Commun. Fac. Sci. Univ. Ank. Series B
V. 43. pp. 11-22 (1997)

SOLUBILITY OF LEAD SILICATE GLASSES IN AQUEOUS MEDIA

F.A. KHALIFA and A.A. EL-KHESHEN

Glass Research Laboratory, National Research Centre, Dokki, Cairo, EGYPT

(Received March 19, 1997; Revised July 11, 1997; Accepted July 15, 1997)

ABSTRACT

Chemical durability of some selected lead silicate glasses were investigated using hydrochloric acid and sodium hydroxide as the attacking solutions. Different factors were studied such as the glass composition, concentration of the attacking solution and conditions of the immersion process.

The experimental results obtained expressed in terms of the weight loss may be mainly attributed to the change of the corrosion rate with the change in the strength of the attacking solution.

INTRODUCTION

Inorganic oxide glasses are of commercial importance and the lead silicate glasses are of great particular scientific and technological interest for many years, because of their wide applications as glass soldes, shielding for nuclear radiation and in optical uses.

The resistance of glass to corrosion in different aqueous solutions or the chemical durability as it is often called has been the subject of investigation by several authors.[1,2] They studied the chemical properties of glass with the aim of throwing some light on this problem. It was concluded that[1] the chemical durability of glass in different media depends on many factors, the more important of which are the chemical composition of the glass and nature of attacking medium. It was also stated that[3] the chemical durability of lead glasses was found to depend on the bond strength, field strength and volume of the various cations present in the glass. Also, the rates of corrosion by aqueous solutions have been studied for some lead oxide-silica glasses and it has been concluded that[4] the change in the rate of attack with the glass composition is believed to be due to a change in the role played by lead oxide in the glass structure. For understanding the glass corrosion mechanism, several theories have been put forward.[5,6] In the present work, the corrosion of some selected lead silicate glasses in 0.1 N HCl and in 0.1 N NaOH solutions have been studied with the aim of exploring the different factors which contribute to the rate of corrosion in relation to glass composition and to different aqueous solutions. The extent of corrosion is expressed in terms of the weight loss from glass grains.

EXPERIMENTAL

Preparation of the glass samples

Raw materials used were of chemically pure grade. Lead oxide was introduced in the form of Pb_3O_4, silica was introduced in the form of finely pulverised Dutch-silver sand washed with 1:1 hydrochloric followed by 5% hydrofluoric solution. Each glass was melted in platinum 2% Rh crucible in an electrically heated furnace at 1100°C for four hours. Then the molten mass was poured as slabs which were annealed at the appropriate temperature at about 380°C and cooled to room temperature at a rate of 20°C/hour.

Experimental Procedure of Durability Test

1. Preparation of glass grains for leaching

The glass pieces were crushed in an agate mortar using vertical crushing movements. After crushing, the glass grains were sieved on B. S sieves No. 300 (pore diameter 0.300 mm). The portions of grains passing through sieve No. 600 and retained by sieve No. 300 were kept in a desiccator. This process was repeated by crushing the grains retained, by sieve No. 600. The grains collected from each glass sample were washed three times by absolute ethyl alcohol and then with a few milliliters of pure dry diethyl ether. This process helped to remove any dirt or very fine particles which might stick to the glass grains during the crushing mechanism. The grains of each glass were dried in an air drying oven at about 120°C for 2 h and then stored in a 50 mL weighing bottle inside a dessiccator.

2. Procedure for Leaching Method of Glass Grains

A regulated water bath was used to heat the water, which was continuously stirred by an electric stirrer. The temperature of the bath was controlled to 60° or 90°±0.5°C, as required. Four polyethylene beakers (250 mL) with covers were suspended in the bath through adjusted holes in the water bath lid (Figure 1).

