Factors Affecting the Hydration of Silicate Glass

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The glasses in the systems Na_2O–SiO_2, Na_2O–MO–SiO_2, Na_2O–K_2O–SiO_2 and Na_2O–MgO–M_2O_3–SiO_2, where M is divalent or trivalent element, were hydrated in an autoclave at the temperatures ranging from 100° to 200°C for 3 to 72 hrs. The hydrated glass layer increased nearly linearly with time under a fixed condition of temperature and pressure. The factors affecting the penetration rate of water were investigated and discussed.

The penetration rate was larger in the glass containing more amount of Na_2O in the Na_2O–SiO_2 system and it was decreased by the substitution of MO for Na_2O or M_2O_3 for MgO, irrespective of the kind of M. The apparent activation energy for water penetration was very close to that for Na^+ ion diffusion. The dependence of penetration rate on water vapor pressure suggests that almost all water penetrates into the glass as water molecule.

KEY WORDS: Hydration of Glass/ Silicate Glasses/ Factor Affecting Hydration/

I. INTRODUCTION

Hydrated glasses which contain much amount of water exhibit plasticity at relatively low temperature and have forming potentiality on heating. Thus they can be used for producing polishing-free optical lenses,[1] hollow glass microspheres,[2] hydraulic cements[3] and spontaneously degradable containers.[4]

When the silicate glass is placed in the steam atmosphere, water penetrates into the glass to form hydrated glass. The penetration rate of water depends upon the composition of glass, the steam temperature and pressure and so on. In this paper the effects of such factors on the penetration rate of water are shown and discussed. The hydration mechanism is also briefly argued.

II. EXPERIMENTAL

The glasses in the systems Na_2O–SiO_2, Na_2O–MO–SiO_2, Na_2O–K_2O–MgO–SiO_2 and Na_2O–MgO–M_2O_3–SiO_2, where M is divalent or trivalent element, were melted in platinum crucibles in an electric furnace. Glass rods of about 3 mm in diameter were drawn from the melts. The rods of about 5 cm in length were placed in an autoclave of the volume of about 500 ml with 10 ml (or 25 ml) of water and heated at the temperatures ranging from 100° to 200°C for 3 to 72 hrs. In Fig. 1 are shown an illustration of the inside of autoclave and the relations between pressures ($P_{(eq)}$ and $P_{(air)}$) and temperature under the usual condition, where $P_{(eq)}$ is the

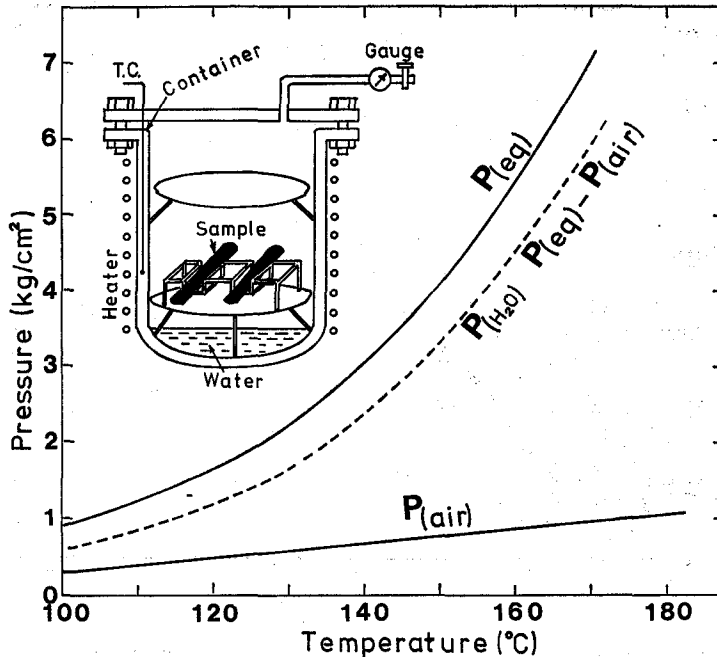* 守屋喜郎: *Government Industrial Research Institute, Osaka, Midorigaoka 1–8–31, Ikeda, Osaka.*

Fig. 1.   Illustration of the inside of autoclave and the relations between pressures
$(P_{(eq)}$ and $P_{(air)})$ and temperature.

equilibrium pressure at a fixed temperature and $P_{(air)}$ is the pressure measured under the condition without water.   The usual condition here means one that $P_{(air)}$ before heating was one atmospheric pressure or 0 Kg/cm^2 in gauge pressure.   Under the usual condition the total pressure, $P_{(total)}$, equals to $P_{(eq)}$.

