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BEHAVIOR OF VARIOUS IONS IN PORE SOLUTION IN NaCl-BEARING MORTAR WITH AND WITHOUT REACTIVE AGGREGATE AT EARLY AGES

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ABSTRACT

It is important from the use of sea-dredged sands and gravels as an aggregate to elucidate the mechanisms of effects of added NaCl on the alkali silica reaction in concrete. Analyses of the pore solution in mortars with and without reactive aggregate were carried out to investigate the details of behavior of various ions in the mortars in the presence of NaCl. Relatively high SO_4^{2-} ion concentrations were found to be maintained in the pore solution in reactive aggregate-free mortars made with a high alkali cement. However, the second reduction in SO_4^{2-} ion concentration following the first rapid reduction for the period of 4 to 12 hours occurred only in the mortars containing reactive aggregate, suggesting the formation of ettringite. *Copyright © 1997 Elsevier Science Ltd*

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Introduction

In relation to the use of sea-dredged sands and gravels contaminated with sodium chloride, some workers have proposed explanations for the exacerbation of the alkali silica reaction due to sodium chloride added at the mixing stage in mortars containing reactive aggregate (1, 2, 3).

Nixon, Page et al. (1) concluded that an elevation of OH^- ion concentration of the pore solution caused by the introduction of sodium chloride at the mixing stage aggravates the damage of concrete from the alkali silica reaction. This conclusion was derived on the basis of pore solution composition of various cement pastes cured for a relatively long period of 84 days.

Kawamura and Ichise (2) related the behavior of OH^- and Cl^- ions in the pore solution in mortars with a highly reactive aggregate of Beltane opal to their expansions, leading to a somewhat peculiar conclusion that the alkali silica reaction progressed in the early stage of the process without greater reduction in OH^- ion concentration in reactive aggregate-containing mortars than reactive aggregate-free mortars. In their study, leakage of OH^- and Cl^- ions from specimens with reactive aggregate was not taken into consideration, as pointed out by Helmuth and Stark (3). However, their results of pore solution composition obtained from specimens exposed to a moist environment for periods up to at least 24 hours may be reliable because amounts of ions leaking out from specimens were not so great during such a short period. In their study, however, it remained ambiguous whether chloride-bearing ettringite was formed during early stages of cement hydration in the presence of a highly reactive aggregate and a large amount of NaCl.

Diamond and Penko (4) revealed the processes of the conversion of the alkalies in cement to alkali hydroxide in relation to the alkali silica reaction by pursuing the details of behavior of Na^+, K^+, OH^- and SO_4^{2-} ion in pore solutions of pastes prepared with various cements. Such an approach is also useful to elucidate effects of added NaCl on the alkali silica reaction in mortar.

In this study, detailed analyses of pore solutions expressed from mortars with and without reactive aggregate were carried out for deeper understanding of effects of NaCl on the processes of the alkali silica reaction in mortar and its expansion.

Experimental

Materials. Blue Circle calcined flint and Beltane opal were used as a reactive aggregate. The former has a size fraction of 2.5 mm to 0.6 mm; the latter less than 0.6 mm. The results of chemical test for the reactive aggregates are given in Table 1. The Japanese standard sand was used as a non-reactive aggregate. A high alkali cement with an equivalent percentage of Na_2O of 1.12 was used. Its chemical composition is given in Table 2.

Mix Proportion of Mortar. Mortars were prepared with a total aggregate:cement ratio of 0.75 and water:cement ratio of 0.45. In the mortars with reactive aggregate, the calcined flint and Beltane opal were introduced at a pessimum proportion of 65% and 10%, respectively, which had been determined in advance. The chloride addition level was 1% by mass of cement.

Expansion Test. Mortar bars, 25.3 mm by 25.3 mm by 285.5 mm, were demoulded about 24 hours after casting and, then sealed in polyethylene sacks for preventing the alkalies, OH^-, Cl^- ions from leaking out. Length changes of mortar bars were measured storing them in a moist atmosphere at 38°C.

