Mechanism of Carbonation of Concrete

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SYNOPSIS

The paper points out that there is a fundamental error in the explanation by many researchers that the mechanism of carbonation of concrete is predicted on the solubilities of calcium hydroxide and calcium carbonate in water of pH value close to 7. Furthermore, based on the chemistry of pore solution which has come to be studied actively in the field of concrete engineering, it is deduced that the rate of carbonation becomes higher the higher the value. This deduction is next verified through experiments.

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1.INTRODUCTION

Factors influencing the rate of carbonation of concrete may be broadly divided into environmental factors such as humidity, temperature, and carbon dioxide concentration, and material and work execution factors such as type of cement, water cement ratio, amount of entrained air, curing conditions, and degree of consolidation, and the research reports that have explained the effects of these factors amount to an enormous number. In Japan, the equations below (Kishitani's Formula[1]) are generally being used for estimating the rate of carbonation of concrete, and it has been confirmed that good estimates can be obtained for concrete structures, built at least prior to the middle 1960s.

$$t = 0.3 \ (1.15 + 3X)/(X - 0.25)^2 \ C^2 \qquad (\ X \geq 0.6)$$

$$t = 7.2 \ /(4.6X - 1.76)^2 \ C^2 \qquad (\ X \leq 0.6)$$

where, C = depth of carbonation (cm)
       t = exposure time (years)
       X = water cement ratio

Meanwhile, in the past several years in Japan, as problems of early deterioration of concrete structures due to alkali-aggregate reaction and chloride corrosion of reinforcing steel have been arisen, there has been a rush to carry out investigations of the degree of deterioration of concrete structures. Accordingly, there have been many reports published which have disclosed the results of measuring carbonated depths, and conspicuous among these are reports which have pointed out that rates of carbonation are abnormally higher than the estimated values obtained by the above-mentioned equations. Fig.1 is an example, which shows the results of investigation of carbonation depths made with cores collected from viaducts of a Shinkansen
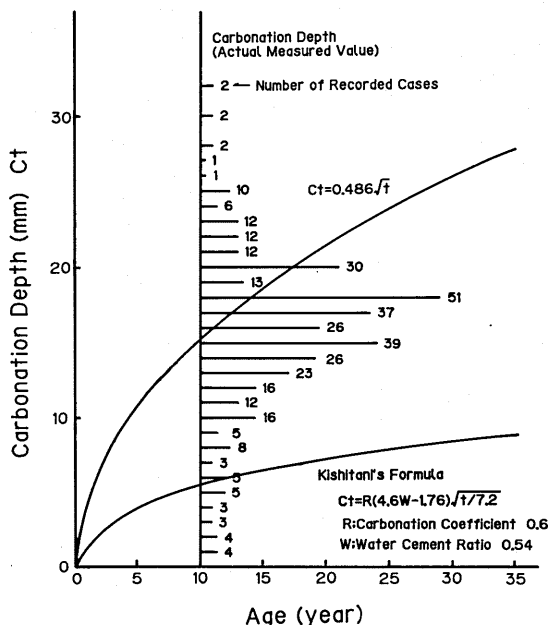

Fig. 1

Increase in depth of carbonation with time for concrete structures

railway line constructed in the middle of the 1970s[1]. This shows the distribution of carbonation depths 10 years after construction of the structures, and it can be seen that the depth of carbonation are about 3 times the values estimated by the above-mentioned equations. However, among the investigation reports are those which have pointed out that carbonation has progressed at a rate 10 times as fast as that estimated with the equations. This paper, based on the chemistry of pore solutions which is now becoming a new field in concrete engineering, points out that there has been a fundamental error in the mechanism of concrete carbonation as explained by many researchers in the past. At the same time, it discloses that there is pH of pore solution as a new factor governing the carbonation of concrete, and that the rate of carbonation is higher the higher this pH value. The pH of pore solution of concrete is basically dependent on the amount of alkali in the cement used. In the 1970s, practically all of the cement plants in Japan finished switching their methods of manufacturing cement from wet system used until then to dry system employing SP kilns, and this corresponded to a time when cement of high alkali content was being supplied on the market nationally. The main reason for the rates of carbonation of concrete structures built since this era being so abnormally high may be caused by the change in the method of manufacturing cement and cement of high alkali content coming into use.

