Original Paper

Mechanism of volatilization of fluorides from E-glass melts[1])

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Volatilization of fluorine and boron compounds from E-glass melts containing up to 1.55 wt% fluorine was investigated in a flowing air atmosphere in the temperature range 1250 to 1350 °C employing the transpiration method. The mass loss and the amounts of fluorine and B_2O_3 emitted were determined discontinuously as a function of time. The kinetics of B_2O_3 emission from fluorine-containing as well as fluorine-free E-glass melts can be approximated by the model of a first order process of B_2O_3 with water vapour from the atmosphere at the melt surface. The calculated activation energy of 197 ± 5 kJ/mol for this process is in good agreement with data from literature for fluorine-free E-glass melts.

From the balance of mass loss, fluorine and B_2O_3 losses followed that SiF_4 is the evaporating fluorine compound in dry atmosphere. Measurements in moist atmosphere indicate that the formation of SiF_4 is the dominating mechanism of evaporation in moist atmosphere, too. This result contradicts experience that fluorine emission from the silicate systems studied until now occurs as HF in moist atmosphere. The experimental result is backed up by discussing the conditions under which SiF_4 and HF are formed.

Mechanismus der Emission von Fluoriden aus E-Glasschmelzen

Mit der Transpirationsmethode wurde die Verflüchtigung von Fluor- und Borverbindungen aus E-Glasschmelzen, die einen Massenanteil bis zu 1,55 % Fluor enthielten, im Temperaturbereich 1250 bis 1350 °C in strömender Luftatmosphäre untersucht. Es wurden die Masseverluste der Probe und die emittierten B_2O_3- und Fluormengen diskontinuierlich in Abhängigkeit von der Zeit bestimmt. Die Kinetik der B_2O_3-Emission aus fluorhaltigen und fluorfreien E-Glasschmelzen kann durch das Modell einer Reaktion 1. Ordnung von B_2O_3 mit Wasserdampf an der Oberfläche der Schmelze angenähert werden. In guter Übereinstimmung mit Literaturwerten wurde eine Aktivierungsenergie der B_2O_3-Verflüchtigung von 197 ± 5 kJ/ mol berechnet.

Aus den gemessenen Masse-, Fluor- und B_2O_3-Verlusten wurde geschlußfolgert, daß die flüchtige Fluorverbindung in trockener Atmosphäre SiF_4 ist. Die Messungen in feuchter Atmosphäre lassen darauf schließen, daß auch in Anwesenheit von Wasserdampf die Bildung von SiF_4 der dominierende Verdampfungsmechanismus ist. Dieses Ergebnis steht im Gegensatz zu der Erfahrung, daß die Fluoremission aus den bisher untersuchten Silicatsystemen in feuchter Atmosphäre als HF erfolgt. Anhand der Diskussion der Bedingungen, unter denen SiF_4 bzw. HF gebildet werden, wird das experimentelle Ergebnis untermauert.

1. Introduction

The problem of volatilization of fluorides from glass melts is important because of its effects on refractory corrosion, inhomogeneities in glass composition, the need to add excess fluorides and the pollution of the atmosphere. These problems have been known for a long time. Because of the strict limits of fluorine emission small additions of fluorides and even impurities in the raw materials are of interest [1 to 3] today. E-glass is still produced with fluorspar as an additive [3].

However, the main emphasis of studies on fluorine emission has been on opal glasses, enamels and slag systems, which are all characterized by relatively high fluorine and high alkali or earth alkaline contents. The average wt% composition of E-glass is: 54 SiO_2, 14 Al_2O_3, 22 CaO(+MgO), 10 B_2O_3, 0.5 F and 1 Na_2O+K_2O and is very different from these silicate systems with regard to the amounts of SiO_2 and B_2O_3, especially due to the very low alkali content and the relatively small fluorine content <2 %. The mechanism and kinetics of fluorine emission from this kind of glass has not previously been studied.

Since the amount of fluorine loss and the products volatilized depend decisively on melt composition and fluorine concentration, it is not possible to apply information about mechnism and kinetics of fluorine emission from other melts to the E-glass system. The aim of the present investigation, therefore, was to identify the products of volatilization from a fluorine-containing alkali-free borosilicate melt and to study the effect of temperature, water vapour in the atmosphere and fluorine concentration in the melt on the amount of fluorides volatilized.