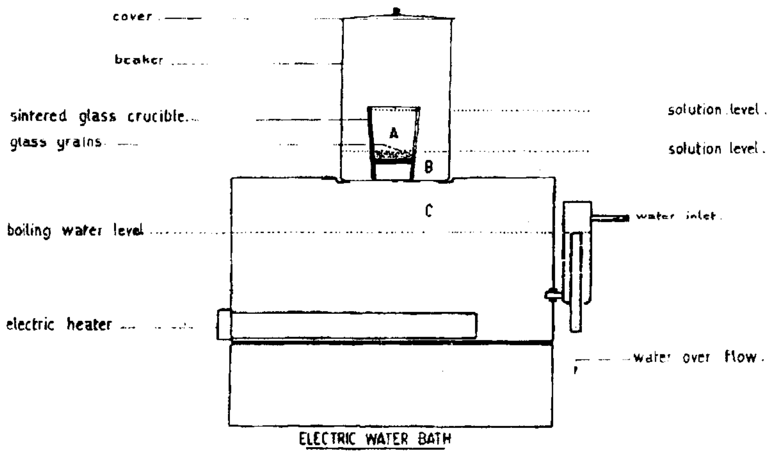

Fig 1. The different parts of the beaker and sintered glass crucible at which temperatures were measured.

1.00 g of the glass grains tested, was accurately weighed in a sintered glass crucible of G4 type which was placed into the polyethylene beaker. 150 ml of the leach solution was introduced to cover the glass grains, and the rest of the solution was placed into the polyethylene beaker.

After the glass grains had been in contact with the attacking solution for the required time, the polyethylene beakers were removed from the water bath. The sintered glass crucible was fitted on a suction pump and the whole solution was pumped through it. The content of the sintered crucible was washed with 10 mL absolute ethyl alcohol, followed by few milliliters of dry ether. The sintered glass crucible was transferred to an air oven at 120°C for 1 h.

Then the sintered glass crucible was reweighed and the total loss was calculated. The volume of the leaching solution was made large enough (150 ml) relative to the weight of the glass grains (1 gm) to avoid the formation of saturated solutions which might prevent further leaching of the glass grains. The reproducibility of the results for representative duplicate samples was ±3%.

RESULTS

The chemical durability of some binary lead silicate glasses, immersed in different aqueous solutions was studied. Different factors were investigated such as the glass composition, type and concentration of the immersion solution, temperature and time of immersion. The weight loss was measured for each glass sample, after the corrosion test was completed. The experimental results obtained can be summarized as follows:

1. Effect of the glass composition

Some lead silicate glasses of the base composition ranging from PbO 70%, SiO_2 30% to PbO 90%, SiO_2 10% (wt. %) were immersed in 0.1 N HCl or in 0.1 N NaOH solutions. The glass samples were kept in the attacking solution at 100°C for 3 hours. The results obtained are given in Table 1 and are shown in Fig. 2 from which it can be seen that the weight loss increases from 0.0309 to 0.0542 g with the gradual increase of the lead oxide content using 0.1 N HCl, while it decreases from 0.0626 to 0.0403 g using 0.1 N NaOH.

Table 1. Chemical compositions and weight loss of a number of lead silicate glasses after immersion in 0.1 N HCl and in 0.1 N NaOH solutions.

Glass No.	Glass Compositions (wt. %)		Weight Loss (g) using	
	PbO	SiO_2	0.1 N HCl	0.1 N NaOH
1	70	30	0.309	0.0626
2	75	25	0.0355	0.0572
3	80	20	0.0408	0.0526
4	85	15	0.0473	0.0475
5	90	10	0.0542	0.0403

