - mutual reactions between the evaporated components and the products of fuel combustion and, possibly, dust particles which come from the glass batch.

3. Evaporation of glass batch components

Some glass batch components have vapour tension so high that they noticeably evaporate already at relatively low temperatures. In volatilisation of pure substances, the rate of evaporation depends on the value of equilibrium pressure of the gases above solid or liquid substances at the given temperature. The following table shows data for some easily volatile compounds, which characterise their behaviour when being heated (melting point T_m, and the temperature at which they start evaporating, defined as a temperature at which equilibrium tension reaches the value 133.32 Pa (1 torr), regardless of the physical state in which they are at that temperature) [5]. In some instances the data were complemented by information about the molecular form in which the compound is predominantly found in a gaseous phase [6].

Table I Equilibrium evaporation of some pure substances

compound	T_m (K)	$T_{133,.32}$ (K)	gaseous phase composition
P_4O_{10} (hexag)	693	462	
As_2O_3	551	475	
Se	494	617	Se_6, Se_2
P_4O_{10} (rhomb)	843	657	
Sb_2O_3	929	850	Sb_4O_6
KOH	673	990	KOH, $(KOH)_2$
NaOH	593	1012	NaOH, $(NaOH)_2$
LiCl	883	1020	
CdO	900	1020	
NaCl	1074	1140	
KF	1130	1190	
PbO	1158	1205	PbO, Pb_2O_2, Pb, O_2
LiF	1121	1310	
NaF	1269	1350	

Majority of these compounds enter into chemical reactions already at lower temperatures, and hence the originally very volatile components are fixed as less volatile compounds. This opportunity is denied to volatile components with high vapour tension, particularly selenium, oxides of phosphor, arsenic and antimony, in which significant losses by evaporation at relatively low temperatures must be assumed (e.g. in case of selenium, the losses might be as high as 90% of the original quantity in the glass batch).
The cause of the increased evaporation of some glass batch components might be the transformation of the originally non-volatile compound into one with a high vapour tension as a consequence of a chemical reaction. An example is a formation of volatile sodium hydroxide by the decomposition of sodium carbonate by water vapour:

$$Na_2CO_3\ (s) + H_2O\ (g) \rightarrow NaOH\ (g) + CO_2\ (g)$$

This reaction can take place in parallel with a reaction between soda and silicate sand already at temperatures around 900°C. Reactive evaporation at the presence of water vapour occurs already at relatively low temperatures also in some other glass batch components (Sb_2O_3). The significance of chemical reactions taking place in the melt for vaporisation is also evidenced by evaporation of melts which contain fluorides. With the presence of fluorides, the following reaction takes place [7]:

$$SiO_2\ (l) + 4\ F^-\ (l) \rightarrow SiF_4\ (g) + 2\ O^{=}\ (l)$$

4. Evaporation from two- and three-component melts

Majority of volatile compounds are a product of reactions which take place between components of the batch already in a solid state, or in the melt. The following table summarises evaporation data of some simple melts, which are not affected by their reactions with gaseous phase components. The selected model systems demonstrate evaporation of main components of common silicate melts.

Table II Equilibrium composition of vapors above model melts

melt	temperature range (K)	composition of gaseous phase
$Na_2O.\ x\ SiO_2$	1163 - 1500	Na, O_2
Na_2O - B_2O_3	1248	$NaBO_2$, $(NaBO_2)_2$
SiO_2 - B_2O_3	1390 - 1590	B_2O_3
Na_2O - CaO - SiO_2	1240 - 1670	Na, O_2
Na_2O - B_2O_3 - SiO_2	1100	Na, $NaBO_2$, $(NaBO_2)_2$
Na_2O-K_2O-CaO-SiO_2	1240 - 1670	Na, K, O_2
PbO - SiO_2	1773	PbO, $(PbO)_2$

The table shows that the main volatile components are alkaline oxides, boron oxide, sodium borate and lead oxide.