To achieve experimental conditions similar to those in the furnace atmosphere, the transpiration method was chosen. This method allows measurements in a flowing atmosphere containing water vapour and collection of the products of volatilization by condensation downstream of the sample and by absorption in a solution.

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[1]) Presented in German under the title "Emissionen von Fluor und Bor aus E-Glasschmelzen" on October 20, 1993 at the Meeting of the Technical Committee VI of DGG in Würzburg (Germany).

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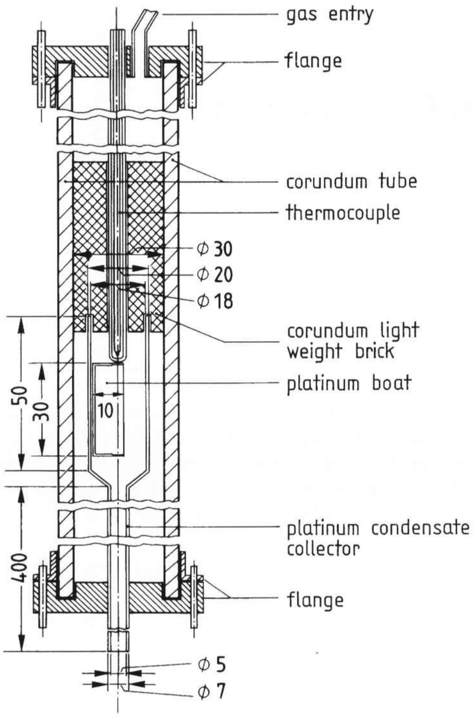


Figure 1. Schematic of the experimental set-up.

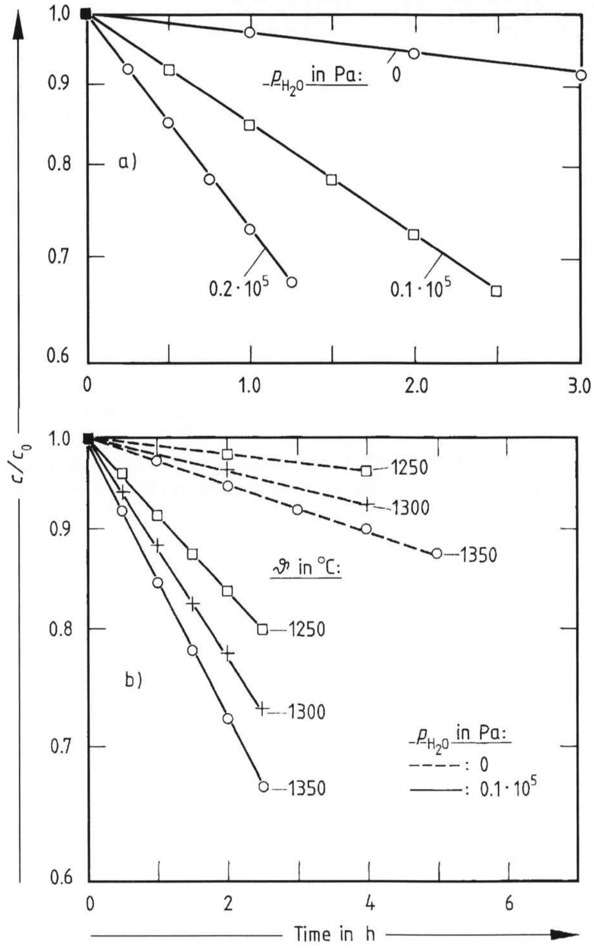
2. Experimental procedure

A schematic diagram of the transpiration apparatus is shown in figure 1.

Dry or moist flowing air was passed over the sample situated in a platinum tube. The flow velocity of the carrier gas (23 to 26 cm/s at reaction temperature) was chosen to be high enough to make evaporation rate independent of velocity.