Analysis of Pore Solution. Mortar cylinders, ϕ 40 mm by 100 mm, sealed in polyethylene sacks were stored in a moist atmosphere at 38°C for prescribed periods. At early ages up to 3 hours, pore solutions were centrifugalized from mortars by the use of special containers. After that, pore solutions were expressed under the pressure of 400 to 500 MPa by the high pressure apparatus. The Na^+, K^+ and Ca^{2+} ion concentration were determined by atomic absorption, the OH^- ion concentrations by titration with HCl, and SO_4^{2+} and Cl^- ion

TABLE 1

Chemical Composition of Cement (%)

CaO	$Si0_2$	Al_2O_3	Fe_2O_3	SO_3	MgO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	Ig • Loss
62.5	20.1	4.7	3.2	3.3	2.5	0.41	1.08	0.26	0.06	0.06	1.2

TABLE 2

Alkali : Reactivity of Reactive Aggregate (ASTM C289)

	Rc(m mol/l)	Sc(m mol/l)
Beltane Opal	225	1200
Calcined Flint	70	1063

concentrations by ion chromatography. No adjustment for reduction in water content through progressive hydration was made. All of the mortar cylinders were tightly sealed by polyethylene sacks so that little ions leaked out during storage.

Results and Discussion

Behavior of Various Ions in Reactive Aggregate Free-Mortars. Fig. 1 shows changes of OH^-, Cl^-, SO_4^{2-} ion concentration with time in the pore solutions expressed from reactive aggregate-free mortars with and without NaCl. As already revealed by Diamond and Penko (4), the results indicating the process of generation of high alkali hydroxide concentration as a consequence of the formation of ettringite were obtained in the mortars without NaCl. However, an attention should be paid to relatively great differences in SO_4^{2-} ion concentration between the mortars with and without NaCl. The rapid and progressive reduction in SO_4^{2-} concentration with time occurred for the period of 4 to 12 hours in both mortars with and without NaCl. However, the SO_4^{2-} ion concentration (0.14N) in the mortar with NaCl did not reduce to so low level as in the mortar without NaCl (0.034N). Since the reduction in SO_4^{2-} ion concentration in pore solution is due to the formation of ettringite (4), less reduction in SO_4^{2-} ion concentration in the mortar with NaCl than without NaCl indicates that a part of C_3A in NaCl-bearing mortar was consumed through the formation of other complex than ettringite, e.g. calcium chloroaluminate. Furthermore, as shown in Fig. 1, the SO_4^{2-} ion concentration gradually increased with time at later than 72 hours. This may be an apparent phenomenon caused by the reduction in water content through slowly progressive hydration.

The OH^- ion concentrations in the pore solutions in mortars with NaCl slightly exceeded those in mortars without NaCl at later than 24 hours. Only a little increase in OH^- ion concentration caused by the addition of a large amount of NaCl to considerably high alkali cement mortars can be explained by the exhaustion of C_3A in the high alkali cement mortar, as Nixon and Page et al. gave the same explanation to a similar result (1). Such small differences in OH^- ion concentration between mortars with and without NaCl must give rise to little difference in the extent of the alkali silica expansion between both, unless other mechansims than the rise of OH^- ion concentration due to the addition of NaCl are taken into consideration.

The Cl^- ion concentration slowly decreased with time expect that it increased for the period of 3 to 6 hours. The increases in Cl^- ion concentration during the period may partly reflect the rapid reduction in water content through active progress of hydration. The slow reduction in Cl^- ion concentration indicates the formation of calcium chloroaluminate. The formation of the product accompanies the consumption of C$_3$A. Thus, this fact does not contradict with less reduction in SO$_4^{2-}$ ion concentration in mortars with NaCl.

Behavior of Various Ions in Reactive Aggregate-Containing Mortar. In order to reveal effects of reactive aggregate on the behavior of various ions in the mortars with and without NaCl, the OH$^-$, SO$_4^{2-}$ and Cl$^-$ ion concentrations in pore solutions expressed from the mortars containing the two types of reactive aggregate with different reactivity are plotted against time, as shown in Figs. 2 and 3. The behavior of these ions in the mortars with different reactive aggregates is found to be different from each other.

As shown in Figs. 2 and 3, differences in SO$_4^{2-}$ ion concentration between the mortar with and without NaCl at 12 hours were about 0.1N, which was almost the same in the reactive aggregate-free mortar (Fig. 1). However, the behavior of SO$_4^{2-}$ ions in the pore solutions for periods later than 12 hours was different for the mortars with different aggregates.