In case of **evaporation from a binary sodium-silicate melt**, we can describe the reaction as follows:

$$x\ (Na_2O\ .2SiO_2\ )\ (l) \rightarrow 2\ Na\ (g) + \tfrac{1}{2}\ O_2\ (g) + (Na_2O)_{x-1}\ .\ 2x\ (SiO_2)\ (l)$$

This mechanism was confirmed by a study of evaporation of an $Na_2O.2SiO_2$ melt using a high-temperature mass spectrometer. The study revealed that the only evaporating components in this system were sodium and oxygen [8]. Similar conclusions can be derived from the data on evaporation of sodium-silicate systems with a higher contents of SiO_2 [9]. An analogous mechanism has been confirmed for evaporation of potassium oxide from binary systems K_2O-SiO_2 and from the ternary Na_2O - K_2O - SiO_2 system [9]. Values of alkaline oxides pressures are very low (less than 1 Pa) up to the temperatures of approximately 1300 ^{0}C (see Fig. 1). Hence equilibrium incongruent evaporation of alkaline oxides is for overall losses by evaporation negligible. In practice, vaporisation losses depend on chemical reactions and on some kinetic factors and can reach considerably higher values [10].

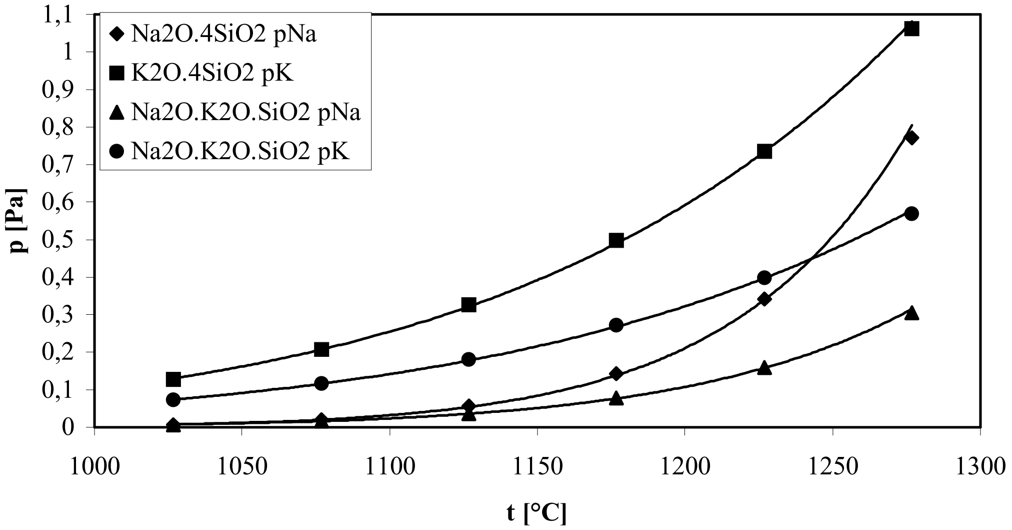

Fig. 1: Equilibrium pressure of sodium and potassium above alkaline silicate melts

Of borate compounds, relatively least volatile in a neutral environment is boron oxide, the equilibrium vapours tension of which, is approximately comparable with alkaline oxides [6] . Considerably higher vapour tension has sodium borate, $NaBO_2$, which evaporates congruently and very fast. The $NaBO_2$ vapour pressure values excess 1 kPa at 1100 ^{0}C and the loss of evaporation reaches about 100 g .m $^{-2}$ .h $^{-1}$ at the same temperature [11] (see Fig. 2). From melts containing sodium borate together with sodium oxide, first evaporates sodium borate in the form of a monomer or a dimer [12]. Evaporation of alkaline boron-silicate melts in an inert environment is probably preceded by reactions which create volatile components:

$Na_2O\ (l) + B_2O_3\ (l) \rightarrow NaBO_2\ (l) \rightarrow NaBO_2\ (g)$ or $(NaBO_2)_2\ (g)$

$Na_2O\ (l) + K_2O\ (l) + 2\ B_2O_3\ (l) \rightarrow 2\ Na\,K\,(BO_2)_2\ (l) \rightarrow 2\ Na\,K\,(BO_2)_2\ (g)$