The E-glass investigated was melted from technical raw materials. First a fluorine-free E-glass with the composition (wt% from analysis) 54.23 SiO_2, 9.63 B_2O_3, 13.39 Al_2O_3, 22.15 CaO, 0.23 MgO, 0.16 Na_2O, 0.18 K_2O, 0.24 Fe_2O_3, 0.12 TiO_2 was obtained by melting in an electric furnace, cooling and crushing. Fluorine-containing glasses were produced by adding defined amounts of fluorspar and remelting 20 min at 1450 °C. Their fluorine and boron contents were determined analytically. 2 g samples of crushed glass in $(30 \times 10 \times 10)\,mm^3$ platinum boats were heated for 15 min at 1200 °C for melting down. The samples were cooled in a desiccator and the starting weight was determined.

80 to 90 % of the volatilized fluorine were collected by passing the gas through absorbers containing 0.1 mol/l NaOH solution. The boron compounds were retained partly in the narrow part of the platinum tube and, in moist atmosphere, partly in the connection to the first absorber as well as in the absorption solution. The proportion of boron compounds retained in the solutions was 70 to 85 %. The loss in weight of the sample and the fluorine and boron contents in the washings from the platinum tube and its connections as well as in the absorption solutions were determined as a function of time. The fluorine analysis was made with a standard method [4] by means of a fluorine-sensitive electrode. Boron contents were analyzed using a difference photometric method [4].



Figures 2a and b. Kinetics of B_2O_3 volatilization from fluorine-free E-glass melts at a) 1350 °C, b) different temperatures.

The measurements were carried out at temperatures from 1250 to 1350 °C. The water vapour pressure was varied from 0 Pa to $0.2 \cdot 10^5$ Pa. The glasses investigated contained 0 to 1.55 wt% fluorine.

3. Compounds volatilizing from an E-glass melt

Boron volatilizes from fluorine-free E-glass melts as B_2O_3 in a dry atmosphere and as HBO_2 in moist atmospheres [5 and 6]. In agreement to [5] the kinetics of B_2O_3 loss can be described as a first order process (figures 2a and b)

$$\ln \frac{c}{c_0} = k \cdot t \qquad (1)$$

with c = B_2O_3 concentration in the melt at time t, c_0 = B_2O_3 concentration in the melt at time t=0, and k = reaction rate constant.

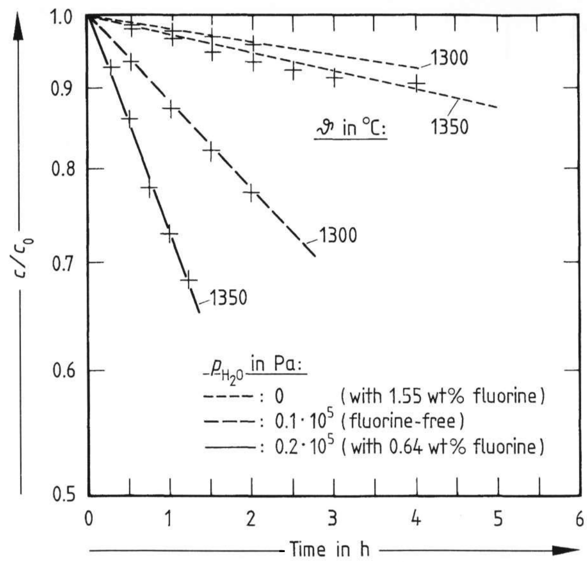


Figure 3. Comparison of kinetics of B_2O_3 volatilization from fluorine-free and fluorine-containing E-glass melts.

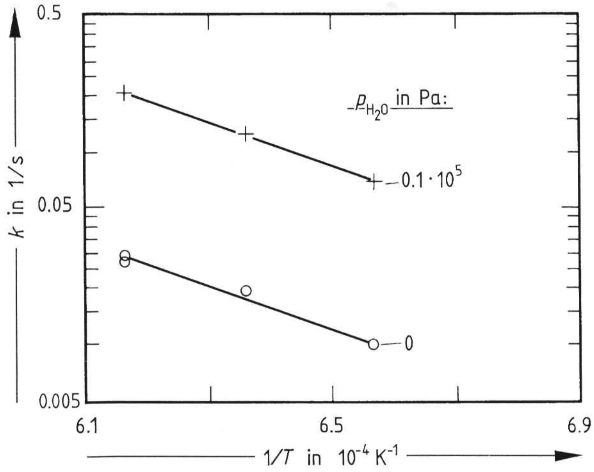


Figure 4. Arrhenius plot of temperature dependence of reaction rate constant for B_2O_3 volatilization.