2. PRESENT STATE OF CONCEPT AND THE POINTS AT ISSUE CONCERNING CARBONATION MECHANISM OF CONCRETE

Carbonation of concrete is the phenomenon of calcium compounds (in general, calcium hydroxide) in cement hydration products reacting with carbon dioxide in the air to change to calcium carbonate. And the reason that this phenomenon is viewed with importance in the field of concrete engineering is that its progress has a close relationship with corrosion of reinforcing steel. In effect, it is because when the pH value of pore solution filling the capillary voids of concrete falls below a certain critical value, the passive film formed at the surface layer of reinforcing steel is broken and the steel becomes completely defenseless against corrosion.
The reaction of carbonation of concrete is generally expressed, by Eq.(1)

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O \qquad (1)$$
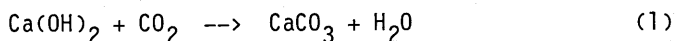
The mechanism of pH value of pore solution in concrete being lowered by this reaction is often explained in the following manner. That is, "the pH of the pore solution of concrete which has not been carbonated, is maintained in a range of 12.5 to 13.5 by the calcium hydroxide dissolved, but with penetration and reaction of carbon dioxide, the pH is decreased and the pH of the carbonated portion becomes approximately 8.3". Or, "a concrete which has not been carbonated has an alkalinity of approximately 12.6 in terms of pH value, but concrete which has been carbonated has its pH value lowered to 8.3, and becomes closer to a neutral states"[3].
Recently, however, with the purpose of explaining the mechanism of alkali-aggregate reaction, analysis of pore solutions of concrete by high-pressure extraction methods are being actively done, and many results have been reported [4]. Tables 1 and 2 give typical examples of such results, all of which used cement of low alkali type. Both of these tables show that the components of the pore solutions are almost all Na^+, K^+, and hydroxide ions which are in equilibrium with these, while Ca^{++} ions exist only in extremely small quantities. This is because solubility of calcium hydroxide is low in relation to the solubility of alkali sulfates supplied from the cement, and especially because the calcium hydroxide has a solubility product relationship as shown

below, with the concentration of Ca^{++} reduced more the higher the pH value of pore solution, so that the solubility of calcium hydroxide is lowered.
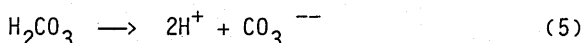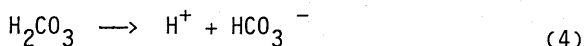
$$Ca(OH)_2 \longrightarrow Ca^{++} + 2OH^- \qquad (2)$$
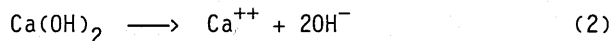
$$Ksp = [Ca^{++}] [OH^-] = const. \qquad (2')$$

As is clear from the above, the pH of pore solution depends principally on the concentration of Na^+ and K^+ supplied by the alkali sulfate in cement, and not on Ca^{++}. Then the question is why such values as 8.3 and 12.6 are cited regarding pH of pore solutions of carbonated and, non-carbonated concrete.
It is because the point that the condition produced by the carbonation reaction is a solution of high pH is ignored, and a reaction occurring in a solution close to neutral has been assumed. In other words, a pure water in which substances such as alkali metal ions which greatly affect progress of carbonation are not dissolved is considered. The solubility of calcium hydroxide in such water at normal temperature is approximately 1350 ppm (corresponding to 1820 ppm of calcium carbonate), and the pH value in this case is 12.6. On the other hand, the solubility in such water of calcium carbonate is 63 ppm, and the pH value in this case will be 8.5.
Based on the foregoing, it is considered that when the saturated calcium hydroxide solution has reached a state of equilibrium, 100 x [(1820 − 63)/1820] = 96% is precipitated as calcium carbonate.

