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## VOLATILIZATION OF BORIC OXIDE FROM BOROSILICATE GLASSES

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Volatilization studies of three borosilicate glasses having  $B_2O_3$  (wt.%) 3.14, 5.88 and 8.79% have been carried out in clay grog crucibles at 1400°, 1450° and 1500° for 10, 20, 30 and 40 hr. of heating in a gas fired furnace. The percent loss of boric oxide due to volatilization has been determined by chemical analysis of the melt. It has been observed that loss is directly proportional to temperature, time and concentration of boric oxide in the glass. The loss of  $B_2O_3$  due to volatilization is affected by the formation of scum at the surface of melt which is mainly silica. Results have been drawn as percent loss versus time (t) (hr) and  $\sqrt{t}$  (hr).

**Key words:** Volatilization from glasses, Boric oxide, Borosilicate glasses.

### Introduction

Volatilization from glass melts has long been of interest to glass technologists because such losses change the composition and the properties of glasses [1]. Volatilization losses may lead to serious problems with cords [2] and surface devitrification [3]. Many glasses contain one or more constituents, volatile during melting. The most common volatile constituents are alkalis, boric oxide, lead oxide, halides, sulphur and selenium. Both sodium oxide and boric oxide evaporate rapidly from borosilicate glass surface and cause serious cord difficulties. The loss of these constituents is increased when flames across the surface of the glass and some times the loss is so great that the remaining glass begins to crystallize.

Kruithof *et al.* [2] observed how easily convection can influence the rate of volatilization from borosilicate glasses. Oldfield and Wright [3] published very good results for borosilicate glasses and showed how silica scum was formed because of volatilization of boric oxide. Barlow [4] showed a clear dependence of loss on the rate of gas flow over the sample. Rate of loss varied by about a factor of 5 over the range of gas flow rates that he used. Barlow also showed the loss of  $B_2O_3$  to be proportional to the square root of water-vapour partial pressure. This may be attributed to a reaction of the form



It may be noted that most volatilization studies [5-7] have been made in electric furnaces under very controlled conditions and therefore, are not of much practical use as far as glass melting in gas furnace is concerned. The present studies on volatilization has been carried out in a gas fired furnace where conditions are much closer to melting of borosilicate glasses in a factory. This work is a part of the project being carried out in PCSIR Laboratories Complex, Lahore, on the development

of the laboratory glass-ware of pyrex type. Borosilicate glasses are very important and useful due to their unique properties as compared to soda-lime-silica glasses. Three borosilicate glass compositions containing  $B_2O_3$  3.41, 5.88 and 8.79% were melted and the volatilization studies have been carried out at 1400°, 1450° and 1500° for 10, 20, 30 and 40 hr. of heating in a gas fired furnace.

### Experimental

**Glass preparation.** The chemicals used in the preparation of glass batches were of commercial grade. Silica sand from Daud Khel, District Mianwali showed 0.025%  $Fe_2O_3$  after water washing. Limestone from pampoka - Swat contained 0.007%  $Fe_2O_3$ . Glass batches were mixed thoroughly on a plastic sheet and then in a bottle by moving to-and-fro. The chemical composition of the batches is given in Table 1 under B. Glasses were melted in molachite clay crucibles specially prepared for melting these glasses. The temperature of the gas fired furnace was kept at 1500° during melting for about 6 hr. till the melt was free of seeds completely. The glass melt was poured on to a stainless steel plate, annealed at 550°, crushed, sieved and the fraction between 0.5 and 0.2mm retained to be used in the present work. Glass grains were cleaned with 3N HCl, water and finally with acetone to remove free iron and dirt. The glass grains were analysed and the chemical analysis is given in Table 1 under (A). MgO and excess CaO and  $Al_2O_3$  are mainly from sand and in traces from refractory.

**Chemical analysis.** Chemical analysis was carried out by the methods given by Tooley [8] and Bennet [9] for the analysis of glasses containing boron. Silica was determined by fusing glass with sodium carbonate followed by double dehydration. Methyl alcohol was added during dehydration for the removal of boron.

Alumina [8,9] was determined gravimetrically precipitating the aluminium hydroxide. Iron [8,9] was estimated spectrophotometrically using 1.10-Orthophenanthroline for

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colour development. Magnesium [9] and calcium were determined by EDTA method sodium [8,9] was determined by flame photometer. The estimation of boron was carried out according to the methods given by Tooley [8] and B.S. [10]. As boric oxide is the main subject of this paper, therefore, procedure for its determination is given in detail as appendix.

