

Hydration of phosphate and borate glasses at high temperatures and pressures

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The kinetics of hydration of $\text{CaO}-\text{Al}_2\text{O}_3-\text{P}_2\text{O}_5$ and $\text{Na}_2\text{O}-\text{CaO}-\text{B}_2\text{O}_3-\text{Al}_2\text{O}_3$ glasses in an autoclave at high temperatures and pressures have been investigated. A linear time dependence of the depth of hydrated layer has been found for the glasses used in the present study. This implies that the hydration process is governed by the chemical reaction at the interface between the unhydrated and the hydrated glass phases. It is indicated that the hydration of the phosphate glasses may occur as a result of hydrolysis of glass constituents to form orthophosphate crystals. Water vapour can easily reach the interface through the crystalline aggregates, which are loosely packed. Cabal glasses which do not contain any alkali oxides have shown quite a high resistance to water. Substitution of sodium for calcium has resulted in deterioration of the chemical durability of cabal glasses. This can be explained by the difference in stability between sodium and calcium ions in the hydrated layer.

1. Introduction

The hydration of alkali silicate glasses at high temperatures and pressures has been investigated as it is possible that hydrated glasses might be formed into any desired shape at a much lower temperature than the glass transition temperature of their unhydrated counterparts [1-4]. The authors studied the hydration of various silicate glasses in an autoclave, finding that the hydration kinetics depend on the composition of the glass and the temperature and pressure of hydration. For instance, some glasses showed a reaction-controlled process at lower temperatures and a diffusion-controlled process at higher temperatures, while others exhibited a reaction-controlled process at all temperatures up to about 220°C [5]. It was also shown that the hydration of glass in water vapour is not caused by ion exchange between alkali ions in the glass and hydronium ions, but is caused by the penetration of water molecules through the hydrated glass layer, in

contrast to the ion exchange in the water solution.

Calcium phosphate glasses are examined because of their use as biomaterials, while calcium aluminosilicate glasses with no alkali oxide have high ultraviolet transmittance [6]. $\text{CaO}-\text{B}_2\text{O}_3-\text{Al}_2\text{O}_3$ glasses, called cabal glasses, have quite high d.c. resistivity equivalent to silica glass. Utilization of phosphate and borate glasses is limited due to their low chemical durability. However, little work has been carried out on the hydration of non-silicate glasses such as phosphate and borate glasses at high temperatures and high pressures.

In the present study, the hydration of $\text{CaO}-\text{Al}_2\text{O}_3-\text{P}_2\text{O}_5$ and $\text{Na}_2\text{O}-\text{CaO}-\text{B}_2\text{O}_3-\text{Al}_2\text{O}_3$ glasses has been investigated in the temperature range 120 to 220°C and at pressures between 1.4 atm and 12.5 atm. On the basis of the experimental results, the hydration kinetics and mechanism of these glasses were discussed and compared with those for silicate glasses [5].

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TABLE I Compositions and properties of glasses used in the study

Glass	Composition (mol%)					T_g (°C)	α ($\times 10^7$ °C ⁻¹)	Water content* (wt %)	ΔE^\dagger (kcal mol ⁻¹)
	Na ₂ O	CaO	Al ₂ O ₃	P ₂ O ₅	B ₂ O ₃				
P1	—	10	20	70	—	575	52.0	—	—
P2	—	23.3	15.1	61.6	—	575	74.7	18.9	16.9
P3	—	38	7	55	—	541	85.1	23.3	15.3
P4	—	41.7	5.2	53.1	—	531	87.2	24.3	14.5
B1	—	40	20	—	40	608	65.6		
B2	10	30	20	—	40	512	80.4		
B3	15	25	20	—	40	475	97.5		
B4	20	20	20	—	40	450	113.4	15	
B5	25	15	20	—	40				
B6	30	10	20	—	40				
B7	20	—	5	—	75				
B8	20	—	10	—	70				
B9	20	10	—	—	70			22	

*Water content (wt %) in the hydrated glass layer.

†Activation energy for hydration.