During heating water penetrates uniformly into the glass to form hydrated swollen glass, keeping the sharp boundary between the hydrated and unhydrated parts of glass.   After heating the glass rods were taken out of the autoclave and the diameter of unhydrated part (d) was measured.   The depth of hydrated galss layer (L) was calculated by the equation $L = (d_0 - d)/2$, where d_0 is the initial diameter of glass rod. The water content in hydrated glass was determined from the weight loss after strong heating.   It ranged about from 30 to 45 wt% on the dry basis depending upon the hydration condition and the composition of original glass.

III.   RESULTS

1.   Change in the depth of hydrated glass layer with the hydration time

Figures 2a and 2b show the changes in the depth of hydrated glass layer with the hydration time on several compositions of glass (in mol% basis).   Within the experimental error, the depth of hydrated glass layer (L) seemed to increase linearly with the time (t) under a fixed atmospheric condition.   Hence, the penetration rate of water (R) can be approximately expressed by $R = L/t$.
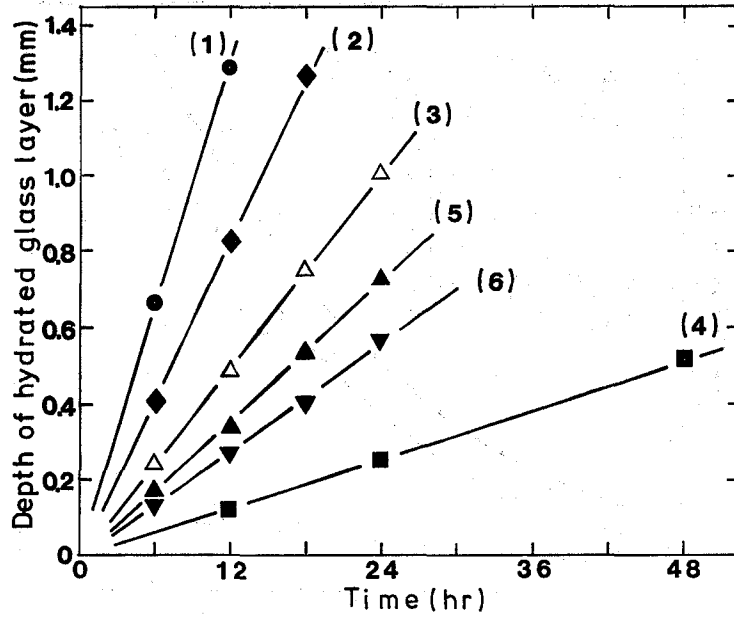
Fig. 2a. Changes in the depth of hydrated glass layer with the hydration time.

(1) $30Na_2O \cdot 70SiO_2$ (120°C),　(2) $25Na_2O \cdot 5MgO \cdot 70SiO_2$ (140°C),
(3) $25Na_2O \cdot 5CaO \cdot 70SiO_2$ (140°C),　　(4) $20Na_2O \cdot 10MgO \cdot 70SiO_2$
(130°C),　　(5) $20Na_2O \cdot 10MgO \cdot 70SiO_2$ (150°C),　　(6) $20Na_2O \cdot$
$9MgO \cdot 1Al_2O_3 \cdot 70SiO_2$ (150°C).

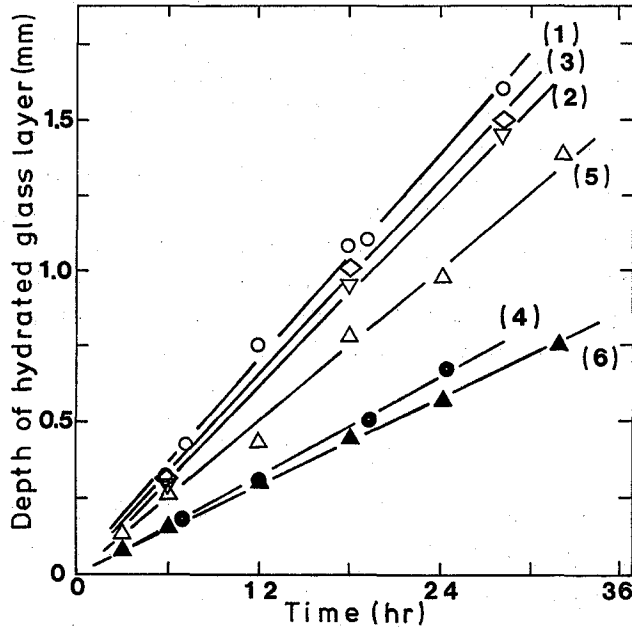
Fig. 2b. Changes in the depth of hydrated glass layer with the hydration time.