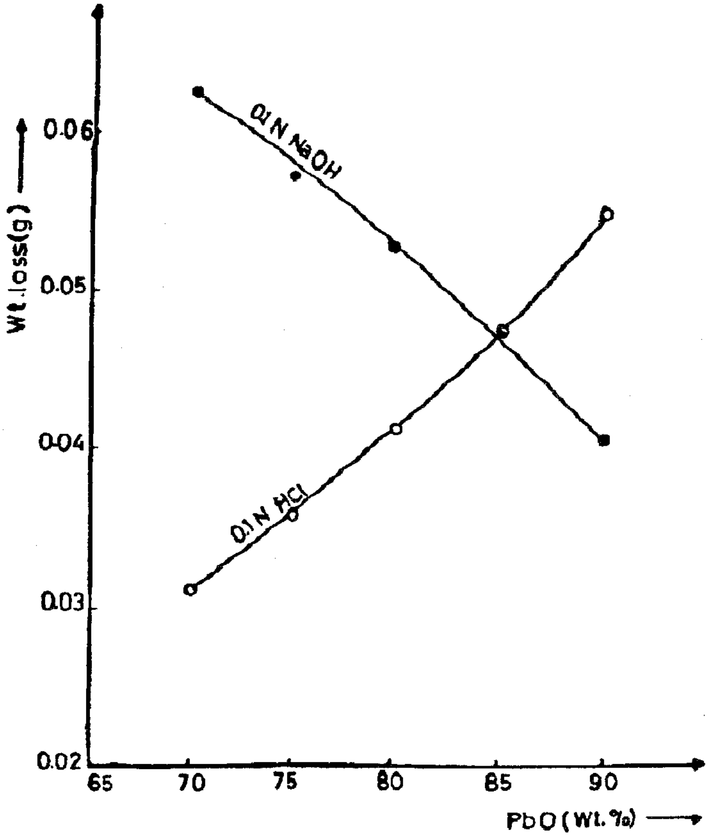

Fig 2. Solubility of lead silicate glasses in the attacking solution versus the lead oxide content.

2. Effect of the concentration of the immersion solution

A lead silicate glass of the base composition PbO 80%, SiO_2 20% (wt. %) was immersed in HCl or NaOH solutions of different concentrations ranging from 0.1 to 2N. The temperature of immersion was 100°C for three hours. The results obtained are given in Table 2 and are shown in Fig. 3, from which it can be seen that the weight loss increases the concentrations of HCl and of NaOH solutions from 0.1 to 2 N, respectively.

Table 2. Weight loss of lead silicate glass of the base composition PbO 80%, SiO_2 20% (wt. %) after immersion in HCl and NaOH solutions of different normalities at 100°C for three hours.

Glass No.	Glass Compositions (wt. %)		Normality of the immersion solution	Weight Loss (g) using	
	PbO	SiO_2	(N)	HCl	NaOH
3	80	20	0.1	0.0408	0.0526
3	80	20	0.5	0.0437	0.0624
3	80	20	1.0	0.0511	0.0669
3	80	20	2.0	0.0612	0.0717

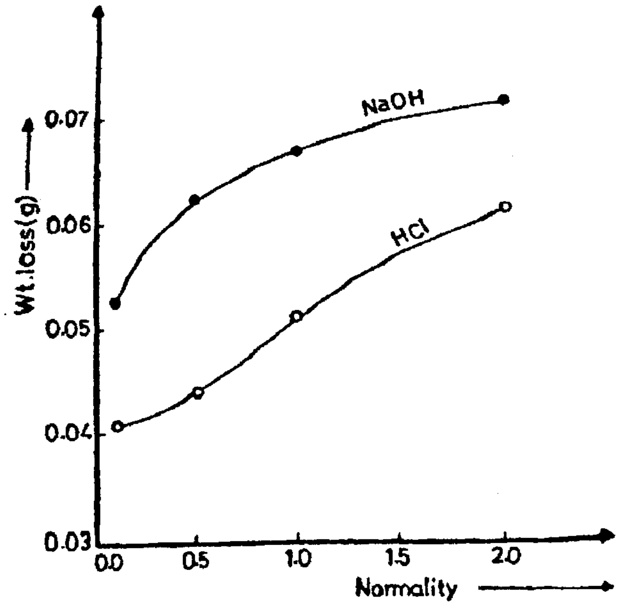

Fig 3. Solubility of a lead silicate glass of the base composition PbO 80%, SiO_2 20% in different concentrations of the attacking solution used at 100°C for three hours.