3. COMPOSITION OF PORE SOLUTION OF CONCRETE AND PROGRESS OF CARBONATION

A question would be what kinds of reaction occur when carbon dioxide acts on pore solutions of compositions as shown in Table 1. This is a point which is of extreme importance in this paper and will be examined below in somewhat detailed form. Carbon dioxide is dissolved in water to become carbonic acid as indicated in Eq.(3), and this dissociates into ions as shown by Eq.(4) and (5) to act as acid. Here, the carbonic acid dissociated as in Eq.(5) in case the pH value of the solution is high.

$$CO_2 + H_2O \longrightarrow H_2CO_3 \qquad (3)$$

$$H_2CO_3 \longrightarrow H^+ + HCO_3^- \qquad (4)$$

$$H_2CO_3 \longrightarrow 2H^+ + CO_3^{--} \qquad (5)$$

The reaction of these hydrogen carbonate ions or carbonate acid ions with alkali metal ions existing in large quantity in pore solution, as shown by Eq.(6), is that alkali carbonate is first formed, but since its solubility is fairly high, it is immediately dissolved in the pore solution and again dissociates into ions. Therefore, the reaction of Eq.6 does not progress to the left side, and the concentration of alkali metal ions is hardly changed.

$$2R^+ + HCO_3^- (CO_3^{--}) \longleftrightarrow R_2CO_3 \qquad (6)$$
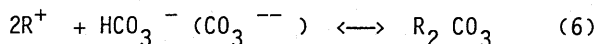
where, R : Na or K
However, in the reaction with calcium ions which exist only in minute quantity in the pore solution, calcium carbonate which is almost completely water-insoluble is precipitated as shown in Eq.(7).

$$Ca^{++} + HCO_3^- (CO_3^{--}) \longrightarrow CaCO_3 \qquad (7)$$
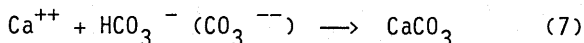
The concentration of Ca^{++} in the pore solution is lowest because hydroxide existing in the solid phase is dissolved in the pore solution by the amount of reduction in concentration. Meanwhile, the calcium carbonate formed is deposited at the wall of pores. Carbonation progresses as such a process is repeated, and calcium carbonate continues to grow along with this inside the pore. When carbonation of concrete progresses with such a mechanism, the concentrations of the various ions in the pore solution are not greatly altered until the calcium hydroxide in the vicinities of the pores disappears, while even during progress of carbonation, what prescribe the pH value of the pore solution are hydroxide ions in a state of equilibrium with alkali metal ions. When looked at in this way, calcium hydroxide itself does not decide the pH of pore solution, but plays the role of fuel for maintaining the pH value. As a consequence, the final decline value starts abruptly from the time that calcium hydroxide in the solid phase disappears.

4. INFLUENCE OF PORE SOLUTION pH VALUE ON RATE OF CARBONATION

4.1 Outline

Now, if it is by such a mechanism that carbonation of concrete progresses, it can be expected that the rate of carbonation will be higher the higher the pH of the pore solution. To explain this point in more detail, it will be as described below. That is, if it were to be assumed that the absolute quantity of calcium hydroxide in the solid phase is the same, the rate of carbonation is greatly affected by the degree of ease with which the calcium hydroxide is leached out into the pore solution. As shown in Fig.2, the state in which carbonic acid exists as ions differs depending on the pH value of the solution, and when pH is high, it exists as CO_3^{--}, the ratio of existence as HCO_3^- becomes high. This means that with calcium salts, they exist as calcium carbonate when pH is high, and as calcium bicarbonate when pH is low, and because bicarbonate is readily dissolved in water, it may be considered that solubility of calcium carbonate is increased when pH becomes low. That is, it may be said that the pH of pore solution has a close relationship with the solubility of calcium carbonate, and the concentration of Ca^{++} in the pore solution is lowered along with precipitation of calcium carbonate to make it easier for calcium hydroxide in the solid phase to be dissolved, and carbonation is accelerated. The mechanism of such carbonation shown in schematic form is Fig.3.
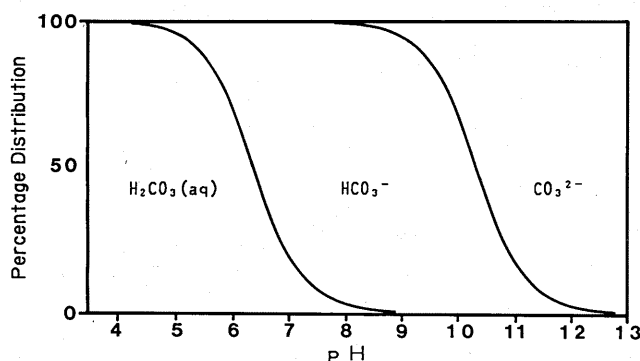