(1) $20Na_2O \cdot 10MgO \cdot 70SiO_2$ (160°C),　　　(2) $20K_2O \cdot 10MgO \cdot 70SiO_2$
(160°C),　(3) $10Na_2O \cdot 10K_2O \cdot 10MgO \cdot 70SiO_2$ (160°C),　(4) $20Na_2O \cdot$
$8MgO \cdot 2Al_2O_3 \cdot 70SiO_2$ (160°C),　(5) $15Na_2O \cdot 15MgO \cdot 70SiO_2$ (200°C),
(6) $15Na_2O \cdot 13MgO \cdot 2Al_2O_3 \cdot 70SiO_2$ (200°C).

2. Dependence of the penetration rate on the composition of glass

Figure 3 shows the changes in the penetration rate with the hydration temperature in the xNa$_2$O$\cdot$(100$-x$)SiO$_2$ glasses. It is clear that the penetration rate is larger in the glass containing more amount of Na$_2$O.

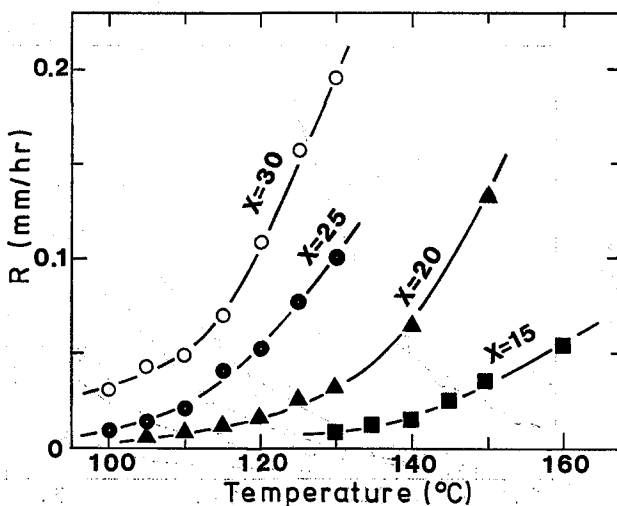
Fig. 3. Changes in the penetration rate with the hydration temperature in the xNa$_2$O$\cdot$(100$-x$)SiO$_2$ glasses.

Fig. 4. Changes in the penetration rate with the hydration temperature in the 25Na$_2$O$\cdot$5MO$\cdot$70SiO$_2$ glasses.

Figure 4 shows the changes in the penetration rate with the hydration temperature in the $25Na_2O \cdot 5MO \cdot 70SiO_2$ glasses. The substitution of MO for Na_2O always decreased the penetration rate and the decreasing effect was larger in the order $MgO < BaO < SrO \approx CaO \approx PbO < ZnO$.

Figure 5 shows the changes in the penetration rate with the hydration temperature in the $(30-x)Na_2O \cdot xMgO \cdot 70SiO_2$ glasses. In the same figure, the case con-
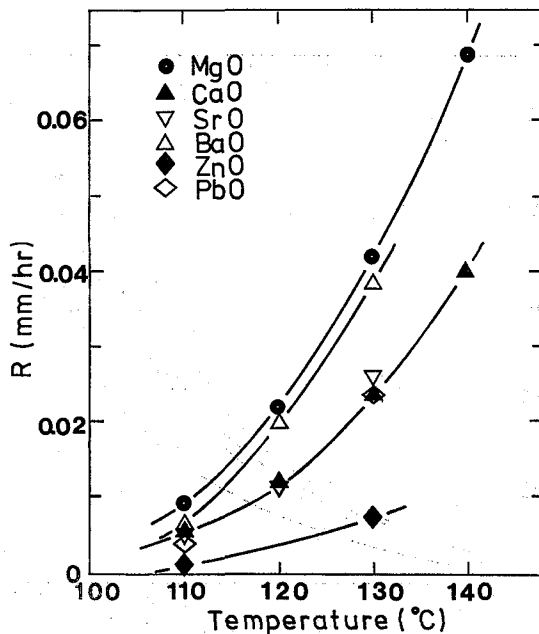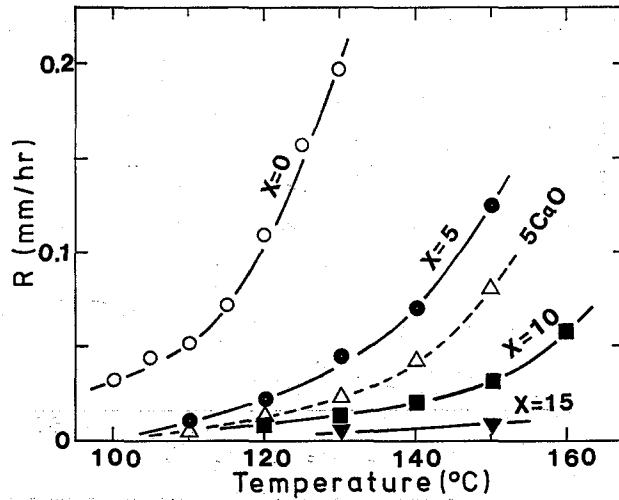