3. Effect of the temperature and duration of immersion

The lead silicate glass of the base composition PbO 80%, SiO_2 20% (wt. %) was immersed in 0.1 N HCl and in 0.1 N NaOH solutions under the following conditions:

i- For three hours at different temperatures ranging from 20° to 100°C.

ii- At 100°C for different periods of times ranging from 60 to 540 minutes.

The results oftained are given in Tables 3 & 4 and are shown in Figs. 4, 5. They can be summarized as follows:

a- The weight loss of the glass sample increases from 0.0125 to 0.0408 g and from 0.0355 to 0.0526 g with gradual increase of the immersion temperature from room temperature 20 to 100°C for three hours using 0.1 N HCl or 0.1 N NaOH as attacking solutions, respectively.

b- The weight loss, of the glass sample, increases form 0.0277 to 0.0659 g and from 0.0408 to 0.0689 g with gradual increase of the immersion duration from 60 to 540 minutes at 100°C using 0.1 N HCl or 0.1 N NaOH as attacking solution, respectively.

Table 3. Weight loss of lead silicate glass of the base composition PbO 80%, SiO_2 20% (wt. %) after immersion in 0.1 N HCl and in 0.1 N NaOH solutions at different temperatures for three hours.

Glass No.	Glass Compositions (wt. %)		T°C of the experiment	Weight Loss (g) by attacking solution	
	PbO	SiO_2		0.1 N HCl	0.1 N NaOH
3	80	20	20	0.0125	0.0335
3	80	20	30	0.0184	0.0388
3	80	20	40	0.0220	0.0442
3	80	20	75	0.0241	0.0496
3	80	20	85	0.0326	0.0513
3	80	20	100	0.0408	0.0526

Table 4. Weight loss of lead silicate glass of the base composition PbO 80%, SiO_2 20% (wt. %) after immersion in 0.1 N HCl and in 0.1 N NaOH solutions of different duration at 100°C.

Glass No.	Glass Compositions (wt. %)		Immersion time	Weight Loss (g) using	
	PbO	SiO_2	t (min.)	0.1 N HCl	0.1 N NaOH
3	80	20	60	0.0277	0.0408
3	80	20	180	0.0378	0.0526
3	80	20	300	0.0447	0.0603
3	80	20	420	0.0530	0.0652
3	80	20	540	0.0659	0.0689

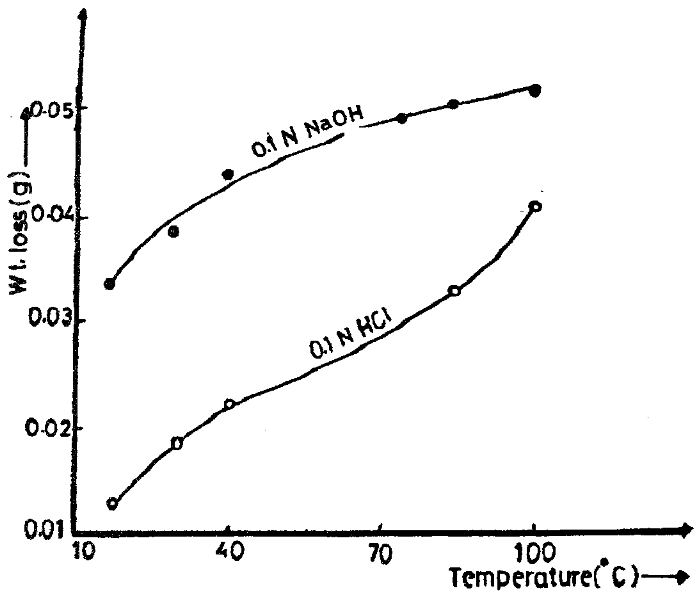

Fig 4. Solubility of a lead silicate glass of the base composition PbO 80%, SiO_2 20% after immersion in the attacking solution versus the immersion temperature (°C) for three hours.

