THE MECHANISM OF FIXING Cl⁻ BY CEMENT HYDRATES
RESULTING IN THE TRANSFORMATION OF NaCl TO NaOH

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1. Introduction

It is known that the alkali aggregate reaction is enhanced by introducing NaCl into mortar or concrete[1, 2, 3]. A possible reason for this enhancement is the transformation of NaCl to NaOH in the pore solution resulting from the fixing of Cl⁻ by cement hydrates [3, 4, 5]. The mechanism by which NaCl is transformed to NaOH due to the fixing of Cl⁻, however, has not been thoroughly investigated. Furthermore the mechanism leading to fixing of Cl⁻ is not yet completely understood, either.

To understand the alkali aggregate reaction within concrete structures in an environment where NaCl is prevalent, such as in a marine environment, it is very important to determine the mechanism by which Cl⁻ is fixed leading to the transformation of NaCl to NaOH.

In this paper, this mechanism is discussed based on the results of the pore solution analysis of mortar using a high pressure pore solution expression technique.

2. Experimental

2.1 Procedures and Materials

The pore solution was extracted from the mortar, stored in airtight polypropylene containers, at ages from 30 minutes to 112 days after mixing using a high pressure pore solution extractor, and the concentration of OH⁻, K⁺, Na⁺, and Cl⁻ ions in the extracted pore solution was measured. As the mixing water, distilled water with three different initial NaCl addition, 0M, 0.52M, and 2.84M was used. The water-cement ratio was 50% and the sand-cement ratio was 1.43. Table 1 shows the chemical composition of the ordinary Portland cement used in the experiments. Silicious sand with a specific gravity of 2.61 and fineness modulus of 1.25 was used.

2.2 Extraction of pore solution

The pore solution from mortar between 5 and 6 hours after mixing was extracted by centrifuging. A high pressure pore solution extractor, shown in Fig. 1, was used for mortar aged more than 12 hours. The extractor was a press-fit double cylinder with an internal design pressure of 4000 kg/cm^2 and an internal diameter of 43 mm.

2.3 Analysis of pore solution

The Cl^- concentration was analyzed using the coulometric titration technique with a silver electrode (Corning model 921). The concentration of Na^+ and K^+ ions was analyzed using a flame photometer (Corning model 100). The measurement of OH^- ion concentration was carried out by titration with nitric acid using phenolphthalein as an indicator. The extracted pore solution was kept in airtight polypropylene sample bottles. The test for OH^- ions was completed on the same day as the pore solution was extracted to minimize the effects from carbonation.

3. Results

Figs. 2 to 5 show the changes in the concentration of OH^-, K^+, Na^+, and Cl^- ions. The concentration of OH^- ions changed slightly during the period 5 to 6 hours after mixing but increased remarkably thereafter up to 12 hours after mixing. The increase in the concentration of OH^- thereafter and up to the age of 112 days depended on the presence of NaCl. The mortar not containing NaCl exhibited a moderate increase after 12 hours as compared with the increase during the 6-12 hour period after mixing, and the concentration became stable at the age of 50 days. By contrast OH^- concentration of the mortar containing NaCl after the age of 12 hours increased significantly than that of the mortar without NaCl. This trend was affected little by the NaCl content, i.e., 0.52M and 2.84M. This marked increase in the concentration of OH^- ions after the age of 12 hours indicates that the addition of NaCl contributes to the increased concentration of OH^- ions in the pore solution. It is thought that several other mechanisms contribute to the OH^- increase besides the addition of NaCl. These mechanisms, however, are not mentioned here since they are outside the scope of this paper; they are presented elsewhere[5].

As to the concentration of K^+ ions, almost no change was seen until 12 hours after mixing, when the concentration began to increase moderately, reaching a constant at the age of 10 to 20 days. No rapid increase, as seen in the concentration of OH^- ions, was observed in the concentration of K^+ ions during the period between 5 or 6 hours and 12 hours after mixing.