Fig. 5. Changes in the penetration rate with the hydration temperature in the $(30-x)Na_2O \cdot xMgO \cdot 70SiO_2$ glasses.

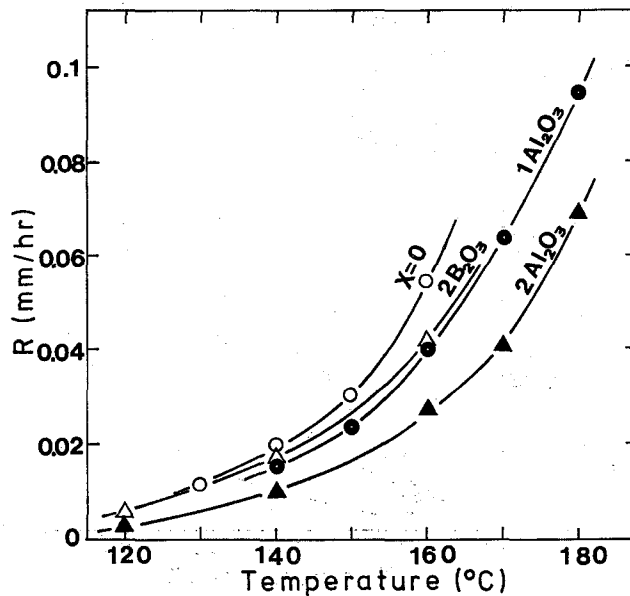Fig. 6. Changes in the penetration rate with the hydration temperature in the $20Na_2O \cdot (10-x)MgO \cdot xM_2O_3 \cdot 70SiO_2$ glasses.

taining CaO is also shown. At a fixed temperature, the penetration rate decreased with the increase of MgO. This tendency was the same in the glasses containing divalent or trivalent metal oxide other than MgO. The substitution of MgO for Na_2O was the most favorable in respect of obtaining the transparent and chemically durable hydrated glass, though it decreased the penetration rate to some extent. In the $Na_2O-MgO-M_2O_3-SiO_2$ system, the penetration rate was larger in the glasses containing B_2O_3 rather than Al_2O_3 in the same content of M_2O_3 as shown in Fig. 6.

The substitution of K_2O for Na_2O decreased slightly the penetration rate in the $(20-x)Na_2O \cdot xK_2O \cdot 10MgO \cdot 70SiO_2$ glasses as seen in Fig. 2b. A phenomemon like the mixed alkali effect was indistinctly observed.

3. Dependence of the penetraion rate on the water vapor pressure

Two series of experiments were undertaken. In the first series the hydration was carried out by changing the $P_{(air)}$ before heating. Figure 7 shows the effects of relative water vapor pressure $(RH=P_{(H_2O)}/P_{(total)})$ on the penetration rate. The points corresponding to the number 0, 1, 2 or 4 in Fig. 7 show the penetration rates when the $P_{(air)}$ before heating was 0, 1, 2 or 4 Kg/cm^2 in gauge pressure. The penetration rate decreased with the decrease of RH in spite of the increase of $P_{(total)}$.