The presence of fluorine in the melt does not significantly effect this relation as is indicated by the comparison of the plots for fluorine-free E-glass melt and data for fluorine-containing melts in figure 3. As the kinetics of volatilization are not diffferent the mass transfer constants are also equal. Arrhenius plots of the resulting temperature dependence of the constants are shown in figure 4. From the plot an activation energy of 197 ± 6 kJ/mol is obtained which is in agreement with the value of 204 ± 5 kJ/mol determined by Barlow [5].

These results suggest that the mechanism of boron emission is not changed by the presence of fluorine in the E-glass melt. Boron still volatilizes as HBO_2 or B_2O_3 from melts containing fluorine.

The mass balance can then be written as follows

Table 1. Possible fluorine compounds and chemical reactions for fluorine-containing E-glass melts

no.	chemical reaction
1	$1B_2O_3\,(l) + 1H_2O\,(g) \rightleftharpoons 2HBO_2\,(g)$
2	$1CaF_2\,(l) + 1H_2O\,(g) \rightleftharpoons 2HF\,(g) + 1CaO\,(l)$
3	$1CaF_2\,(l) \rightleftharpoons 1CaF_2\,(g)$
4	$1CaF_2\,(l) + 1/2SiO_2\,(l) \rightleftharpoons 1/2SiF_4\,(g) + 1CaO\,(l)$
5	$1CaF_2\,(l) + 1SiO_2\,(l) \rightleftharpoons 1SiOF_2\,(g) + 1CaO\,(l)$
6	$1CaF_2\,(l) + 1/3B_2O_3\,(l) \rightleftharpoons 2/3BF_3\,(g) + 1CaO\,(l)$
7	$1CaF_2\,(l) + 1B_2O_3\,(l) \rightleftharpoons 2BOF\,(g) + 1CaO\,(l)$
8	$1CaF_2\,(l) + 1B_2O_3\,(l) \rightleftharpoons 2/3(BOF)_3\,(g) + 1CaO\,(l)$
9	$1B_2O_3\,(l) \rightleftharpoons 1B_2O_3\,(g)$
10	$1CaF_2\,(l) + 1CaSiO_3\,(l) \rightleftharpoons 1SiOF_2\,(g) + 2CaO\,(l)$
11	$1CaF_2\,(l) + 1/2CaSiO_3\,(l) \rightleftharpoons 1/2SiF_4\,(g) + 3/2CaO\,(l)$
12	$1CaF_2\,(l) + 1/3Al_2O_3\,(l) \rightleftharpoons 2/3AlF_3\,(g) + 1CaO\,(l)$
13	$1CaF_2\,(l) + 1Al_2O_3\,(l) \rightleftharpoons 2AlOF\,(g) + 1CaO\,(l)$

$$\Delta m_{B_2O_3} + \sum x_i \, \Delta m_{F,i} = \Delta m_{total} \qquad (2)$$

where $\Delta m_{B_2O_3}$ is the B_2O_3 loss from the melt, $\Delta m_{F,i}$ is the loss of fluorine as fluorine compound i, x_i is a factor, and Δm_{total} is the mass loss of the sample,