The concentration of Na^+ ions was constant in the initial stages, increased at a moderate rate, and finally reached a constant value at the age of 50 days. The Na^+ ions observed in the mortar not containing NaCl originated from the cement and reached a final concentration of 0.12M. The concentration of Na^+ ions in the mortar containing 0.52M NaCl finally reached 0.62M. In the case of the mortar containing 2.84M NaCl, the concentration of Na^+ ions increased by 1.26M and totalled 4.10M. This increase is not solely due to the emission of Na^+ ions from the cement, since it is clear that the quantity of water is reduced as the cement hydrates, and this enriches the ion concentration in the pore solution. The increase in the concentration of Na^+ ions which cannot be attributed to emissions from the cement is considered due to this process.

The concentration of Cl^- ions in the mortar containing 0.52M NaCl did not change for a period of 12 hours after mixing. It dropped sharply thereafter, reached 0.26M at the age of 50 days, and was constant thereafter. The concentration of Cl^- ions in the mortar containing 2.84M NaCl increased to 3.9M by the age of 7 days but gradually declined to a value of 3.7M at the age of 56 days. The Cl^- decrease in the case of mortar containing 0.52M NaCl after the age of 12 hours indicates that Cl^- ions are fixed by the cement hydrates. In the case of mortar containing 2.84M NaCl the concentration of Cl^- ions had increased by the age of 7 days as the enrichment of pore solution due to the hydration of cement surpassed the fixing effect. The decrease in the concentration after the age of 7 days, however, shows that Cl^- ions were fixed.

As is clear in the experiment on mortar containing 0.52M NaCl, the concentration of Cl^- ions dropped steeply while that of Na^+ ions increased. This means that it is not Na^+ ions but Cl^- ions which are fixed by cement hydrates when NaCl is added to the mortar. When NaCl addition was 2.84M, the difference in the concentration between Na^+ and Cl^- ions was about 0.5M at the age of 112 days. It is difficult to explain this amount simply by the Na^+ ions originating in the cement. This also indicates that Cl^- ions are fixed when NaCl is added.

4. Discussion

4.1 Equilibrium between free and fixed Cl^- ions

The equilibrium between free and fixed Cl^- ions is considered at the age of 112 days when no change is taking place in the Cl^- concentration. If the quantity of fixed Cl^- ions is deemed to be the difference between the initial and final Cl^- concentration, errors will be introduced by the enrichment of pore solution due to the hydration of cement. Therefore, the quantity of fixed Cl^- ions was obtained by the concentration difference between Na^+ and Cl^- ions; the Na^+ ions attributable to cement was assessed to be 0.12M (the Na^+ concentration of the specimen without NaCl). According to this method, the quantity of fixed Cl^- ions in the mortar containing 0.52M NaCl was 0.24M at the age of 112 days (the quantity of free Cl^- ions was 0.26M). The quantity of fixed Cl^- ions in the mortar containing 2.84M NaCl was 0.38M (the quantity of free Cl^- ions was 3.63M). Fig. 6 shows the relationship between fixed Cl^- ions and free Cl^- ions based on these results including the results of Diamond [6]. The Diamond data, however, bases the quantity of fixed Cl^- ions on the difference between the initial and final concentrations; errors due to enrichment of the pore solution are included. The relationship between fixed Cl^- ions and free Cl^- ions is almost linear until the concentration of free Cl^- ions reaches 0.5M. When the concentration of free Cl^- ions exceeds 0.5M, the concentration of fixed Cl^- ions no longer increases. Although Fig. 6 seems inadequate due to the limited number of data and errors included, it qualitatively indicates the basic relationship between fixed and free Cl^- ions.

4.2 OH^- increase resulting from Cl^- fixing

The Cl^- concentration in the mortar with 0.52M NaCl started to fall at the age of 12 hours, indicating that fixing of Cl^- ions began at this age. The difference in the increase in the OH^- concentration between the cases with NaCl addition and without it became pronounced at the same age; the mortar containing NaCl exhibited a considerable increase in the OH^- concentration. These results indicate that the concentration of OH^- ions increases as Cl^- ions are fixed. The increase in the concentration of OH^- ions in the mortar containing
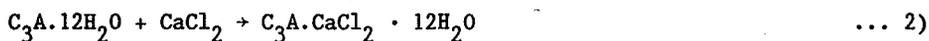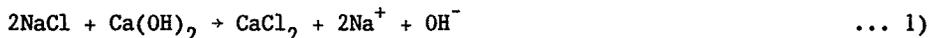
0.52M NaCl during the period from the age of 12 hours up to 112 days was 0.26M, and that of the mortar containing 2.84M NaCl was 0.27M. These increases in OH^- ion concentration nearly the same as the previously mentioned quantity of Cl^- ions fixed. Thus, OH^- ions equal to the quantity of fixed Cl^- ions are formed as the fixing of Cl^- ions proceeds.