In the second series the autoclave was evacuated beforehand to remove almost all air and then heated $(P_{(air)} \approx 0)$. When it reached a fixed temperature, an exhaust valve of autoclave was opened to lower the pressure to a desired one. The points plotted in Fig. 8 were obtained under this condition. As shown, the penetration rate increased almost linearly with the increase of water vapor pressure when the $P_{(air)}$ was about 0 and the ratio of the $P_{(H_2O)}$ to the $P_{(air)}$ shown in Fig. 1 was less than about
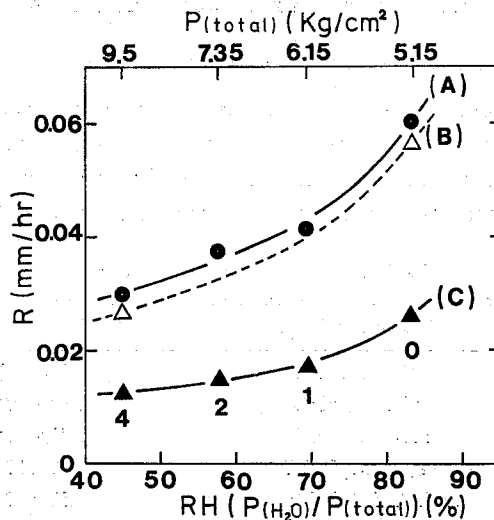

Fig. 7. Effects of the relative water vapor pressure on the penetration rate at 160°C.

(A) $20Na_2O \cdot 10MgO \cdot 70SiO_2$, (B) $20K_2O \cdot 10MgO \cdot 70SiO_2$,
(C) $20Na_2O \cdot 8MgO \cdot 2Al_2O_3 \cdot 70SiO_2$.
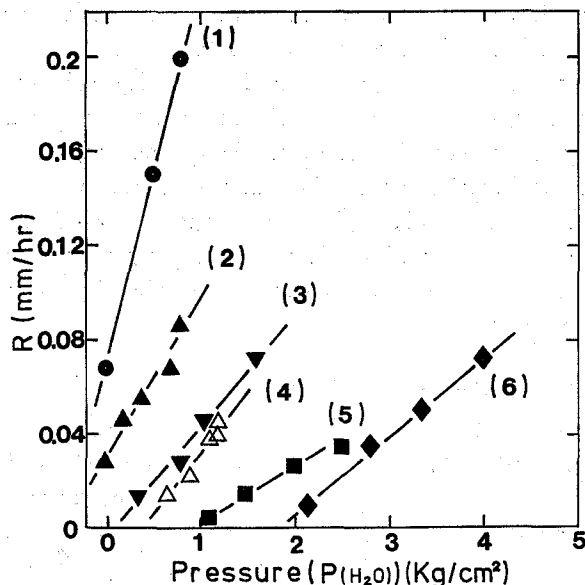
Fig. 8. Dependence of the penetration rate on the water vapor pressure when $P_{(air)}$ is about 0 and $P_{(H_2O)}/P_{(eq)}$ is less than about 0.7.
(1) $30Na_2O \cdot 70SiO_2$ (120°C), (2) $25Na_2O \cdot 75SiO_2$ (120°C),
(3) $20Na_2O \cdot 80SiO_2$ (140°C), (4) $25Na_2O \cdot 5MgO \cdot 70SiO_2$ (120°C),
(5) $20Na_2O \cdot 10MgO \cdot 70SiO_2$ (140°C), (6) $20Na_2O \cdot 10MgO \cdot 70SiO_2$ (160°C).

0.7. The linear relation between the penetration rate and the $P_{(H_2O)}$ suggests that almost all water penetrates into the glass as water molecule.[5]

4. Dependence of the penetration rate on the hydration temperature

As seen in Figs. 3, 4, 5 and 6, the penetration rate increases with the increase of hydration temperature. It was found that under the equilibrium pressure, the relation between the penetration rate (R) and the absolute temperature (T) could be approximately expressed by the Arrhenius type equation $R = R_0 \exp - E/RT$. Re-