with

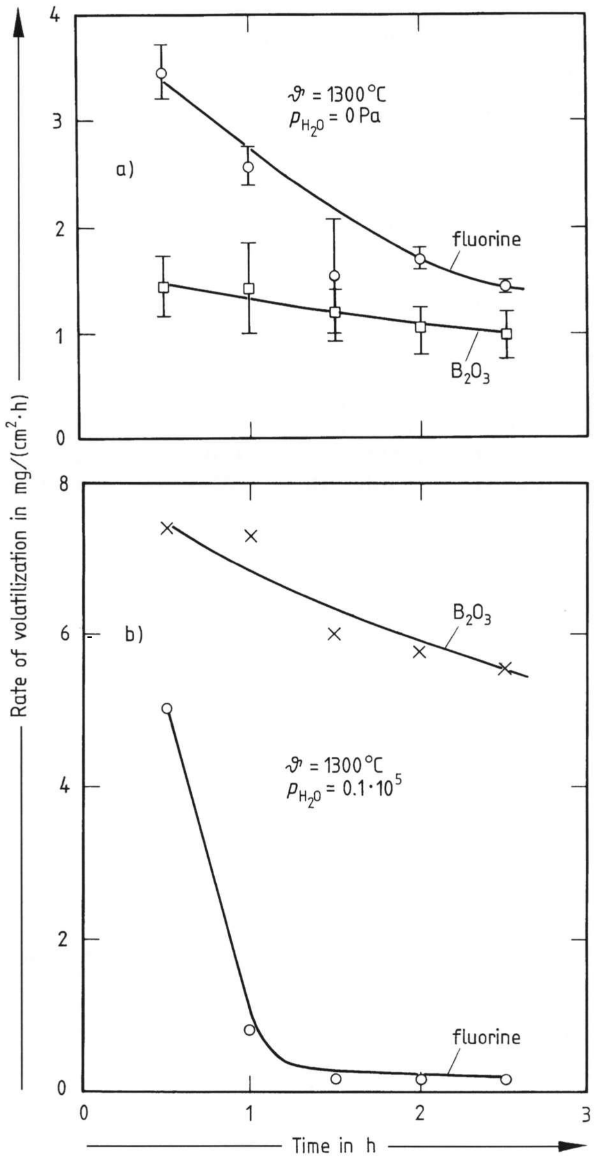
$$x_i = \frac{M_{fluoride}}{M_{fluorine}} \qquad (3)$$

where $M_{fluoride}$ = molecular mass of fluorine compound volatilizing and $M_{fluorine}$ = molecular mass of fluorine.

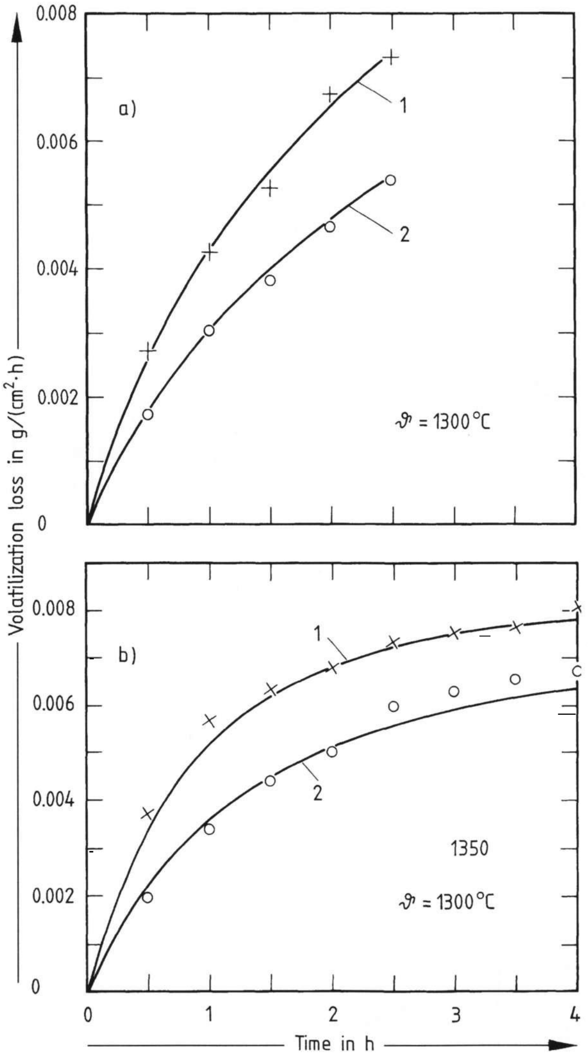
Due to the E-glass composition the fluorine compounds evaporating may be aluminium, calcium, silicon and boron fluorides and oxyfluorides, if the impurities are excluded. Table 1 lists the thermodynamically most stable fluorine compounds which were chosen by calculation of simultaneous reaction balances for a fluorine-containing E-glass melt.