4.3 Fixing mechanism of Cl^- ions

From the results of experiments the following four phenomena are found to occur as Cl^- ions are fixed. The mechanism by which Cl^- ions are fixed must be consistent with all these observations.

(1) When NaCl is added to mortar, Cl^- ions are fixed but Na^+ ions are not.
(2) Fixed Cl^- ions and free Cl^- ions are in equilibrium as shown in Fig. 6.
(3) As Cl^- ions are fixed, the concentration of OH^- ions increases.
(4) The quantity of fixed Cl^- ions is almost equal to the increase in OH^- ions.

The C_3A hydrate formed by the fixing of Cl^- ions may have the form $C_3A.CaCl_2.12H_2O$. A possible mechanism for the formation of such a complex by the fixing of Cl^- ions when NaCl is added is expressed by the following equations.

$$2NaCl + Ca(OH)_2 \rightarrow CaCl_2 + 2Na^+ + OH^- \qquad \cdots 1)$$

$$C_3A.12H_2O + CaCl_2 \rightarrow C_3A.CaCl_2 \cdot 12H_2O \qquad \cdots 2)$$

This mechanism satisfies all the observations mentioned above except (2). However, it is difficult to explain phenomenon (2) in terms of the dissolution of the complex.

The relationship between fixed and free Cl^- ions is very similar to the Langmuir adsorption isotherm. According to the theory that Cl^- ions are fixed by adsorption, proposed by Ramachandran[7], Cl^- ions are fixed by chemical adsorption of C_3S hydrates. Based on the experiments using pure C_3S, however, Goto[8] and Lambert[9] showed that the contribution of C_3S hydrates to the fixing of Cl^- ions is negligible. The relationship given in Fig. 6 suggests that it may be necessary to investigate the possibility of adsorption of Cl^- ions onto C_3A hydrates. According to Daimon[10] and Lee[11], monosulfate type C_3A hydrates such as $C_3A.CaCl_2.12H_2O$ have a common structure in which inter-layer substances are present between the plate-like crystals of $Ca_2.Al(OH)_6$, as schematically illustrated in Fig. 7; the inter-layer substances may be OH^-, Cl^-, or SO_4^{2-}. If Cl^- ions are in fact adsorbed by C_3A hydrates, they must be adsorbed by these plate-like crystals and take up inter-layer positions. This mechanism of adsorption of Cl^- ions onto C_3A hydrates can explain phenomena (1) and (2). It is difficult, however, to explain the increase in OH^- ion concentration as Cl^- ions are fixed using this mechanism. It is possible that Cl^- ions are adsorbed resulting in OH^- increase if both Ca^{2+} and Cl^- in equations 1) and 2) above are adsorbed simultaneously. However, it is improbable that positive and negative ions are adsorbed at the same time. In conclusion a mechanism in which Cl^- ions are fixed due to the adsorption of C_3A hydrates must be discarded.