2. Experimental details

The glass compositions used in the experiment are shown in Table I. Compositions of glasses P1 to P4 fall almost on the tie line between Al₂O₃·3P₂O₅ and CaO·P₂O₅ in the phase diagram of the CaO—Al₂O₃—P₂O₅ system. In going from P1 to P4, the component of Al₂O₃·3P₂O₅ decreases and that of CaO·P₂O₅ increases. The phosphate glasses were melted in an alumina crucible at 1000 to 1100°C for 1 to 2 h. Reagent grade chemicals of Al(PO₃)₃, CaCO₃, Al₂O₃ and Ca(H₂PO₄)₂·H₂O were used as starting materials. The borate glasses were melted in a platinum crucible at 1100 to 1200°C for 1 h. Reagent grade chemicals of CaCO₃, Al₂O₃ and B₂O₃ were used. Excess of 5 wt % B₂O₃ over the calculated quantity was added to the glass batch to compensate for the loss of B₂O₃ due to evaporation during melting [7–9].

After melting, the glass melt was poured into a graphite mould. The glass block was annealed near its glass transition temperature and then cut into

plates of 10 mm × 10 mm × 3 mm. Both surfaces were ground and finished with no. 1000 alumina powder.

A schematic diagram of the apparatus for the hydration of the glasses is shown in Fig. 1. It consists of a reaction vessel (1 l) and a boiler (10 l) which are connected together by a stainless steel tube. This construction makes it possible to control independently the temperature and pressure of the reaction vessel [5]. Maximum operating temperature and pressure are 220°C and 16 atm, respectively. Glass samples which were placed on the stainless steel holder covered with teflon were hydrated in the reaction vessel in the following manner: the reaction vessel was evacuated and heated to a desired temperature and then filled with water vapour of desired pressure sent from the boiler through the tube.

The thickness of the hydrated layer was determined by subtracting the thickness of the unreacted glass core from that of the original glass

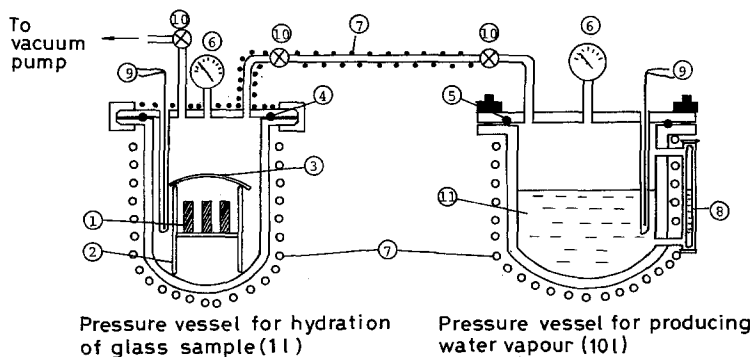


Figure 1 Schematic diagram of the apparatus for hydration of glass at high pressures and temperatures. 1, glass sample; 2, sample holder; 3, Teflon sheet cover; 4, O-ring (Viton); 5, O-ring (Teflon); 6, pressure gauge; 7, heater; 8, level; 9, thermocouple (CA); 10, valve; 11, water.

sample. The hydrated layer of phosphate glasses was easily removed after hydration. In contrast with phosphate glasses, the hydrated layer of borate glasses could not be removed when the hydrated glass sample was taken out of the reaction vessel. Therefore, the surface layer was foamed by heating the sample at 450°C for 30 min and then scraped off.

The water content of the hydrated layer was estimated from the equation:

$$\text{wt \% H}_2\text{O} = \frac{W_2 - W_1}{W_2 - W_3} \times 100 \quad (1)$$

where W_1 and W_2 are the sample weights before and after hydration and W_3 is the weight of the unhydrated glass core.

The hydrated layer of phosphate glasses was analysed using X-ray diffraction to correlate the crystal phase precipitated and the hydration kinetics.

As no appreciable hydrated layer was observed for the borate glass with no alkali oxide (cabal glass), infrared (IR) spectroscopy was used to determine whether or not water had been introduced into the glass.

3. Results

3.1. Appearance and properties of the hydrated glasses

Phosphate glasses were hydrated at 120 to 200°C under water vapour pressure of 1.4 to 11.1 atm. All phosphate glasses used in the experiments showed distinct, opaque, hydration layers. The layers could easily be separated from the unhydrated glass. The X-ray analysis indicated that crystals are precipitated in the opaque hydrated layers, as depicted in Fig. 2.

Crystalline phases precipitated in the hydrated layer of the phosphate glasses are listed in Table II. The crystalline phase changes with the glass composition; increase in $\text{Al}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5$ promotes the precipitation of AlPO_4 , while increase in $\text{CaO} \cdot \text{P}_2\text{O}_5$ that of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$.