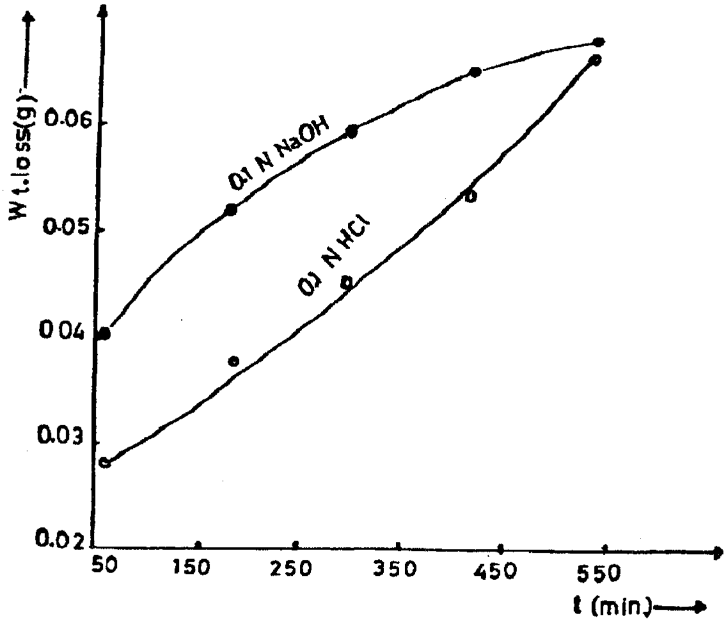

Fig 5. Solubility of a lead silicate glass of the base composition PbO 80%, SiO_2 20% after immersion in the attacking solution versus the immersion time (min.) at 100°C.

DISCUSSION

The term chemical durability of the glass has been used conventionally to express its resistance towards the attack by water, acids, alkalis, salt solutions and gases including water vapour and carbon dioxide in the atmosphere. The chemical durability of different types of glasses depends on several factors such as the composition of the glass, nature of attacking agents, temperature of the attacking solution and duration for which it is kept in contact with it.[8] Several theories have been introduced for better understanding of the glass corrosion mechanism.[5,6] In fact, any particular reaction usually involves two chemical mechanisms, "Leaching" which is an ion exchange process characteristic of acid attack and "etching" which is a first order reaction characteristic of alkaline attack, one or the other predominating. The stability diagram of the lead oxide in different aqueous solutions indicates that,[8] in acidic medium lead dissolves as Pb^{2+} (aq.) and PbO^{+} (aq.) while in alkaline medium lead forms $HPbO_2$ (aq.).

According to the above mentioned considerations, the results obtained can be explained in the following manner.

1. Effect of the glass composition

When a glass of the base composition PbO 80%, SiO_2 20% (wt. %) is immersed in 0.1 N HCl, a diffusion controlled ion exchange process is expected. The procedure of this reaction involves the exchange of the easily detachable lead in (Pb^{2+}) from the glass by the hydronium ion from acid solution. This process can be represented as follows:[5]

$$Pb^{2+} + 2\ HCl \rightarrow PbCl_2\ (aq.) + 2H^{+} \qquad (1)$$

In this case the back bone silicate network remains unreacted.