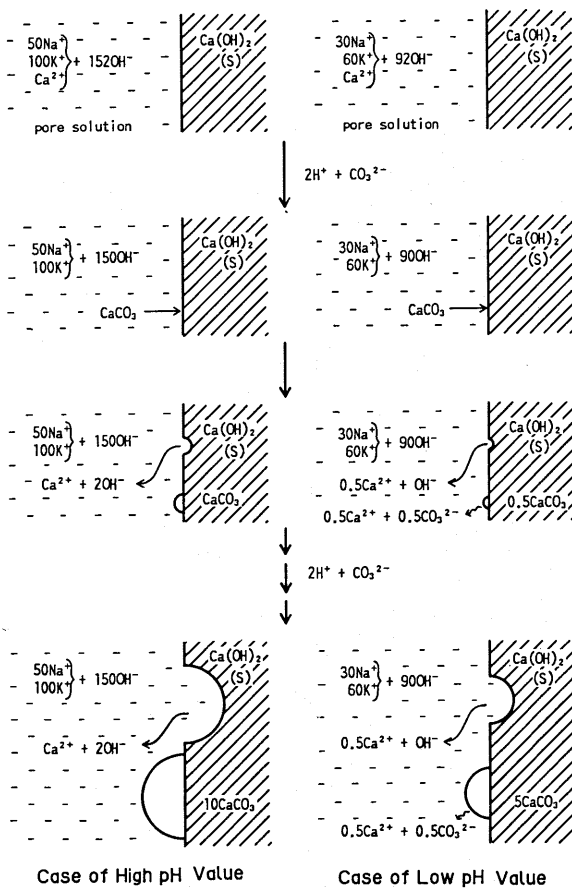Fig. 2 Carbonate ion speciation as a function of pH
(25 °C,1 atm pressure)[5]

Fig. 3

Case of High pH Value

50Na$^+$
100K$^+$ } + 152OH$^-$
Ca^{2+}

pore solution

Ca(OH)$_2$
(S)

2H$^+$ + CO$_3$$^{2-}$

50Na$^+$
100K$^+$ } + 150OH$^-$

CaCO$_3$ →

Ca(OH)$_2$
(S)

50Na$^+$
100K$^+$ } + 150OH$^-$

Ca^{2+} + 2OH$^-$

Ca(OH)$_2$
(S)

CaCO$_3$

2H$^+$ + CO$_3$$^{2-}$

50Na$^+$
100K$^+$ } + 150OH$^-$

Ca^{2+} + 2OH$^-$

Ca(OH)$_2$
(S)

10CaCO$_3$

Case of High pH Value

Case of Low pH Value

30Na$^+$
60K$^+$ } + 92OH$^-$
Ca^{2+}

pore solution

Ca(OH)$_2$
(S)

30Na$^+$
60K$^+$ } + 90OH$^-$

CaCO$_3$ →

Ca(OH)$_2$
(S)

30Na$^+$
60K$^+$ } + 90OH$^-$

0.5Ca^{2+} + OH$^-$

0.5Ca^{2+} + 0.5CO$_3$$^{2-}$ ←

Ca(OH)$_2$
(S)

0.5CaCO$_3$

30Na$^+$
60K$^+$ } + 90OH$^-$

0.5Ca^{2+} + OH$^-$

0.5Ca^{2+} + 0.5CO$_3$$^{2-}$

Ca(OH)$_2$
(S)

5CaCO$_3$

Case of Low pH Value

Fig. 3

Effect of pH of pore solution on progress of carbonation

H$_2$O(pH=13)