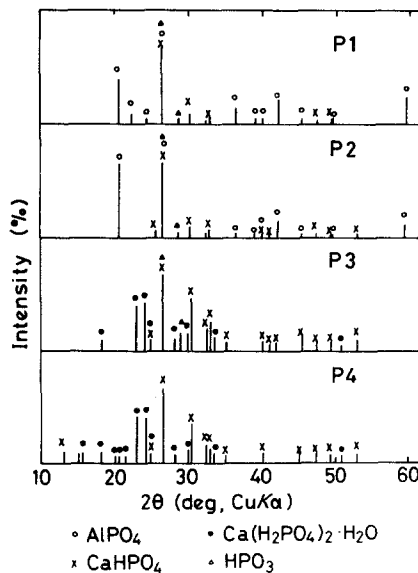


Figure 2 X-ray diffraction patterns of the hydrated layers of phosphate glasses hydrated at 200°C for 48 h.

No distinct hydrated layer could be observed using an optical microscope for borate glasses containing less than 15 mol% Na_2O , when they were treated in the pressure range of 7 to 16 atm at 180 to 220°C. Infrared spectra of glasses B1 (0 mol% Na_2O) and B3 (15 mol% Na_2O) in the wave number range of 4000 to 1900 cm^{-1} are shown in Fig. 3. The absorption band at about 3450 cm^{-1} due to water in the glass increases after hydration [10], indicating that water enters the borate glasses containing less than 15 mol% Na_2O even though the hydrated layer is not distinctly observed. Assuming that the extinction coefficient of the 3450 cm^{-1} water peak for the present borate glasses is equal to that for binary $\text{PbO}-\text{B}_2\text{O}_3$ glasses [10], the amounts of water contained in glasses B1 and B3 are estimated as 1.5×10^{-6} and $4.0 \times 10^{-6} \text{ g cm}^{-3}$, respectively. The amount of water in P1 and 20 $\text{Na}_2\text{O} \cdot 10 \text{ CaO} \cdot 70 \text{ SiO}_2$ glasses treated under the same conditions as above [11] were 1×10^{-4} and $4 \times 10^{-4} \text{ g cm}^{-3}$,

TABLE II Crystalline phases in the hydrated layer of the phosphate glasses

Glass	Crystalline phase				Component in glass	
	AlPO_4	CaHPO_4	$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$	HPO_3	$\text{Al}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5$	$\text{CaO} \cdot \text{P}_2\text{O}_5$
P1	MJ	MI	ND	MI	↑	↓
P2	MJ	MI	ND	MI		
P3	ND	MJ	MJ	ME		
P4	ND	MJ	MJ	ND		

MJ, major phase; ME, medium phase; MI, minor phase; ND, not detected. Arrows show direction of increase.

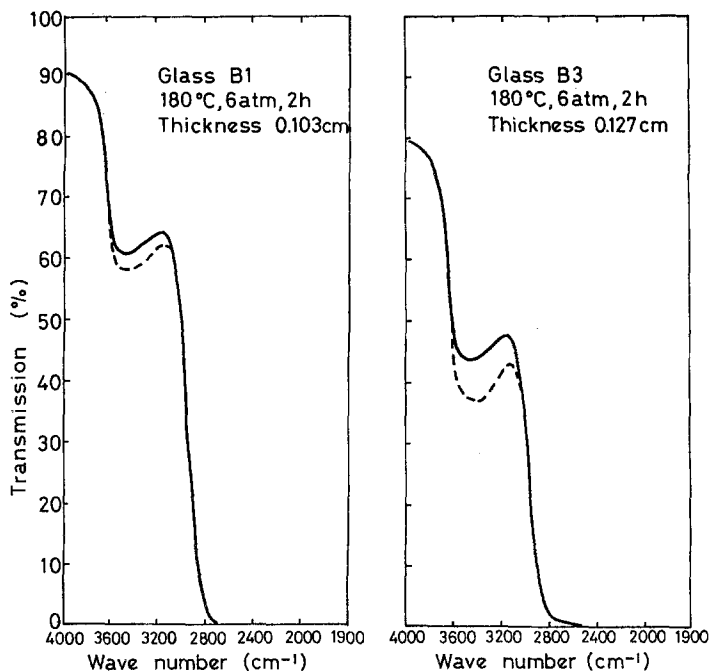


Figure 3 Infrared spectra of borate glasses before (—) and after (---) hydration.

respectively, suggesting that much less water enters the borate glasses containing less than 15 mol% Na_2O .