**Method.** An ordinary gas fired furnace was used in the present studies. It was cylindrical with an I.D. of 1 foot, its height was 3 feet with an opening at the top for placing and removing the glass crucibles and a small hole at the bottom for the burner.

Three clay crucibles containing different glasses were placed side by side in the furnace before firing. Zero time was taken when the temperature reached 1000° and after this the temperature was raised quickly to actual experimental temperature within 1/2 hr. The temperature was controlled by adjusting the gas-air ratio. At the end of the experiment, the crucibles were removed from the furnace to stop further volatilization. After this, each crucible was broken very carefully and whole glass was crushed to determine the percentage loss of  $B_2O_3$  [8,10] due to volatilization. The experiments were carried out at 1400, 1450 and 1500° for 10, 20, 30 and 40 hr. Results are given in Table 2. Results have also been drawn as % loss of  $B_2O_3$  against  $t$ (hr.) and  $\sqrt{t}$ (hr) in Figs. 1-5.

### Results and Discussion

During the investigation, a whitish surface scum was noticed on all the melts. It was observed that the intensity of surface scum was dependent on time, temperature and boron

TABLE 1. CHEMICAL COMPOSITION OF GLASSES BEFORE MELTING AND AFTER MELTING.

Chemical constituents	G-1		G-2		G-3	
	B	A	B	A	B	A
SiO <sub>2</sub>	75.5	75.85	75.5	76.05	75.50	76.25
Al <sub>2</sub> O <sub>3</sub>	2.5	2.53	2.5	2.59	2.50	2.64
B <sub>2</sub> O <sub>3</sub>	4.0	3.41	7.0	5.88	10.0	8.79
Na <sub>2</sub> O	14.0	13.97	11.0	10.95	8.0	7.93
CaO	4.0	4.21	4.0	4.39	4.0	4.28
MgO	—	0.05	—	0.08	—	0.07

B=Before, A=After

TABLE 2. PERCENTAGE LOSSES OF BOROSILICATE GLASSES.

Time (hr.)	B <sub>2</sub> O <sub>3</sub> : 3.41%			B <sub>2</sub> O <sub>3</sub> : 5.88%			B <sub>2</sub> O <sub>3</sub> : 8.79%		
	1400°C	1450°C	1500°C	1400°C	1450°C	1500°C	1400°C	1450°C	1500°C
10	1.9	4.5	7.4	3.75	6.75	9.69	8.82	12.72	17.51
20	3.41	6.35	10.12	6.25	10.25	14.52	12.42	16.81	20.67
30	4.5	7.8	12.05	8.75	13.0	17.75	15.82	19.5	22.8
40	5.1	9.2	13.0	11.5	15.0	19.51	17.41	21.0	24.25

Weight of sample : 300 g, Area of surface : 46.10 cm.

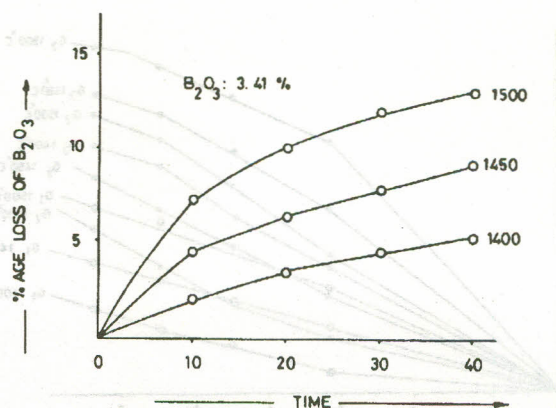


Fig. 1. Percent loss of  $B_2O_3$  as a function of time and temperature for G-1.

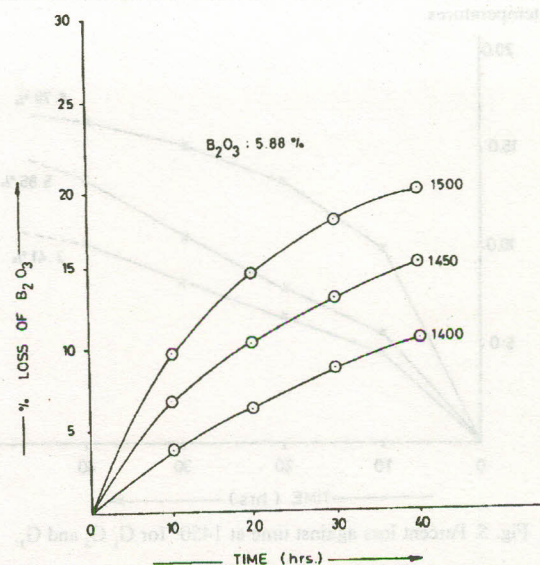


Fig. 2. Percent loss of  $B_2O_3$  as a function of time and temperature for G-2.