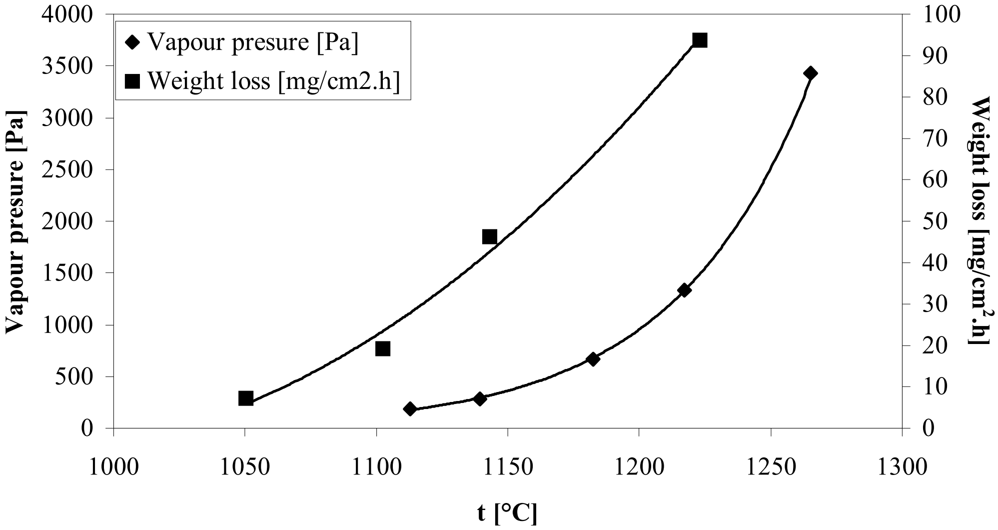

Fig. 2: Equilibrium vapours pressure and mass losses by evaporation of $NaBO_2$ as a function of temperature (adapted from [11])

These reactions take place also in ternary systems Na_2O-B_2O_3-SiO_2 [6]. From melts with lower contents of Na_2O evaporate metaborates (monomer and dimer). Partial pressure of the dimer $(NaBO_2)_2$ is lower and shows an increase with a growing content of boron oxide in the melt (Fig. 3)..

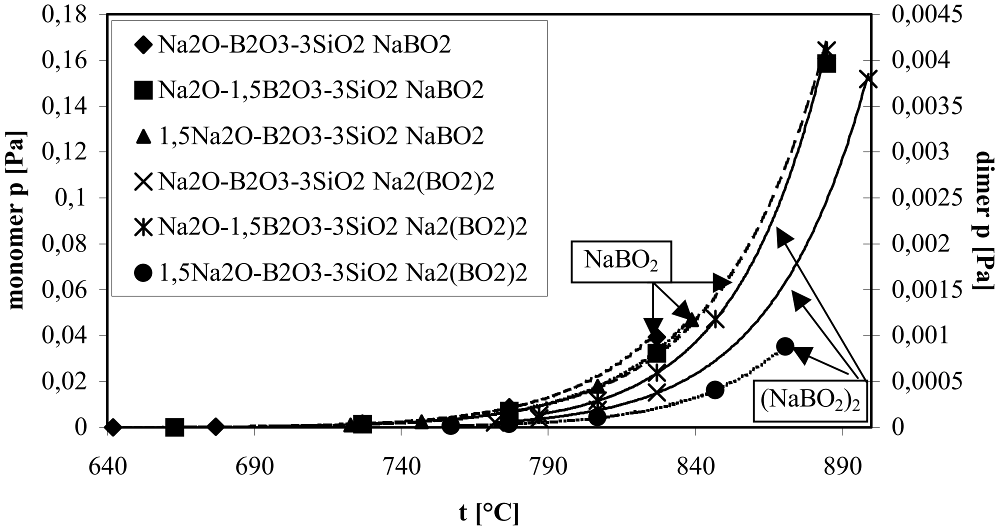

Fig. 3: Equilibrium vapors pressure of $NaBO_2$ and $(NaBO_2)_2$ above melts of the Na_2O-B_2O_3-SiO_2 system as a function of temperature (adapted from [6])

Considerable losses by evaporation occur in melts containing **lead oxide**. This oxide evaporates congruently and its vapours have a tendency to form dimers, trimers and tetramers $(PbO)_n$. The tendency to form polymolecules PbO grows with increasing temperature. Lead oxide evaporates very intensively and its equilibrium pressure is in the order of kPa already at temperatures around 850 - 900°C [12] as it is seen from the Fig.4.