CO$_2$ H$_2$O   H$_2$O   CO$_2$

CO$_2$ H$_2$O   H$_2$O   CO$_2$
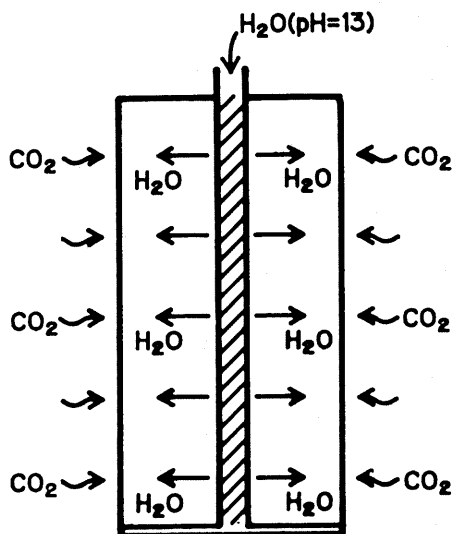
CO$_2$ H$_2$O   H$_2$O   CO$_2$

Fig. 4

Specimen modelling migration of pore solution (Thick-shell cylinder)

4.2 Method of Verification

The authors, in order to confirm the foregoing by experiments, made with pH
values of pore solutions raised by addition of sodium hydroxide to mixing water
and carried out accelerated carbonation tests. However, it has been pointed out
that when sodium hydroxide is added the hardened cement in mortar will be more
porous compared with the case of no addition, and even though a results of
carbonation of mortar with pH value of pore solution raised by addition of
sodium hydroxide, there is fear that it will become unclear whether it was
accelerated because of raising of the pH of pore solution, or because of the
increased porosity of the constitution. Therefore, it was decided to adopt the
technique of performing accelerated carbonation tests supplying solution of high
pH value to the carbonation front of a specimen such as shown in Fig. 4 after
that specimen of mortar using cement of comparatively low alkali content had
been thoroughly hardened, comparing the results obtained by this with the
results of accelerated carbonation tests performed using ordinary specimens not
supplied with such high-alkali solution, thus extracting only the pure effect of
pH of pore solution on the carbonation. Furthermore, in this study, the
technique of adding sodium chloride with which it is possible to raise pH of
pore solution without making hardened cement paste porous was also used.

4.3 EXPERIMENTAL

Two kinds of ordinary portland cement of Na_2O equivalent content(R_2O) of 0.31%
and 0.57% were used. Silica sand was used as fine aggregate, and ion-exchanged
water was used as mixing water. Mix design of mortar had water cement ratios of
0.40, 0.50, and 0.60, and unit water content were selected so that flow would be
180 for all mixes. The sodium hydroxide and sodium chloride used to raise pH of
the pore solution were converted by weight to Na_2O equivalent content, and were
added dissolved in mixing water so that the values adding R_2O of cement would be
0.9, 1.2 and 1.5 percent, respectively. The specimens were cylinders of ¢ 5 x 10
cm, with fog curing done at 20°C for 28 days after casting, and these were
furnished for accelerated carbonation tests and exposure tests in normal room
air. The accelerated carbonation tests were performed under the conditions of
carbon dioxide concentration 10%, relative humidity 60%, and temperature 20°C.
For thick-shelled cylinder specimens as shown in Fig.4, aqueous solution of pH =
13 was supplied throughout the period of carbonation from the holes provided at
the centers. Measurement of carbonation depth was performed by splitting to
obtain fractured surfaces of 5 x 10 cm, spraying immediately with 1% ethanol
solution of phenolphthalein, measuring the carbonated area using an image
analyzer with the uncolored portion as the carbonated area, and carbonation
depth was obtained from this value.