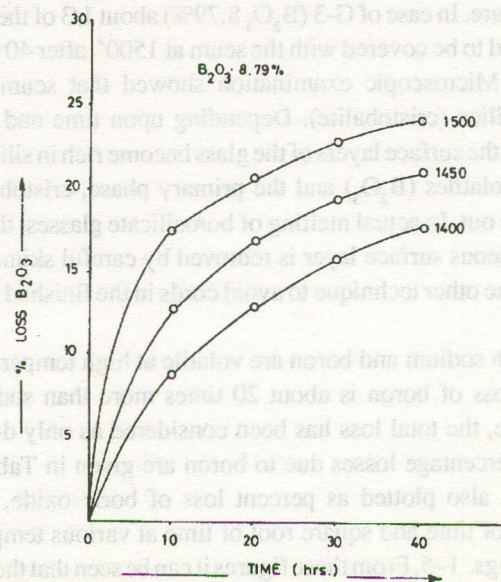


Fig. 3. Percent loss against time (hr.) for G-3.



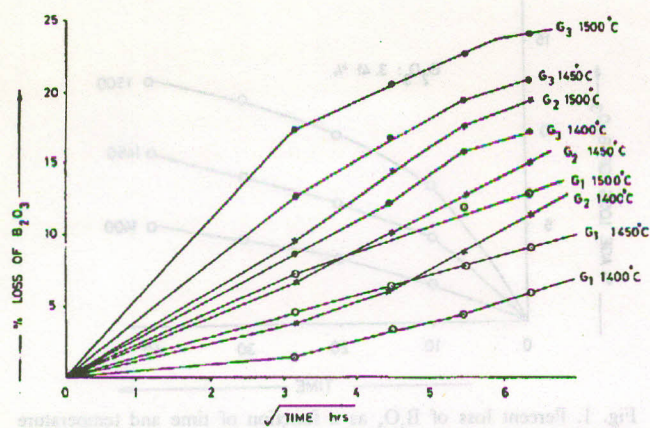


Fig. 4. Percent loss of boric oxide as a function of square root of time at various temperatures.

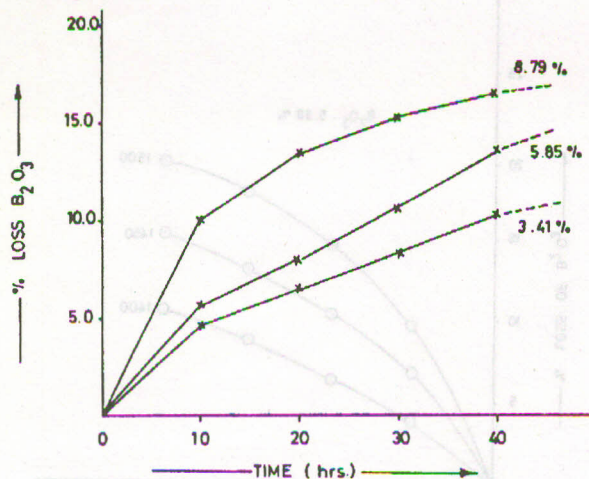


Fig. 5. Percent loss against time at 1450° for  $G_1$ ,  $G_2$  and  $G_3$ .

content of the glass. In  $G-1$  ( $B_2O_3$  3.41%) the scum was almost 0 at 1400° for 10 hr. of heating but it increased with time and temperature. In case of  $G-3$  ( $B_2O_3$  8.79%) about 1/3 of the melt was found to be covered with the scum at 1500° after 40 hr. of heating. Microscopic examination showed that scum was mainly silica (cristobalite). Depending upon time and temperature, the surface layers of the glass become rich in silica by loss of volatiles ( $B_2O_3$ ) and the primary phase, cristobalite, separates out. In actual melting of borosilicate glasses, the inhomogeneous surface layer is removed by careful skimming or by some other technique to avoid cords in the finished glass wares.