Phenomenon (4), that is, the fact that the OH^- concentration increases by an amount almost equal to the quantity of Cl^- ions fixed, indicates the possibility of ion-exchange between Cl^- and OH^- ions. The equation below is thought

to express the affinity between negative ion-exchangers and Cl^-, OH^-, and SO_4^{2-} ions[12].

$$SO_4^{2-} > Cl^- \gg OH^- \qquad \ldots 3)$$

According to the equation, Cl^- ions easily replace the OH^- ions in negative ion-exchangers. Equation 3) can also explain how So_4^{2-} ions are fixed preferentially when both SO_4^{2-} and Cl^- ions coexist (e.g., in a marine environment). The negative ion-exchange between Cl^- and OH^- ions can be expressed by the following equation:

$$R-OH^- + Na^+ + Cl^- \rightarrow R-Cl^- + Na^+ + OH^{-H} \qquad \ldots 4)$$
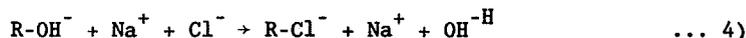
where R is an ion-exchanger. If the monosulphate type C_3A hydrate is an ion-exchanger, R is $Ca_2 \cdot Al(OH)_6$, the plate-like crystal described above. According to this reaction, NaCl added to concrete or mortar transforms to NaOH while Cl^- ions are fixed.

The mechanism by which Cl^- ions are fixed by ion-exchange can explain phenomena (1), (3), and (4). To make this theory fit the observations, the phenomenon (2), the relationship between fixed and free Cl^- ions as shown in Fig. 6, must be explained. The fact that the quantity of fixed Cl^- ions remains constant at the Cl^- concentrations higher than 0.5M can be explained by the assumption that the ion-exchange capacity of the negative ion-exchanger is exceeded at that stage and therefore ion-exchange no longer takes place even if the concentration of free Cl^- ions increases. It may be considered that ion-exchange is in equilibrium within the region where there is a nearly linear relationship between fixed Cl^- ions and free Cl^- ions. Fig. 6 indicates that the distribution coefficient Kd, defined by the following equation, is almost constant until the concentration of free Cl^- ions reaches 0.5M.

$$Kd = [Cl^-] \text{ fixed} / [Cl^-] \text{free} \qquad \ldots 5)$$

Since Kd is observed to be approximately 1, the quantity of fixed Cl^- ions is equal to the free Cl^- ions in the equilibrium condition. Though further study is required to find exact Kd value, the relationship indicated in Fig. 6 can be well explained by ion-exchange. Thus, the ion-exchange reaction between Cl^- and OH^- ions as expressed by equation 4) is a mechanism consistent with the four observations described above. The authors propose this as the mechanism of fixing Cl^- ions in concrete and consequently transforming NaCl into NaOH.

According to the experiments of Diamond[6], the concentration of OH^- ions in the pore solution when NaCl is added is higher than that when $CaCl_2$ is added. This can also be explained by the ion-exchange mechanism. When $CaCl_2$ is added, $Ca(OH)_2$ is formed by the reaction in equation 4). Since the pore solution is always saturated with $Ca(OH)_2$, even if the reaction of equation 4) does not occur, the formation of $Ca(OH)_2$ due to this reaction does not contribute to the increase in concentration of OH^- ions. This results in the observed difference in the concentration of OH^- ions.

5. Conclusion

The following four phenomena are observed when the fixing of Cl^- ions occurs.

(1) When NaCl is added to mortar, Cl^- ions are fixed but Na^+ ions are not.
(2) Fixed and free Cl^- ions are in equilibrium as shown in Fig. 6.
(3) When Cl^- ions are fixed, the concentration of OH^- ions increases.
(4) The quantity of fixed Cl^- ions is almost equal to the increase in the concentration of OH^- ions.

As a mechanism for the fixing of Cl^- ions which is consistent with all the above phenomena, the authors propose the ion-exchange reaction for Cl^- and OH^- ions as follows;

$$R - OH^- + Na^+ + Cl^- \rightarrow R\text{-}Cl^- + Na^+ + OH^-$$
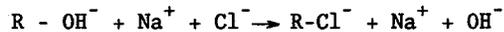
The NaCl added to mortar or concrete follows this reaction and NaOH is formed, which results in enhancement of the alkali aggregate reaction.