Vapour pressures of gaseous compounds in equilibrium with a melt consisting of SiO_2(l), CaO(l), Al_2O_3(l), B_2O_3(l) and CaF_2(l) were determined by calculation of simultaneous reaction balances [7]. Thermodynamic data of the components in the liquid state were extrapolated to the temperature range 1250 to 1400 °C. The thermodynamically most stable compounds were chosen from the resulting vapour composition. Volatilization of these compounds is described by the equilibrium reactions in table 1. The equilibrium constants and the vapour pressures for all reactions were calculated for temperatures greater than the melting temperatures of all reacting partners [7]. The structure of the melt was taken into consideration by estimating the activities of the components in the melt. Vapour pressures at 1250 to 1400 °C were obtained by extrapolation.

These calculations contain a great error due to extrapolation over a wide temperature range and uncertain thermodynamic data (especially CaO(l)). Furthermore,



Figures 5a and b. B_2O_3 and fluorine loss rates of E-glass with 1.55 wt% fluorine as a function of time; a) in dry atmosphere, b) in moist atmosphere.



Figures 6a and b. Calculated differences of $\Delta m_{\text{total}} - \Delta m_{B_2O_3}$ (curves 1) and the amounts of fluorine Δm_F (curves 2) at p_{H_2O} = 0 Pa as a function of time for E-glass with 1.55 wt% fluorine at a) 1300 °C, b) 1350 °C.

the utility of thermodynamic calculations for the investigation of the mechanism of volatilization is limited because the kinetics of volatilization may have a strong influence on the kind of volatilizing compounds. Thermodynamic calculations are not given being of no interest in the context of this paper.

The mass balances following to equation (2) deduced from the chemical reactions in table 1 confirm that boron evaporates as B_2O_3 or HBO_2 because the evaporation of BF_3 and BOF can be excluded. This assumption is supported by the different kinetics of fluorine and boron evaporation (figures 5a and b), which indicate two practically independent processes.

Assuming that one fluorine compound dominates the process of fluorine volatilization and that boron is lost as B_2O_3, relation (2) can be rearranged to

$$\frac{M_{\text{fluoride}}}{M_{\text{fluorine}}} = \frac{\Delta m_{\text{total}} - \Delta m_{B_2O_3}}{\Delta m_F} . \tag{4}$$

The volatilizing fluorine compound can be derived from the quotient on the right side of equation (4). The difference $\Delta m_{\text{total}} \approx \Delta m_{B_2O_3}$ and the amount of fluorine Δm_F are plotted as a function of time in dry atmosphere in figures 6a and b. The quotient obtained from the plots is approximately 1.4 to 1.5. This value is in good agreement with the value $M_{\text{fluoride}}/M_{\text{fluorine}} = 1.37$ for SiF_4.

The conclusion that SiF_4 must be the major volatilizing fluorine compound is also supported by spot check analyses of the solutions for cations. Significant amounts of silicon and small amounts of calcium were found whereas the analysis for aluminium was negative. The data of analysis of silicon, fluorine, boron and the weight losses for one series of experiments are contained in table 2. The fluorine : silicon proportions are near the theoretical value for SiF_4 which is 2.7.

Table 2. Volatilized fluorine, silicon and B_2O_3 amounts from analyses of absorption solutions at 1300 °C and $p_{H_2O} = 0$ Pa

time in h	fluorine loss in g	silicon loss in g	ratio F: Si in g/g	B_2O_3 loss in g	sum $F+Si+B_2O_3$ losses in g	weight loss in g	difference (sum − weight loss)	
							absolute in g	relative in wt%
0.5	0.00607	0.00213	2.80	0.00232	0.0105	0.0117	0.0012	10.1
1.0	0.00392	0.00152	2.57	0.00088	0.0063	0.0065	0.0002	2.7
1.5	0.00161	0.00123	1.31	0.00078	0.0036	0.0050	0.0014	27.7
2.0	0.00261	0.00104	2.52	0.00136	0.0050	0.0034	0.0016	47.3
2.5	0.00226	0.00093	2.44	0.00129	0.0045	0.0038	0.0007	17.8

Besides the sum of fluorine, silicon and B_2O_3 losses is equal to the measured weight losses of the sample considering the measurement accuracy. The increasing differences in the balances for the longer reaction times can be explained by the greater effect of the absolute error of the boron analyses.