Table I. R_0 and E for several glasses

No. in Fig. 9	Glass composition	R_0 (mm/hr)	E (Kcal/mol)
1	$20Na_2O \cdot 80SiO_2$	1.91×10^{10}	21.6
2	$25Na_2O \cdot 75SiO_2$	1.37×10^{9}	18.6
3	$30Na_2O \cdot 70SiO_2$	7.71×10^{9}	19.5
4	$25Na_2O \cdot 5MgO \cdot 70SiO_2$	5.30×10^{8}	18.6
5	$25Na_2O \cdot 5CaO \cdot 70SiO_2$	3.58×10^{9}	20.6
6	$20Na_2O \cdot 10MgO \cdot 70SiO_2$	1.33×10^{8}	18.6
7	$20Na_2O \cdot 9MgO \cdot 1Al_2O_3 \cdot 70SiO_2$	3.66×10^{7}	17.7
8	$20Na_2O \cdot 8MgO \cdot 2Al_2O_3 \cdot 70SiO_2$	1.35×10^{8}	18.3
9	$20Na_2O \cdot 8MgO \cdot 2B_2O_3 \cdot 70SiO_2$	4.57×10^{7}	17.8
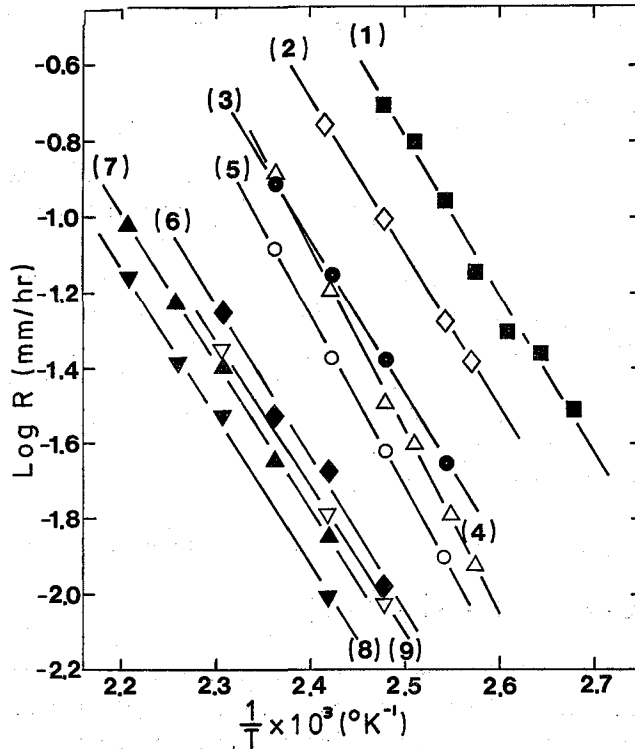
Fig. 9. Plots of the logarithm of penetration rate *vs* the reciprocal of hydration temperature (Glass compositions are given in Table I).

sults on several glasses are shown in Fig. 9 and the calculated R_0 and E are given in Table I. The apparent activation energy ranged about from 18 to 21 Kcal/mol.

IV. DISCUSSION

1. Hydration mechanism

There is a similarity between the hydration in steam atmosphere and the corrosion by water. Therefore the information about the nature of surface attack by water is helpful for understanding of the hydration process in autoclave. According to Charles, when water comes in contact with an alkali containing silicate glass the following reaction takes place. The first step is a substitution of a Na^+ ion in glass by a H^+ ion in water.

$$-Si-O-[Na] + H_2O \longrightarrow -Si-OH + Na^+ + OH^- \qquad (1)$$
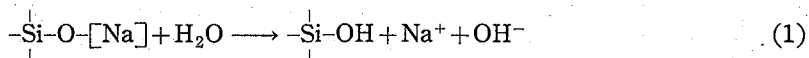
The second step is a breaking of $Si-O-Si$ bond by a free OH^- ion.

$$-Si-O-Si- + OH^- \longrightarrow -Si-OH + -SiO^- \qquad (2)$$
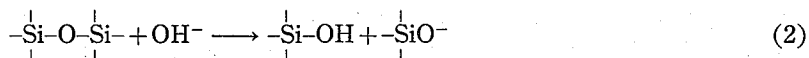
In the reaction (2) is formed another active group, $\geqslant$SiO$^-$, which is capable of reaction with water as

$$-\overset{|}{\underset{|}{Si}}O^- + H_2O \longrightarrow -\overset{|}{\underset{|}{Si}}-OH + OH^- \qquad (3)$$

The OH$^-$ ions released in the reactions (1) and (3) raise the pH in water and the increase in pH helps the dissolution of terminal $\geqslant$SiOH into water as well as the breaking of $\geqslant$Si–O–Siξ bond.[6,7]