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Table 1 Chemical composition of the cement used

Ignition loss	Insoluble residue	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Total alkalies (Na_2O eq.)	TiO_2	P_2O_5	MnO
1.4	0.5	19.0	5.1	2.4	65.0	1.0	2.9	0.19	0.46	0.49	0.22	0.10	0.06
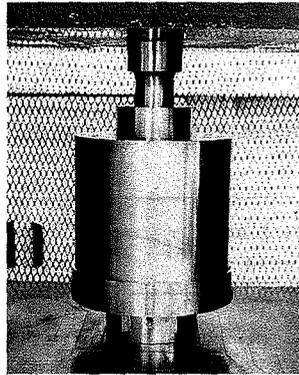
Fig. 1 High pressure pore solution extractor
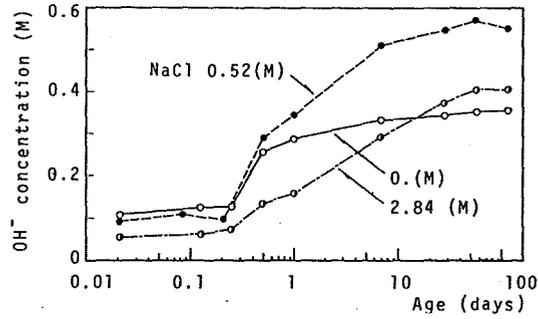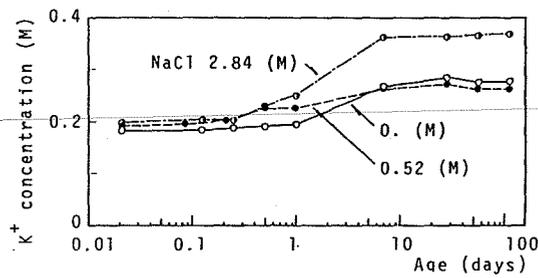

Fig. 2 OH^- concentration in the pore solution

Fig. 3 K^+ concentration in the pore solution
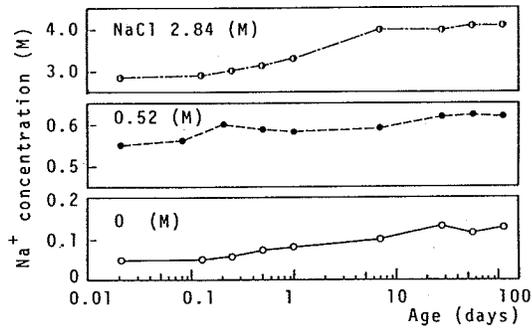
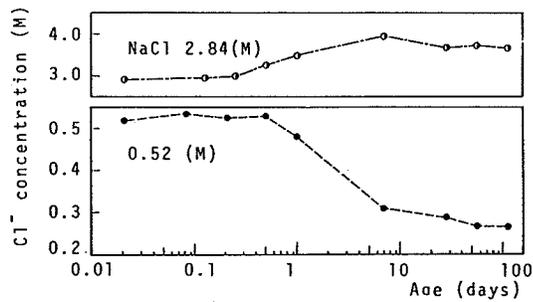Fig. 4 Na⁺ concentration in the pore solution

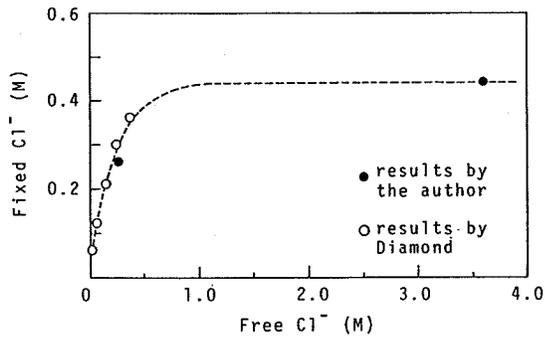Fig. 5 Cl⁻ concentration in the pore solution
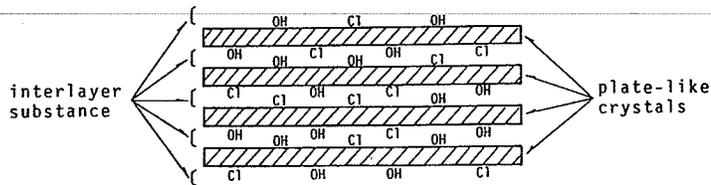

Fig. 6 Relation between fixed and free Cl⁻

Fig. 7 Schematic representation of the lamellar structure
of mono-sulphate type C_3A hydrates