On the other hand when the glass of the same base composition is immersed in 0.1 N NaOH, the reaction is different and the alkaline solution attacks the silicate network and this can be represented as follows:

$$NaOH + (SiO_2) \rightarrow Na_2SiO_3 + H_2O \qquad (2)$$

Thus, from the above two reactions it can be concluded that the increase in the weight loss for the glasses, studied, Table 1 and Fig. 1, using HCl as the immersion solution may be due to the increase in the corrosion rate, while the decrease in the weight loss, Table 1 and Fig. 1 using NaOH as the immersion solution may be attributed to the decrease in the corrosion rate.[1] These conclusions can be understood by taking into consideration that, in the lead silicate glasses containing low proportions of lead oxide, the lead ions will be enclosed within the interstices formed by SiO_4 tetrahedra as Pb^{2+} ions. With higher proportions of lead oxide, a considerable proportion of lead ions can act as double bridges between adjacent SiO_4 tetrahedra or can form PbO_4 building units.

The difference between the effect of HCl and NaOH can be explained as follows. Hydrochloric acid solution attacks lead glasses through preferential leaching of Pb^{2+} ions from glass (ion exchange process) as shown in reaction (1). As this particular glass type is believed to be of very loose structure containing isolated SiO_4 basic building unit, the ionic exchange process is considered to proceed progressively without interference. In the case of alkaline sodium hydroxide solution, the attack goes on as a complete leaching process of all the glass constituents (as shown in reaction 2). However, as the process proceeds, different species including gelatinous silica are expected to be formed which might retard or alter the whole leaching process or reaction rate.

2. Effect of the concentration of the attacking solution

The increase in the weight loss, for the lead silicate glasses of the base composition PbO 80%, SiO_2 20% (wt. %), with the gradual increase of HCl or NaOH concentrations from 0.1 to 2 N, Table 2 and Fig. 2 may be due to the pH value of the attacking solution, since in general, the rate of attack on the glass is quite dependent on the pH value range.(7,8)

It is generally accepted that both ion-exchange and surface dissolution reactions are driven by the attack of H^+ (or H_3O^+). Reaction rates are thus expected to be strongly pH-dependent. Most glasses are observed to dissolve faster in both acid and base solutions than in neutral solutions. The release of alkali and other mobile ions and their replacement by H^+ require an increase in OH^- to maintain charge balance and thus pH tends to rise during a dissolution experiment. If the pH exceeds values between 9 and 10, there will be an increase in dissolution rate due to self-generated alkalinity.

3. Effect of the temperature and duration of immersion

The increase in the weight loss, with the gradual increase in the temperature or duration of immersion may be explained as follows:

i- The increase in the weight loss with the gradual increase of the immersion temperature as shown in Table 3 and Fig. 3 may be attributed to the fact that the extracted amount of easily leachable Pb^{2+} ion from a glass in a given period of time increases with increasing the temperature.(8)

ii- The increase in the weight loss with the gradual increase of the immersion time as shown in Table 4 and Fig. 4 may be due to the fact that the glass constituents have enough time to be released into the immersion solution.(6)

REFERENCES

[1] NEWTON, R.G., *Glass Technol.*, **26**, 21 (1985).

[2] KEDR, A., and ELBATAL, H.A., *J. Amer. Ceram. Soc.*, **79**, 733 (1996).

[3] ABOU EL AZM, A., and HUSSEIN, A.L., *J. Chem. Egypt.*, **5**, 1 (1962).

[4] EL SHAMY, T.M., and TAKI EL DIN, H.P., *Glass Technol.,* **2** (1974).

[5] DOREMUS, R.H., NON-CRYST, *J., Solids*, **19**, 137 (1975).

[6] ERNASBERGER, F.M., 14th Intern. Congress in Glass, Calcutta, India, p. 3119 (1986).

[7] EL HADI, Z.A., GAMMAL, M., EZZ EL DIN, F.M., and MOUSTAFFA, F.A., *Cent. Glass & Ceram. Res. Inst. Bull.*, **32**, 15 (1985).

[8] PAUL, A., *Chemistry of Glasses*, Chapman and Hall, Ltd; London. UK 1982 (1982).

[9] WHITE, W.B., in "*Advances in Ceramics*" Vol. 20, Nuclear waste managements II, the American Ceramic Society; P. 431-442 (1986).