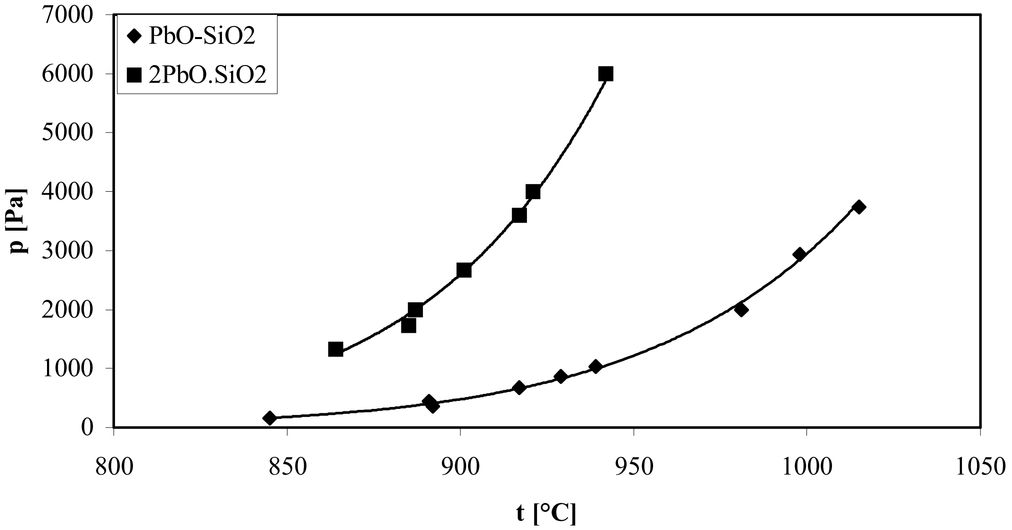

Fig. 4: Equilibrium pressure of PbO above melts $PbO.SiO_2$ and $2PbO.SiO_2$ as a function of temperature (adapted from [12])

5. Reactive evaporation

Water vapour significantly speeds up vaporisation of melts containing alkaline oxides and/or boron oxide. Reactions of pure alkaline oxides with water vapour take place already at temperatures above 500°C, with mainly monomers of corresponding hydroxides being formed, e.g. according to the following equation:

$$Na_2O\ (s) + H_2O\ (g) \rightarrow 2\ NaOH\ (g)$$

With growing temperature, the proportion of dimer in the product vapours grows, while trimer was in small quantities observed only at temperatures above 850°C. The reaction results in the formation of hydroxides, the equilibrium pressure of which reaches the value of 0.1 kPa already at temperatures around 720°C. Reactive evaporation of sodium oxide from binary melt Na_2O-SiO_2 can be expressed by the following equation:

$$x\ [Na_2O.SiO_2]\ (l) + n\ H_2O\ (g) \rightarrow [\ (x-n)\ Na_2O\ .\ x\ SiO_2\ ]\ (l) + 2n\ NaOH\ (g)$$

Data on evaporation of model systems [10] and multicomponent industrial melts [13, 14, 15] show considerable growth of mass losses by vaporisation with growing partial pressure of water vapour in the gaseous phase above melts which contain sodium oxide or sodium oxide together with potassium oxide. Theoretical analysis of these results [14] shows that with the presence of steam, completely dominant becomes an evaporation mechanism associated with the formation of hydroxide, whereas the contribution of a dissociative mechanism (evaporation of Na and O_2) is negligible.

Water vapour also modifies evaporation of melts containing boron oxide. Evaporation of a pure boron oxide melt is accompanied by a formation of metaboric acid HBO_2 and orthoboric acid H_3BO_3. The proportion between these reaction products and hence their contribution to the total pressure above the melt, depends on the partial pressure of the water vapour. With growing water vapour pressure, the contribution of H_3BO_3 to the total pressure P_t increases, as the following relationship applies:

$$P_t = P_{HBO2} + P_{H3BO3} = (K_1 \times P_{H2O})^{1/2} + K_2^{1/2} \times P_{H2O}^{3/2}$$

However, the water vapour does not take place in the evaporation of the $NaBO_2.2SiO_2$ melt, because in this case the main volatile component remains $NaBO_2$ [16]. If the melt contains more sodium oxide than its molar content in $NaBO_2$, evaporation in the form of sodium hydroxide takes place, while the surplus of boron oxide in the melt leads to evaporation in the form of metaboric acid [15, 16, 17, 18].