Contrary to expectation, the borate glasses containing more than 20 mol% Na_2O showed distinct, white, hydrated layers of water content ranging from 15 wt% to 22 wt%, like the phosphate (Table I) and silicate glasses [5]. The hydrated layer of the borate glasses was not crystalline but glassy. The hydrated glass layers came off easily on heating the glass to 450°C .

3.2. Rate of hydration

The variations of the depth of the hydrated layer L with the hydration time t for phosphate glasses are shown in Fig. 4. Linear increases of L with t are clearly indicated for all phosphate glasses. The

rates of hydration $R = L/t$ (mm h^{-1}) estimated from the slope of straight lines in Fig. 4 are plotted against the hydration temperature in Fig. 5. The R 's increase exponentially with increasing temperature. Plots of $\log R$ against $1/T$ (reciprocal of absolute temperature) give straight lines, as shown in Fig. 6. The activation energies ΔE for hydration calculated from the slopes of the lines are listed in the last column of Table I. It is seen that ΔE ranges from 14.5 to 16.9 kcal mol^{-1} .

The variations of L with t for borate glasses are shown in Fig. 7. The borate glasses containing Na_2O also show a linear relationship between L and t , just like the phosphate glasses. Fig. 8 shows the variation of depth of the hydrated layer with the concentration of Na_2O for borate glasses. This indicates that the borate glasses containing more

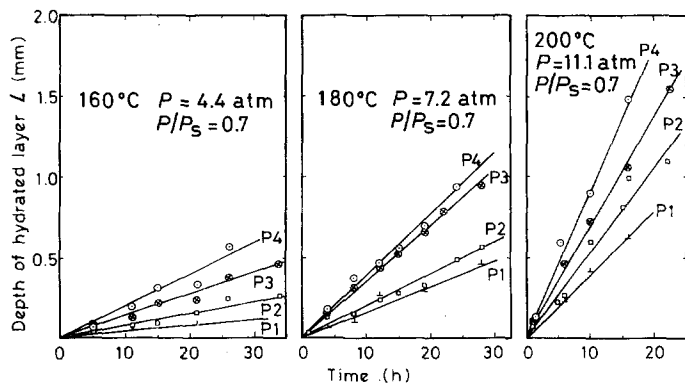


Figure 4 Depth of the hydrated layer plotted against time for phosphate glasses.

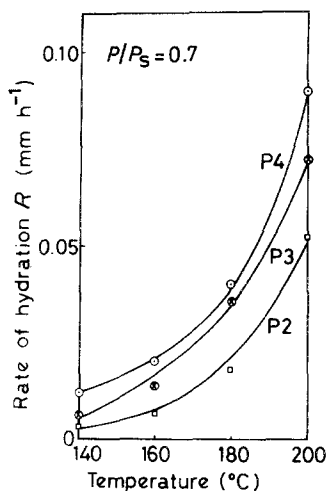


Figure 5 Rate of hydration as a function of temperature for phosphate glasses.

than 15 mol% Na_2O are easily hydrated, especially at higher temperatures.

4. Discussion

4.1. Phosphate glasses

Charles carried out hydration of soda-lime-silica glass at 175 to 250°C and saturation of 90 to 100%. He found an auto-catalytic hydration reaction in which the rates of hydration increases with the hydration time [1]. Bartholomew *et al.* [2] reported square root time dependences of the depth of the hydrated layer and linear per cent saturation dependences of the rate of hydration for the alkali silicate glasses at 225 to 350°C and saturation of 56 to 100%. These results indicate that the hydration kinetics are controlled by a diffusion process of water through the hydrated

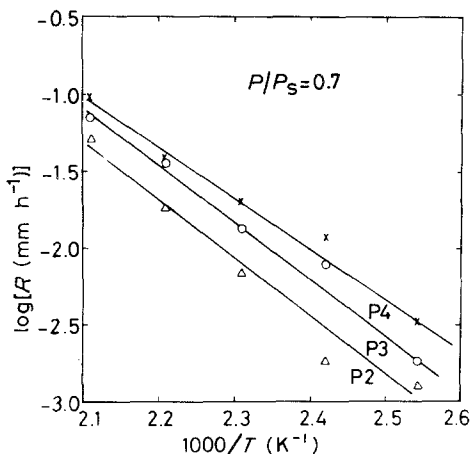


Figure 6 Logarithm of R plotted against the reciprocal temperature for phosphate glasses.