In a moist atmosphere the value of the quotient in equation (4) was approxiamtely 2.0. Silicon was also found in the solutions. If HF was formed by reaction (2) (table 1) the quotient $\Delta m_{total} \approx \Delta m_{B_2O_3}/\Delta m_F$ would be 0.58. A greater contribution of SiO_2 evaporation in moist atmospheres can be excluded as a reason for the results. Consequently, there was no indication that HF is formed as in alkali-containing glass melts under moist atmospheres. A fluorine retention in the solution of 68 % from the total fluorine loss would explain the quotient 2.0, assuming SiF_4 to be the volatilizing compound.

4. Discussion

The preceding conclusions raise questions about the conditions in which SiF_4 and HF are formed.

Hřebíčková and Hřebíček [8] studied the products of volatilization from opal melts in dry and moist flowing nitrogen and in static air as a function of time and temperature also using the transpiration method. From analyses of the sample and weight losses they concluded that NaF, KF and HF are the volatilizing species. However, their analyses for experiments at 1400 °C in moist flowing nitrogen verify a loss of silicon which would explain 22 % of the measured fluorine emissions.

Moreover, their data for fluorine, sodium, potassium, oxygen and weight losses summarized in table 3 do not completely correspond to the following mass and fluorine balances

$$\Delta m_{total} \equiv \Delta m_{NaF} + \Delta m_{KF} + \Delta m_{HF} \tag{5}$$

and

$$\Delta m_{F,total} \equiv \Delta m_{F,NaF} + \Delta m_{F,KF} + \Delta m_{F,HF} \tag{6}$$

where Δm_i is the mass loss of the compund i, and $\Delta m_{F,i}$ is the loss of fluorine by volatilization of compound i.

There exists a significant remainder in the two balances which can be ascribed to an additional fluorine compound. Calculating the quotient

$$\frac{\Delta m_{total} - \Delta m_{fluoride}}{\Delta m_F - \Delta m_{F,fluoride}} \tag{7}$$

with $\Delta m_{fluoride} \equiv$ weight loss calculated from losses by the volatilizing fluorine compounds, and $\Delta m_{F,fluoride} \equiv$ fluorine loss calculated from fluorine losses by the volatilizing fluorine compounds, gives a value between 0.93 and 1.41 equally in dry and moist atmospheres which is reasonably explained by a loss of SiF_4. Parker et al. [9] came to the same conclusion from other data [8] for dry flowing N_2.

Furthermore, the data in table 3 show that at reaction times of 4 h the presence of water vapour in the atmosphere does not influence the amount of fluorine lost. Evidently, the formation of HF in moist atmosphere is linked with a simultaneous decrease of alkali fluoride emission.

The results of Range and Willgallis [10] confirm that HF is only formed under particular conditions. Their measurements in the system $NaF-SiO_2$ (table 4) under equilibrium conditions at 1200 °C led to the following conclusions:

a) SiF_4 is formed in every case even if there is more than 50 mol% NaF.

b) The amount of fluorine lost is not influenced by water vapour in the atmosphere.

c) In moist atmosphere SiF_4, NaF and HF are formed. A simultaneous decrease of NaF loss was observed when HF is formed but the sum of NaF and HF is constant in SiO_2-rich compositions.

d) A considerable increase of the amount of HF in the vapour arises in NaF-rich compositions where the amount of SiF_4 is low. From the fact that all the fluorine is used up before substantial HF formation could take place in SiO_2-rich compositions with low fluorine content it can be deduced that the rate of formation of NaF and SiF_4 is greater than that for HF. Therefore, HF is of little importance in SiO_2-rich compositions where SiF_4 plays the most important role.

e) HF was not formed if the starting mixture consisted of NaF and Na_2SiO_3. Hence, the formation of HF cannot be a direct reaction between NaF in the melt and H_2O in the atmosphere. There must be an intermediate step including the solution of water in the melt which is only possible if a suitable melt structure exists.