Steam reacts with glass faster than water does because of more rapid increase in pH at the steam/glass interface (Ref. 6). However in the steam atmosphere, particularly under the unsaturated condition, the hydrated glass whose composition in dry basis does not much dif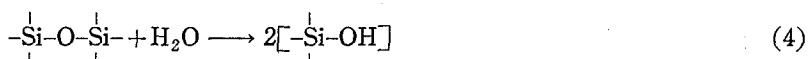fer from that of original glass still remains in the surface. Accordingly the reaction (3′) along with the reaction (3) may occur.

$$-\overset{|}{\underset{|}{Si}}O^- + Na^+ \longrightarrow -\overset{|}{\underset{|}{Si}}-O-[Na] \qquad (3')$$

In any event the overall reaction between steam and glass may be written as

$$-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}- + H_2O \longrightarrow 2[-\overset{|}{\underset{|}{Si}}-OH] \qquad (4)$$

The breaking of $\geqslant$Si–O–Siξ network makes the structure more open (loose) and weaker so that the water molecule can penetrate more easily into such weaker structure under high water vapor pressure. The penetrated water attacks further inside $\geqslant$Si–O–[Na] and $\geqslant$Si–O–Siξ bond through the reactions (1) to (3) leaving the swollen hydrated layer behind. Of course a small amount of alkali ions in the hydrated layer may be lost in the water condenced on the sufrace. Almost all of them, however, remains in the hydrated layer.

2. Time dependence of the increase of hydrated layer

On the time dependence of the increase of hydrated layer several different results have been reported. Charles found that the penetration depth of water accelerates with time at a constant temperature and the acceleration effect occurs in not only the saturated but also unsaturated (90%) atmospheres (Ref. 6), though his data appear to indicate linear dependences on time for both initial and later stages of hydration. Bartholomew confirmed that the penetration depth increased linearly with the square root of time except for short exposure time and the slope of the straight line was almost independent of temperature.[8] Wu classified the rate process of hydration into four types including above two cases.[9]

In present experiments, the penetration depth was found to increase approximately linearly with time as shown in Figs. 2a and 2b, although the experiments were carried out at relatively low temperatures and for relatively short period of time. This linear dependence on time seems to be possible from the following line of reasoning.

As described before, the boundary between the hydrated and unhydrated parts of glass is very sharp, the composition of hydrated glass in dry basis is nearly the same as that of original glass and the hydrated layer has a swollen gel-like structure which

does not greatly impede the transfer of water. On the consistence with these facts, the concentration profile of water (or H^+ ions) is considered to be as shown in Fig. 10. The transfer of water in the hydrated layer is so rapid comparing to that in the unhydrated glass that the diffusion control zone, in which water (or H^+ ions) shows the S-shaped concetnration profile, is thin and the thickness of it is probably almost a constant under a fixed condition of temperature and pressure. Consequently if the increase of penetration depth has a linear dependence on time in the hydrated layer, even though it has a squar root dependence on time in the diffusion control zone, a linear dependence on time eprhaps appears more predominantly.
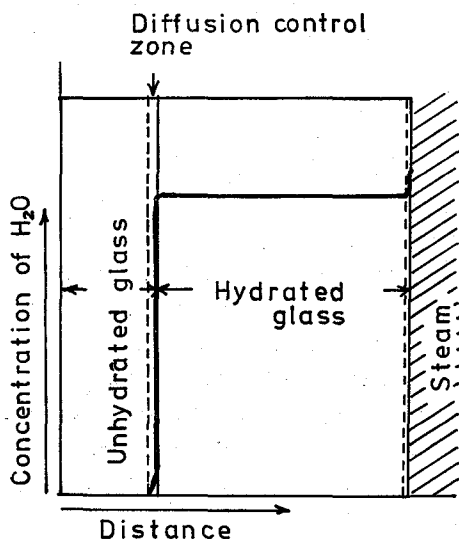

Fig. 10. Assumed concentration profile of water (thick solid line) in the hydrated and unhydrated glasses.

This linear time dependence is phenomenally analogous to that found in the corrosion by alkaline solution where the breaking of $\geqslant$Si–O–Si$\leqslant$ bond is the most important step.[10] For the case of formation of the hydrated layer which has a tight structure (water content is low) and is highly resistant to the transfer of water molecule, the square root dependence on time becomes more likely.