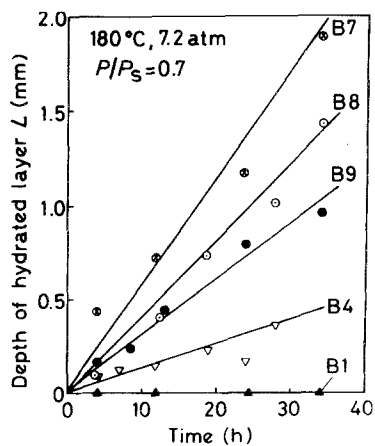


Figure 7 Depth of the hydrated layer plotted against time for borate glasses.

layer. A contradictory result was reported by Moriya and Nogami, who found a linear time dependence of the hydrated layer for the various alkali and alkaline earth silicate glasses [4].

The present authors have examined the hydration of various silicate glasses with different compositions at 150 to 220°C and saturation of 30 to 100%. It was found that the time dependence of depth of the hydrated glass layer depends on the glass composition and the hydration temperature. Certain glasses showed linear time dependences of the depth of the hydrated layer at lower temperatures and square root time dependences at higher temperatures. The temperature of the transition from the former time dependence to the latter depended on the glass composition. According to the reaction kinetic theory [12], the linear

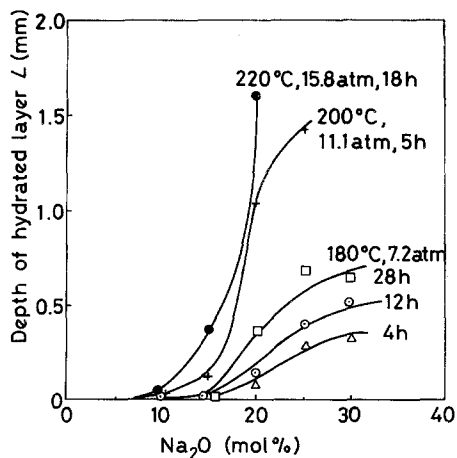


Figure 8 Depth of the hydrated layer as a function of Na_2O content in $x \text{Na}_2\text{O} \cdot (40-x) \text{CaO} \cdot 20 \text{Al}_2\text{O}_3 \cdot 40 \text{B}_2\text{O}_3$ glasses.

time dependence corresponds to the process controlled by the chemical reaction at the interface between the hydrated layer and the unhydrated glass core and the square root time dependence to that controlled by the diffusion of water through the hydrated layer as follows:

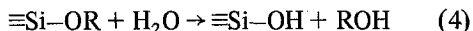
$$L = kC^m t \text{ (chemical reaction controlled) (2)}$$

$$L = a(DCt)^{1/2} \text{ (diffusion controlled) (3)}$$

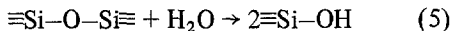
Here, k is the rate constant, C the concentration of the reactant, m the order of the reaction, D the diffusion constant, a the constant and t the time.

In all phosphate glasses used in the present study, hydration is controlled by the chemical reaction. It is assumed that water can easily penetrate the loosely packed layers of crystals in the phosphate glasses. This would make it possible for water molecules to reach the unhydrated glass core, which results in the reaction-controlled hydration kinetics. Then a transition from linear to square root time dependence of the depth of the hydrated layer would not be observed until much higher temperatures, if at all. Conversely such a transition has been observed in some silicate glasses because their hydrated layers are dense and suppress easy access of water molecules to the unhydrated glass core.

The hydration of alkali silicate glasses may occur as a result of the formation of silanol group [1, 13]:



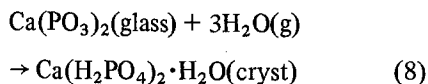
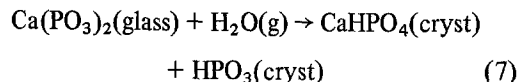
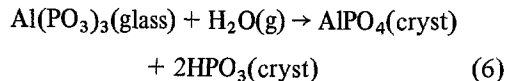
Then, OH^- ions and water may react with siloxane bond $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ to form silanol groups. The total reaction is written as follows:



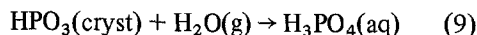
The presence of alkali oxides in glass makes the formation of silanol groups easier [14]. The hydrated glass usually remains glassy.