In melts containing PbO, the effect of water on evaporation is ambiguous. Water vapour reacts with lead oxide forming unstable hydroxide, and hence in melts which apart from PbO contain no other volatile components, its effect on evaporation is rather limited [19]. Multicomponent melts containing more volatile components, especially sodium oxide, show a significant growth in the evaporation rate with a growing partial pressure of water [15, 20].

Water vapour reacts at high temperatures also with other melt components. Even silicon dioxide, regarded as a practically non-volatile component of silicate melts, reacts with water at temperatures above 1200°C yielding gaseous compounds $Si\ (OH)_2$, $SiO\ (OH)_4$ and $Si_2O\ (OH)_4$ [21].

Inert gases, of which most often researched effect was that of nitrogen, can reduce the losses by vaporisation by either partially or completely (according to their respective partial pressures) eliminating reactive evaporation. From the practical point of view, interesting is the effect of carbon dioxide which reduces vaporisation of volatile alkaline oxides, boron oxide and lead oxide [15], [19]. Another oxide affecting evaporation is **sulphur dioxide** which is usually present in the gaseous phase as a result of congruent evaporation, or as a product of the dissociative reaction:

$Na_2SO_4\ (l) \rightarrow Na_2SO_4\ (g)$
$Na_2SO_4\ (l) \rightarrow 2\ Na\ (g) + SO_2\ (g) + O_2\ (g)$

Experimental data [22] show that at low partial pressures of SO_2 (< 500 Pa), dominant is congruent evaporation of sulphate in a molecular form, and the contribution of a dissociative reaction is negligible. When water vapour is present, sodium sulphate decomposes according to the following reaction

$Na_2SO_4\ (l) + H_20\ (g) \rightarrow 2\ NaOH\ (g) + SO_2\ (g) + O_2\ (g)$

Sodium hydroxide evaporates and increases the overall loss by vaporisation. Another reaction which takes place in the melt in parallel with this decomposition reaction is:

$$Na_2SO_4\,(l) + 3\,[\equiv Si - O - Si \equiv]\,(l) + 2\,H_20\,(g) \rightarrow SO_3\,(g) + 4\,[\equiv SiO\text{-}OH]\,(l) + \\ + 2\,[\equiv Si - ONa]\,(l)$$

These reactions affect the concentration of SO_2 in the gaseous phase and thus increase the proportion of reactive evaporation of melts containing sodium oxide. It has been proved by experiments that with an increasing content of sodium sulphate in the melt grow the volatilisation losses of industrial melts [23], particularly when the melt contains NaCl. Sodium chloride is a very volatile compound and can further react with sulphur dioxide in the following reaction:

$NaCl\ (l) + SO_2\ (g) \rightarrow Na_2SO_4\ (l) + HCl\ (g)$

Undesirable consequences of this reaction are obvious, and hence attempts made to reduce the content of NaCl in the glass batch are understandable. Sulphur dioxide is the cause of reactive evaporation also of other silicate melt components, e.g. potassium oxide, lithium oxide and lead oxide.

Redox state of the gas mixture above the melt can also be the cause of reactive evaporation of some components. From reduction gases, the evaporation process can be affected especially by CO. Carbon monoxide shifts the equilibrium of dissociative reaction of sodium oxide and contributes towards an increase of Na concentration in the gaseous phase. And vice versa, in the conditions of oxidation atmosphere, the oxygen present above the melt suppresses the dissociation of Na_2O. A similar effect can be observed in the evaporation of lead oxide.

At high temperatures, carbon monoxide partially reduces silicon dioxide according to the following reaction:

$SiO_2\ (s) + CO\ (g) \rightarrow SiO\ (g) + CO_2\ (g)$

so that in a reduction environment, the otherwise stable silicon dioxide evaporates.

6. Concentration changes in melts by evaporation

Data on changes in concentrations due to vaporisation are not well established and apply rather to vaporisation in laboratory conditions. For lead containing melts, a concentration of PbO was identified in the surface layer after vaporisation under various

conditions [24, 25]. These data show that the decrease in concentration of PbO in a 4 mm thick surface layer is significant and depends mainly on the vaporisation temperature [24].
Also some results of a mathematical simulation of concentration profiles of Na_2O in the melt surface layer were published [4]. These results show that the concentration of sodium oxide in 1 mm thick surface layer of 72 SiO_2 13 Na_2O, 5 MgO, 10 CaO (wt%) melt drops to ¼ of its original value. A similar concentration profile was identified in the $Na_2O.2SiO_2$ melt [25]. Thus is has been confirmed experimentally that in a humid atmosphere the drop in surface concentration of Na_2O is more pronounced.