3. Effect of glass composition on the penetration rate

For the progress of hydration the breakdown of $\geqslant$Si–O–Si$\leqslant$ network by OH^- ions is necessary. This reaction is also indispensable step for the dissolution of glass into water and alkaline solution. So it seems wellgrounded to consider that the glass liable to be attacked by water or alkaline solution has a larger tendency to the hydration in steam atmosphere. This is the case for the $x\mathrm{Na_2O \cdot (100-}x\mathrm{)SiO_2}$ and $(30-x) \cdot$ $\mathrm{Na_2O} \cdot x\mathrm{MgO \cdot 70SiO_2}$ glasses. However the same does not hold for the $(20-x) \cdot$ $\mathrm{Na_2O} \cdot x\mathrm{K_2O \cdot 10MgO \cdot 70SiO_2}$ and $25\mathrm{Na_2O \cdot 5MO \cdot 70SiO_2}$ glasses. In the former the order of dissolution tendency to the water of about 96°C is $20\mathrm{K_2O} > 10\mathrm{Na_2O} \cdot$ $10\mathrm{K_2O} > 20\mathrm{Na_2O}$ containing glass. In the latter that to the water is $\mathrm{BaO} > \mathrm{PbO} >$

SrO>MgO>CaO>ZnO containing glass and also that to the $2N$ NaOH solution of about 90°C is SrO>PbO>CaO≈MgO>BaO>ZnO containing glass. In both systems, the orders do not coincide with the orders of the penetration rate as seen in Figs. 4 and 2b.

Scholze found that the fraction of silanol groups which are not hydrogen-bonded to non-bridged oxygens, r, depends strongly on the field strength of cation in the oxide substituted for SiO_2.[11] On the other hand, Wu showed that the r is smaller in the hydrated glass containing more amount of water.[12] These suggest that the ease of hydration may be related to the factor affecting the r, that is, to the field strength of substituted cations. But this suggestion is not always generally correct as judged from Figs. 4 and 6. An attempt to relate the ease of hydration to the degree of openess of glass structure or the packing density of elements contained in glass was also unsuccessful.

4. Effects of temperature and pressure on the penetration rate

The penetration rate is larger at higher temperature under the usual experimental condition and the relation between $\log R$ and $1/T$ was represented by a nearly straight line. However it is not clear whether or not this result indicates only the effect of temperature because the change in temperature accompanies inevitably the change in water vapor pressure. Nevertheless, the E values given in Table I are nearly the same as that found by Charles (20±4 Kcal/mol for Corning 0080 soda lime glass) (Ref. 6) or that by Lanford (18.9±1.6 Kcal/mol for commercial window glass which was measured in the dissolution process).[13] All these values are very close to the activation energies for Na^+ ion diffusion in similar types of glasses. Therefore it seems highly probable that the Na^+ ion diffusion within glass is responsible for the initial process of hydration, as suggested by Charles (Ref. 6).

Regarding to the water vapor pressure, it is possible to vary only the pressure keeping the temperature a constant. As shown in Figs. 8 and 9, the penetration rate was lower under the condition of lower RH in spite of higher total pressure and also the condition of lower absolute water vapor pressure. The water content in the hydrated glasses obtained under such conditions was slightly lower and the structure of them was somewhat more tight (the degree of swelling was lower) than that in those obtained under the usual conditions. Accordingly the lower rate of penetration is probably due to the lower transfer rate of water within the hydrated layer and the lower concentration of water just outside the unhydrated glass.

V. SUMMARY

The glasses in the systems Na_2O-SiO_2, $Na_2O-MO-SiO_2$, $Na_2O-K_2O-MgO-SiO_2$ and $Na_2O-MgO-M_2O_3-SiO_2$, where M is divalent or trivalent element, were hydrated in an autoclave at the temperatures ranging from 100° to 200°C for 3 to 72 hrs. The hydrated glass layer which has a swollen gel-like structure increased nearly linearly with time under a fixed condition of temperature and pressure. This linear time dependence of hydrated glass layer increase was discussed on the basis that the

diffusion control zone in unhydrated glass was very thin and the transfer of water in thick hydrated glass layer was not greatly impeded.

The penetration rate of water was larger in the glass containing more amount of Na_2O in the Na_2O–SiO_2 system and it was decreased by the substitution of MO for Na_2O or M_2O_3 for MgO, irrespective of the kind of M. It increased with increasing temperature and water vapor pressure under the usual condition. The relation between the logarithm of penetration rate and the reciprocal of hydration temperature could be expressed by the Arrhenius type equation and the apparent activation energies were very close to those for Na^+ ion diffusion. The dependence of the penetration rate on water vapor pressure suggests that almost all water penetrates into the glass as water molecule.

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