On the other hand, the hydration of phosphate glasses with no alkali oxides may differ from that of silicate glasses. The hydration of the phosphate glasses seems to lead to the hydrolysis of glass constituents to orthophosphates (see Table II and Fig. 2). Although phosphate glasses react with water to produce polymers characteristic of their composition at low temperatures and ordinary pressure [15], it might be assumed that at high temperatures and pressures, as in the present

case, phosphate glasses should be hydrolysed to orthophosphates. Actually, AlPO_4 , CaHPO_4 and/or $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ could be found in the hydrated layers of the phosphate glasses, depending on the glass composition. On this basis, the following reactions can be proposed for the hydration of the phosphate glasses used in the study:



Metaphosphoric acid is easily hydrolysed into orthophosphoric acid in the presence of water, as follows:



According to the rate law [16], the slope of the line relating logarithmic reaction rate with logarithmic concentration of the reactant gives the orders of reaction. Applying the idea to the present study, plots of hydration rate R against relative pressure P/P_s , where P is the ambient water vapour pressure and P_s the saturated water vapour pressure at the temperature of interest as a standard state, give the order of hydration reaction n with respect to water through the following equation:

$$\log R = n \log (P/P_s) + A \quad (10)$$

where A is the constant related to the rate constant. The plots for some glasses are shown in Fig. 9. The value of n determined from the slope are listed in Table III. The value of n is about unity, that is 1.2, for P2 glass whose composition is nearly $\text{Al}(\text{PO}_3)_3$ and increases up to about 3

TABLE III Kinetic parameters obtained from the plots of $\log R$ against $\log (P/P_s)$ for phosphate and borate glasses hydrated at 180°C

Glass	n	$\log A$	A (mm h^{-1})
P2	1.2	-1.55	0.029
P3	1.8	-1.11	0.079
P4	3.0	-0.89	0.13
B4	4.2	-0.85	0.14
B9	3.2	-0.94	0.11

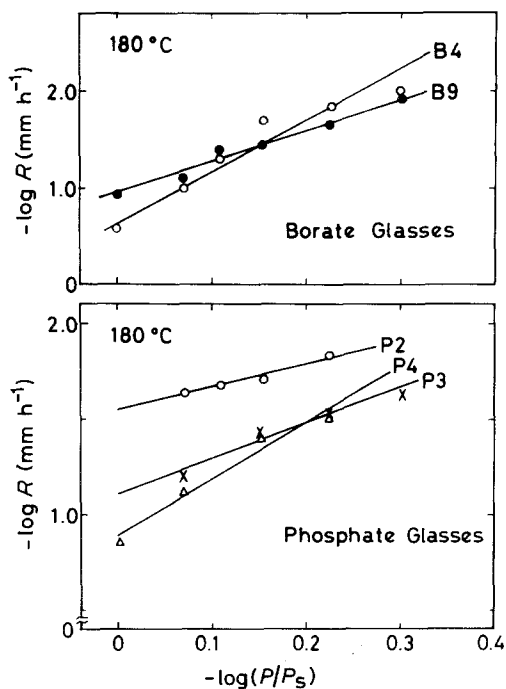


Figure 9 Plots of $\log R$ against $\log (P/P_s)$ for the phosphate and borate glasses.

with increasing $\text{Ca}(\text{PO}_3)_2$ in the glass. This kinetic analysis corresponds well to the Reactions 6 and 8 previously proposed based on the X-ray analysis. That is, the hydration rate for P2 glass is proportional to P^1 , while that for P4 glass, whose composition is rich in $\text{Ca}(\text{PO}_3)_2$, to P^3 . These also confirm that a driving force of hydration for phosphate glasses arises from the hydrolysis of the glass constituents to the corresponding orthophosphate crystals.

As seen in Fig. 4, phosphate glasses P1 and P2 containing more $\text{Al}(\text{PO}_3)_3$ component have higher hydration resistance. This can be reasonably related to the formation of an AlPO_4 group in the glass which has no non-bridging oxygen like silica glass as explained by Kreidl *et al.* [17].