4.4 RESULTS AND DISCUSSION

Figs.5 and 6 both show the influences of alkali content in mortar on the depth
of carbonation, with sodium hydroxide used as alkalinity intensifier in these
cases. As these figures clearly show, in case of comparing mortars of identical
water cement ratios, carbonation is accelerated as alkali content is increased.
Fig.7 similarly shows the influence of alkali on depth of carbonation for
specimens exposed outdoors, and similarly to the cases of Figs.5 and 6 obtained
from accelerated carbonation tests, the tendency for carbonation to be
accelerated the higher the alkali content may be recognized.
It was made clear from the above-mentioned experimental results that alkali in
mortar is a factor for accelerating carbonation. However, as mentioned in 4.2,
it has been pointed out that the proportion of coarse pores in the pore
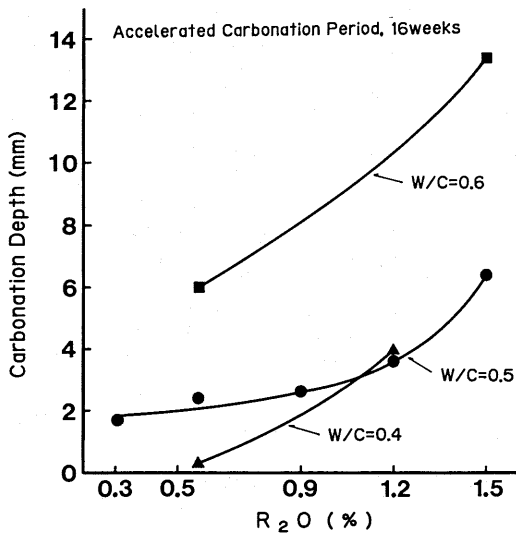
Fig. 5

Carbonation depth – R_2O relationship as influenced by water cement ratio
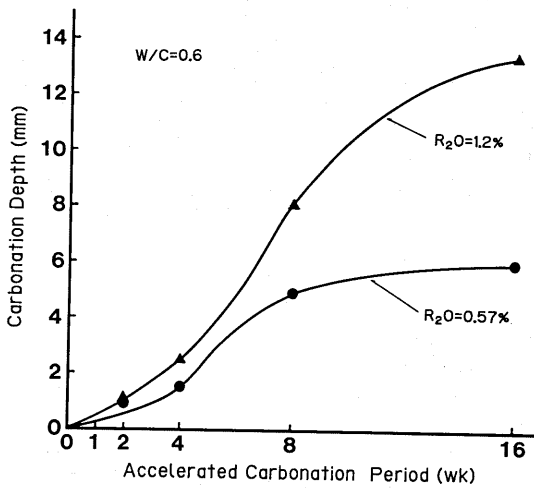

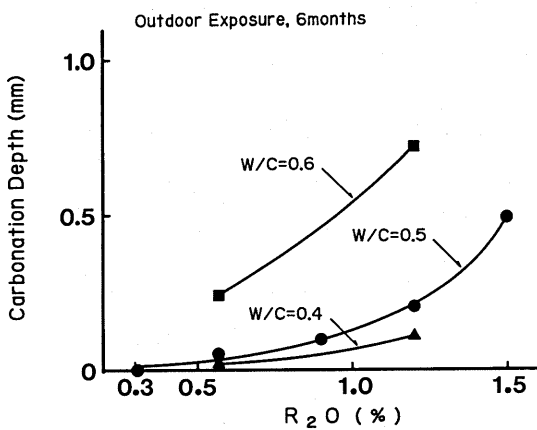Fig. 6

Effect of cement alkali on progress of carbonation

Fig. 7

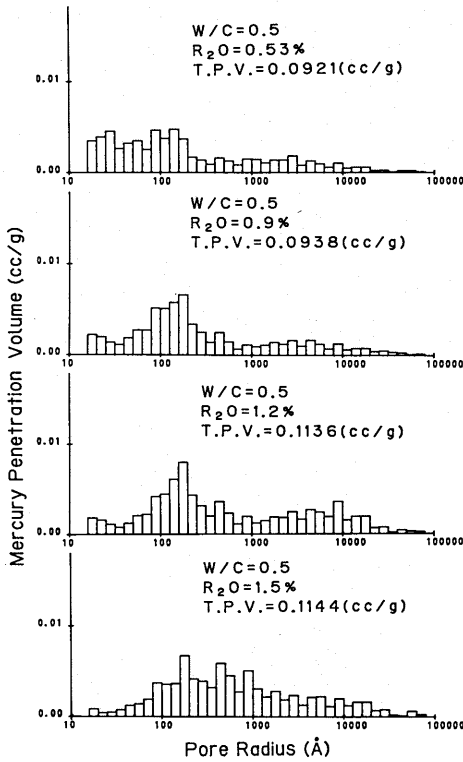Carbonation depth – R_2O relationship as influenced by water cement ratio