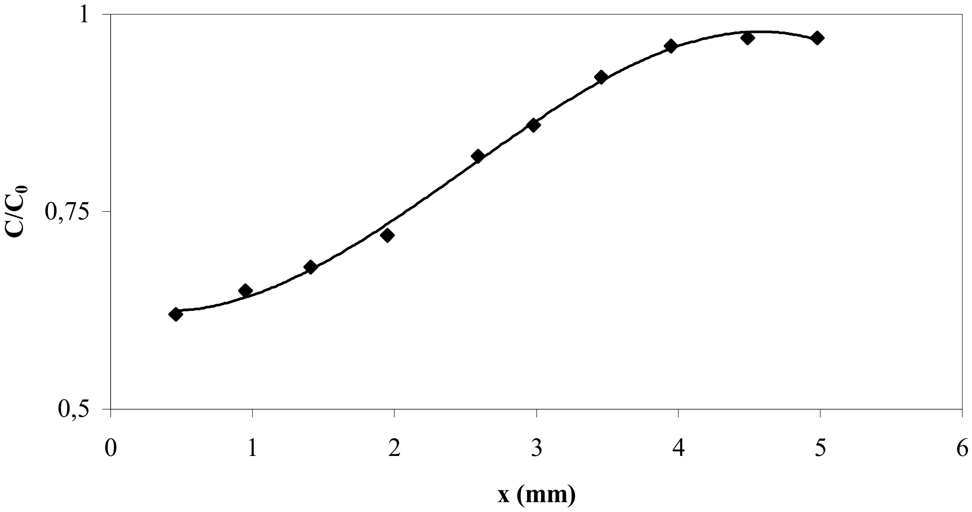

Fig. 5: Concentration of PbO as a function of distance from the surface of the melt

7. Reaction in gaseous phase and condensation of volatile products

In multicomponent gas mixture present in combustion chambers of glass furnaces, a number of chemical reactions take place at high temperatures, which can affect vaporisation by shifting chemical equilibrium of the evaporation reactions in or against the favour of volatile products. We do not have enough information about these reactions, because data on the composition of gaseous phase at high temperatures are very difficult to obtain. From the practical point of view, it is useful to find out at least composition of the condensate after the exhaust gas has cooled off. Several works deal with condensate compositions [4, 26] based on data obtained from experiments. These data agree with information on thermodynamic equilibrium, obtained from computing minimum of the total Gibbs' free system energy. These theoretical computations [27] imply for common sodium-calcium-silicon glass melts the following conclusions:

- sodium starts condensing in the form of Na_2SO_4 at approximately 1120°C and the condensation stops at approximately 900°C. The melt solidifies after being cooled slightly below this temperature (884°C).
- if the gaseous phases contains also potassium compounds (K_2O, KOH), sodium sulphate and potassium sulphate condensate together at temperatures somewhat higher.

- condensation of volatilisation from borosilicate melts can differ, depending on the type and the proportional quantity of volatile components (HBO_2, $NaBO_2$). The condensate then contains a mix of alkaline compounds and borates [26].
- other elements which are commonly found in condensates (Si, Al, Ca, Mg, Fe, Cr, Ba) originate most probably from dust particles which are dissolved in the sodium sulphate melt.

Interesting are also data on reactions undergone by products of vaporisation from lead silicate melts. Lead oxide usually evaporates in the form of PbO molecules, and in this form is also most commonly found in condensates. Due to the presence of carbon dioxide, more complex lead compounds are formed during the process of cooling [28, 29]. With sulphur dioxide present, a certain proportion of PbO condensates in the form of a sulphate [27].

Conclusion

At present we have possess a relatively large amount of knowledge about chemical reactions associated with the process of evaporation of volatile components of silicate melts. To verify these data and obtain further information, it will be necessary to apply more modern methods which allow direct identification of compounds and measuring of their concentrations in melts and in the gaseous phase at high temperatures. Particularly data on concentrations close to the phase interface will be useful for better understanding and more precise description of the volatilisation process.

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