4.2. Borate glasses

Hydration rates of some borate glasses containing Na_2O are shown in Fig. 10, together with those of phosphate and silicate glasses [5]. Silicate glasses which show linear time dependence of the hydration depth have been selected. Obviously, the borate glasses containing more than 20 mol% Na_2O have lower chemical durability. It should be remembered, however, that $\text{CaO-B}_2\text{O}_3\text{-Al}_2\text{O}_3$ glass (cabal) which does not contain any alkali

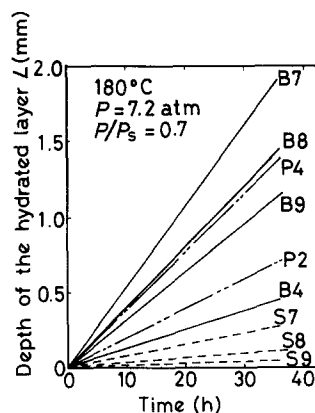
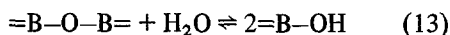
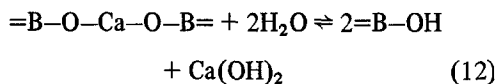
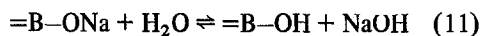


Figure 10 Comparison of the hydration rate in phosphate (P2, P4), borate (B4, B7, B8 and B9) and silicate (S7, S8 and S9) glasses. S7: $20 \text{ Na}_2\text{O} \cdot 10 \text{ CaO} \cdot 70 \text{ SiO}_2$; S8: $20 \text{ Na}_2\text{O} \cdot 5 \text{ Al}_2\text{O}_3 \cdot 75 \text{ SiO}_2$; S9: $20 \text{ Na}_2\text{O} \cdot 10 \text{ Al}_2\text{O}_3 \cdot 70 \text{ SiO}_2$.

oxide shows such a high chemical durability that the distinct hydrated layer could not be detected under the experimental condition used (see Figs. 7 and 8).

Bishop and Bray [18] concluded from the B^{11} NMR measurements on the cabal glasses that boron atoms form both planar BO_3 and tetrahedral BO_4 groups and at the same time aluminium atoms may form tetrahedral AlO_4 as well as octahedral AlO_6 groups, the fraction of the AlO_4 or AlO_6 groups depending on the glass composition. On the basis of the $\text{AlK}\alpha$ fluorescence X-ray spectra for the cabal glasses, one of the authors [19] found that aluminium atoms in the glass with less than 25 mol% B_2O_3 are in tetrahedral configuration and the numbers in octahedral configuration increase with increasing B_2O_3 content. According to the above results [18], 20% of boron atoms and almost all aluminium atoms assume tetrahedral configuration in B1 glass. In short, the high chemical durability of the cabal glass can possibly be attributed to the tetrahedral configurations of boron and especially aluminium atoms just as in the case of alumino-silicate glasses [5, 20] and alumino-phosphate glasses studied in the present work.

The substitution of sodium for calcium atoms, however, led to a marked lowering of the chemical durability of the borate glasses (B2 to B6) as shown in Fig. 8. It is assumed that the hydration of borate glasses proceeds according to the following reaction schemes in analogy to the silicate glasses:



The lower the activities of the products, the larger the shift of the above equilibria to the right – in other words, the more easily the hydration takes place.

Sodium ions become more stable in the presence of water, leading to a decrease in activity. In contrast, since $Ca(OH)_2$ has a lower solubility in water, the activity of Ca^{2+} ions in the hydrated layer will not be lowered as in the case of silicate glasses in water [21]. Moreover, the formation of NaOH in the hydrated layer may raise the pH value to more than 10, resulting in easier hydration of the $=B-O-B=$ bond due to ionization of H_3BO_3 [22].

5. Conclusions

The kinetics of hydration of $CaO-Al_2O_3-P_2O_5$ and $Na_2O-CaO-B_2O_3-Al_2O_3$ glasses in an autoclave at high temperatures and high pressures have been investigated. A linear time dependence of the depth of hydrated layer has been found for the glasses used in the present study. It is concluded from this fact that the hydration kinetics are governed by the chemical reaction at the interface between the unhydrated and the hydrated glass phases.

It has also been indicated that the hydration of the phosphate glasses may occur as a result of hydrolysis of glass constituents as water vapour can easily reach the interface through the crystalline species which are very loosely packed.

Cabal glasses which do not contain any alkali oxide have shown a quite high chemical durability. Substitution of sodium oxide for calcium oxide has resulted in a deterioration of the chemical durability of cabal glasses. This has been explained by the difference in stability between sodium and calcium ions in the hydrated layer.

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