Fig. 8

Effect of R$_2$O on pore size
distribution of non-carbonated
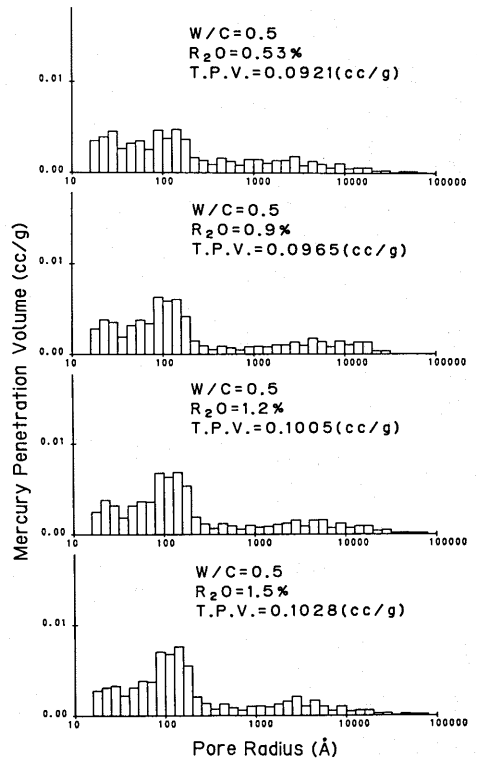mortars with sodium hydroxide
added.

Fig. 9

Effect of R$_2$O on pore size
distribution of non-carbonated
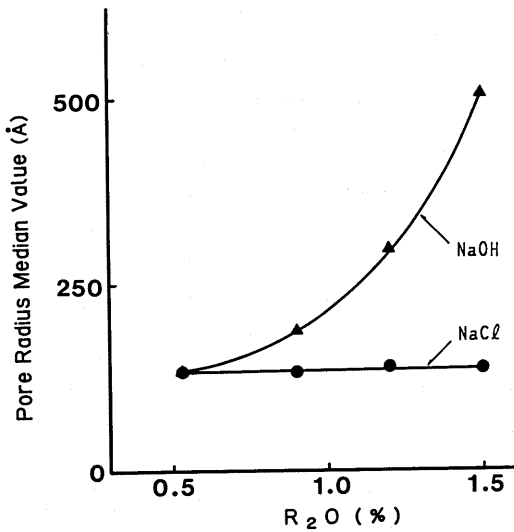mortar with sodium chloride
added.

Fig. 10
Effect of R$_2$O on pore radius
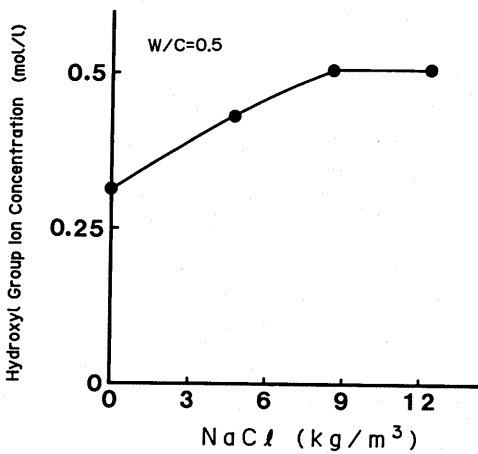median value of mortars with
sodium hydroxide and sodium
chloride

Fig. 11
Effect of sodium chloride
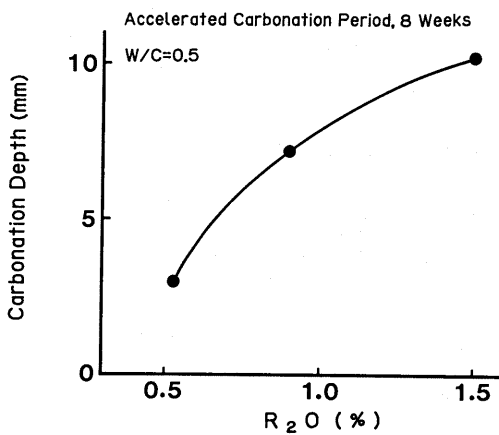content on hydroxil ion
concentration

Fig. 12

Carbonation depth – R$_2$O
relationship of mortar
with sodium chloride added.

structures of the hardened cement paste is increased when sodium hydroxide is added. Because of this, it cannot be judged from only the above-mentioned results whether carbonation had been accelerated by the chemical factor of alkali in pore solution or by the physical factor of increased number of coarse pores. Fig.8 shows pore-radius distributions of mortars with alkalinity intensified using sodium hydroxide, and it can be seen that the proportion made up by coarse pores is increased along with increase in alkali content.