Both sodium and boron are volatile at high temperature but the loss of boron is about 20 times more than sodium. Therefore, the total loss has been considered as only due to boron. Percentage losses due to boron are given in Table 2. They are also plotted as percent loss of boric oxide, as a function of time and square root of time at various temperatures in Figs. 1–5. From these figures it can be seen that the loss is markedly temperature dependent in the first 20 to 30 hr. of

exposure to the atmosphere. The loss after 30 hr. has started decreasing. The percentage loss of boron is not the same in every 10 hr. as it is influenced by the highly viscous silica-rich layer covering the glass melt. From Figs. 1–3, it is also apparent that temperature has great influence on the volatilization loss. It is due to the fact that with the increase of temperature, the viscosity of the melt decreases and therefore volatile ions can diffuse more easily towards the surface and hence the loss is increased. From Table 2, it is also apparent that the percent loss of boric oxide is proportional to the percentage of boric oxide in the original glass. However, losses are not as high as they should have been in view of the original percentage of boric oxide in the glasses.

From the above results, it seems that approximately 10–20% extra  $B_2O_3$  would be needed to compensate the losses for melting  $G-3$  glass ( $B_2O_3$  8.79%) at 1500° on industrial scale. Reynolds [11] has reported 10–15% loss of boron in gas furnace. Similarly additional boron is required to melt pyrex glass ( $B_2O_3$  11.5%). Experiments are in progress in these laboratories to develop a glass similar to pyrex where 25% extra boron is added. Results are satisfactory. Further studies will be continued to find out the techniques to minimize the losses of boron as far as possible to get cord free borosilicate glass comparable with pyrex.

As the rate of loss of some constituents from a complex material is often diffusion controlled, the data were tested for their dependence on the square root of time, often a useful criterion to indicate a simple diffusion process. The temperature dependent straight line relationship shown in Fig. 4 for the various temperatures indicates that diffusion control of volatilization may be occurring. However, after some time, the simple diffusion process is counteracted and becomes more complex by the formation of surface scum. It is assumed that the gradually increasing area of scum has a major influence in decreasing the rate of volatilization with time and that preferential evaporation only occurs through the free surface area.

From the above discussion, it may be concluded that the kinetics of volatilization from borosilicate glasses is complex and two volatilization processes may be occurring in parallel, one is through the "free" surface at a faster rate and the second slower, is diffusion through the highly siliceous glass cristobalite surface layer.

Further studies are to be done for longer periods of heating and for higher concentration of boron, to understand the kinetics of volatilization from borosilicate glasses in depth.

### Appendix

#### DETERMINATION OF $B_2O_3$ [8,10]

- (i). Mix 0.2 g of glass sample with 1.2 g of anhydrous  $Na_2CO_3$  in a platinum crucible covered with lid. Fuse



the mixture at a low temperature and for as short as possible until a clear melt is obtained.

- (ii). Remove the crucible from the burner and rotate so that the melt solidifies in a thin layer.
- (iii). Add 10 ml of warm water and warm gently to disintegrate the melt and transfer the solution to a 250 ml Erlenmeyer flask.
- (iv). Rinse the lid with hydrochloric acid and hot water until no adhering materials remains on the lid.
- (v). Fill the crucible with hydrochloric acid and wash contents into the flask.
- (vi). After the melt has been desolved, add a few drops of methyl red indicator and neutralize the excess hydrochloric acid with a strong solution of NaOH to an approximate pH of 5.
- (vii). Boil gently under reflux for 10 min.
- (viii). Rinse the condenser a few times with a minimum amount of water into the flask.
- (ix). Filter solution through a medium paper in a small Butchner funnel, collecting the filtrate in 500 ml flask.
- (x). Wash the residue and paper several times with hot water.
- (xi). Add 1 drop of methyl red and a few drops of 1:3 HCl (to turn the solution just acidic) and warm, under boiling, on a hot plate.
- (xii). Quantitatively transfer this solution to a 400 ml beaker.
- (xiii). Cool the solution to room temperature and insert pH electrodes attached to pH meter.
- (xiv). Using sodium hydroxide solution and hydrochloric acid, adjust the solution to a stable pH of 5.4.
- (xv). Add approximately 10 grams of mannitol to the solution.
- (xvi). Add standard sodium hydroxide from the burette until

a pH of 6.8 is obtained.

- (xvii). Add a few grams more of mannitol and if the pH decreases, add more standard sodium hydroxide to bring pH back to 6.8.
- (xviii). Repeat step 17 once more and record the burette reading.
- (xix). Also make a blank titration by running the borate procedure on the reagents used.

$$\%B_2O_3 = \frac{(\text{ml NaOH} - \text{Blank}) \times B_2O_3 \text{ Equipment}}{\text{Sample wt.}} \times 100$$

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