Table 3. Volatilization losses from an opal melt [8] and calculated amounts of fluorine compounds (in g/(g cm^2))

	atmosphere at 1400 °C			atmosphere at 1150 °C		
	dry flowing N_2	static air	moist flowing N_2	dry flowing N_2	static air	moist flowing N_2
analyzed loss of:						
Na	15.8	13.2	0.7	5.0	0.6	0.4
K	2.8	1.8	0.0	0.8	0.0	0.0
O	0.0	−1.8	−6.1	0.0	−3.5	−7.0
F	23.1	19.0	21.2	16.7	11.6	16.4
fluorine volatilized as:						
NaF	13.1	10.9	0.6	4.1	0.5	0.3
KF	1.4	0.9	0.0	0.4	0.0	0.0
HF	0.0	4.3	14.5	0.0	8.3	16.6
total fluorine calculated	14.4	16.1	15.1	4.5	8.8	16.9
difference of fluorine analyzed – calculated	8.7	2.9	6.1	12.2	2.8	−0.6
total loss in weight	43.6	32.2	18.3	26.1	8.5	10.5
analyzed loss in weight as:						
NaF	28.9	24.1	1.3	9.1	1.1	0.7
KF	4.2	2.7	0.0	1.2	0.0	0.0
HF	0.0	2.5	8.4	0.0	4.8	9.6
total losses from analysis	33.0	29.3	9.7	10.3	5.9	10.4
difference (weight loss−total calculated)	10.6	2.9	8.6	15.8	2.6	0.1

Table 4. Volatilization losses from NaF–SiO_2 melts at 1200 °C in moist and dry atmosphere as a function of mixture composition [10] (in wt%)

composition		atmosphere: N_2, moist			atmosphere: dry N_2/vacuum	
		volatilization losses			volatilization losses	
NaF	SiO_2	F as SiF_4	F as NaF	F as HF	F as SiF_4	F as NaF
10	90	3.5	0.0	1.0	3.0	1.5
20	80	5.3	1.3	2.4	6.0	3.0
30	70	8.1	3.6	1.9	6.0	7.6
40	60	13.0	5.2	0.0	6.2	11.9
50	50	10.8	9.4	2.1	6.0	16.2
60	40	8.1	10.0	6.9	6.0	21.2
70	30	5.1	10.7	11.6	5.7	26.0
80	20	4.6	12.8	6.0	4.3	31.9
90	10	2.4	15.2	3.0	2.1	38.8

Summarizing the results in [8 and 10] it seems that SiF_4 is formed in dry and moist atmospheres and that HF formation is connected with alkali fluoride emission so that high alkali fluoride losses in a dry atmosphere leads one to expect high HF losses in moist atmospheres. Applying these considerations on E-glass melts, it would not be surprising that HF is not as important because SiF_4 is the dominant volatile fluorine compound in dry atmosphere.

The peculiarity of E-glass melts is that a second compound – B_2O_3 – reacts with the water vapour in the atmosphere at the same time and could influence the fluorine emission. Presumably the surface reaction of B_2O_3 with the water vapour is faster than the formation of HF which demands the immediate step of H_2O dissolution and has a gettering effect for H_2O.

The fluorine emission may also be influenced by the change in melt composition due to loss of B_2O_3.

The formation of SiF_4 is supported by the thermodynamic data in [11]. The compounds in the following equations (8 and 9) are liquid, because the calculations in [11] were done for a slag system with high fluoride content.

From the calculated equilibrium constants for the reactions

$$SiO_2(l) + 2\,CaF_2(l) \rightleftharpoons 2\,CaO(l) + SiF_4(g) \qquad (8)$$

and

$$CaF_2(l) + H_2O(g) \rightleftharpoons CaO(l) + 2\,HF(g) \qquad (9)$$

it follows that the vapour pressure $p_{SiF_4} \equiv 24\cdot 10^5$ Pa, which is substantially greater than $p_{HF} \equiv 2.3\cdot 10^5$ Pa at 1600 °C, at $p_{H_2O} \equiv 10^5$ Pa (for activities: $a_{CaO}/a_{CaF_2} \equiv 2.1\cdot 10^{-4}$ and $a_{SiO_2} \equiv 1.0$).

It is desirable to continue the present investigation by extended experiments for testing the hypothesis discussed which opens a new point of view concerning the mechanism of fluoride volatilization.

More detailed information would be given by investigating an E-glass without impurities, by analysis of vapour composition by mass spectroscopy and by complete analysis of all solutions for silicon.

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