On the other hand, Fig. 9 shows the pore-radius distributions of mortars with sodium chloride added, and in these cases the proportions made up by coarse pores are not increased as in the cases of adding sodium hydroxide. This is clear from Fig. 10 which summarizes the relationship of the two by median values of pore radius. In contrast, Fig. 11 which shows the relationship between amount of addition of sodium chloride and pH of pore solution, indicates that the pH of pore solution is definitely raised by the addition of sodium chloride.

The results above suggest that by carrying out carbonation tests of mortar with alkalinity intensified using sodium chloride, it is possible to investigate whether or not the pH value of pore solution is the factor which accelerates carbonation. Fig. 12 shows the results of accelerated carbonation tests of mortar adding sodium chloride, which indicate that carbonation is accelerated accompanying increase in alkali content, verifying that the pH of pore solution is the factor accelerating carbonation. On the other hand, Fig. 13 shows the results of accelerated carbonation tests in case of using thick-shelled specimens of the kind shown in Fig. 4, and when accelerated carbonation testing is done in a state of high-alkali solution supplied to the carbonation front, it is shown that carbonation of mortar is exceedingly accelerated, and together with the results in Figs.5 and 12, it was verified that the pH of pore solution is the chemical factor accelerating carbonation.
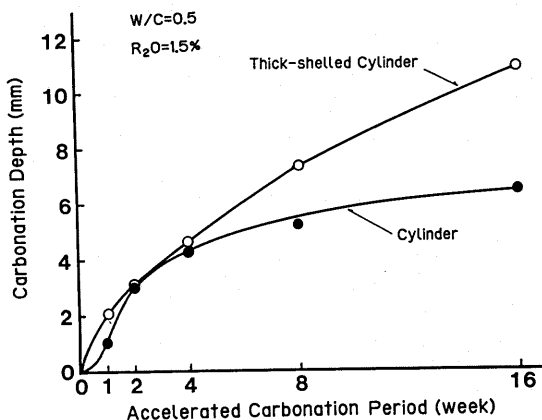

Fig. 13

Progress of carbonation of thick-shell cylinder and of cylinder

5.CONCLUSIONS

1) The rate of carbonation of concrete is governed by the pH value of pore solution, and the rate of carbonation is increased the longer that the condition of high pH of pore solution is maintained.
2) The most general condition for raising the pH of pore solution of concrete is the use of cement of high alkali content, but the sodium chloride introduced in concrete accompanying use of marine sand also raises the pH value of pore solution. Consequently, carbonation progresses rapidly in concrete structures using such materials.

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Table 1 Analysis of pore solution expressed from mortar

$$- R_2O = 0.52\% -$$

Age	Concentration (Equivalent /liter)				
Days	Ca^{++}	Na^+	K^+	$Na^+ + K^+$	OH^-
7	0.028	0.08	0.07	0.15	0.14
28	0.036	0.07	0.05	0.11	0.19
91	0.007	0.05	0.03	0.08	0.08
182	0.001	0.04	0.02	0.06	0.05

1) Cement:Ordinary portland cement
2) Water cement ratio:0.50
3) Sand/cement ratio:2.25
4) Pore solution extracted after storing specimens until specified age in atmosphere of 40°C,100% RH

Table 2 Analysis of pore solution expressed from mortar

$$- R_2O = 0.78\% -$$

Age	Concentration (Equivalent/liter)				
Days	Ca^{++}	Na^+	K^+	$Na^+ + K^+$	OH^-
1	0.008	0.13	0.32	0.45	0.43
3	0.008	0.25	0.41	0.65	0.58
7	0.006	0.27	0.45	0.72	0.64
28	0.006	0.27	0.45	0.71	0.64
72	0.004	0.20	0.45	0.66	0.59

1) Cement:Ordinary portland cement
2) Water cement ratio:0.40
3) Sand/cement ratio:0.75