The OH$^-$ ion concentrations during the first 4 hours in all the three mortars without NaCl were a little higher than in the NaCl-bearing mortars (Figs. 1, 2 and 3). The OH$^-$ ion concentration itself during the period was considerably low. After that, however, the OH$^-$ ion concentration increased to the maximum level of 0.58N to 0.79N. The maximum OH$^-$ ion concentrations were different for different types of reactive aggregate. It was also affected by the addition of NaCl. After the attainment of the maximum level, the OH$^-$ ion concentration in Beltane opal-containing mortars with and without NaCl rapidly reduced to the level of 0.34N and 0.27N, respectively (Fig. 2). This result shows that, for the period up to at least 3 days, the alkali silica reaction actively progressed in the mortars containing Beltane opal. As shown in Fig. 3, slower reduction in OH$^-$ ion concentration from the maximum level in the calcined flint-containing mortars indicates that the alkali silica reaction in the mortars more slowly progressed than in Beltane opal-containing mortars.

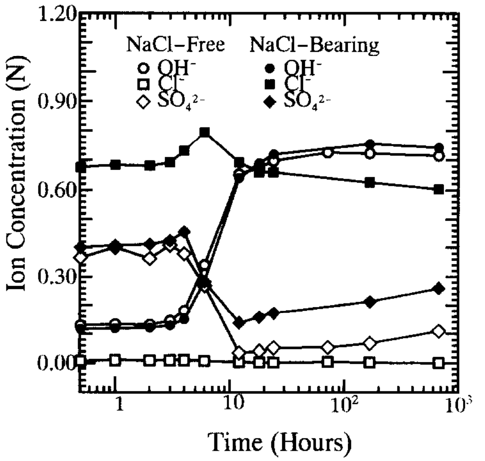

FIG. 1.

Changes of OH$^-$, Cl$^-$, and SO$_4^{2-}$ ion concentrations with time for reactive aggregate-free mortars with and without NaCl.

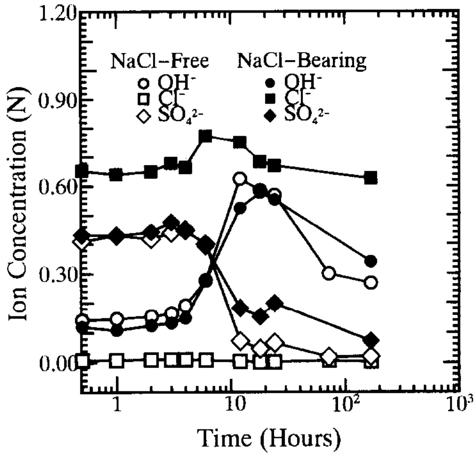

FIG. 2.

Changes of OH$^-$, Cl$^-$, and SO$_4^{2-}$ ion concentrations with time for Beltane opal-containing mortars with and without NaCl.

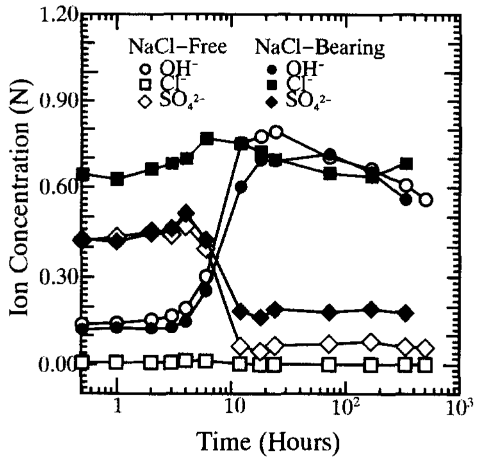

FIG. 3.

Changes of OH$^-$, Cl$^-$, and SO$_4^{2-}$ ion concentrations with time for the calcined flint-containing mortars with and without NaCl.

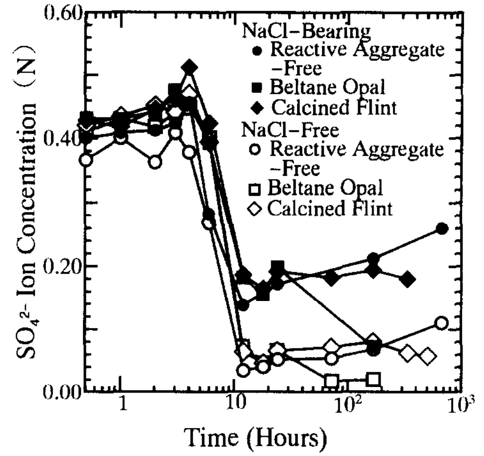

FIG. 4.

Changes of SO$_4^{2-}$ ion concentration with time for various mortars.

Another result to be noted is the behavior of SO$_4^{2-}$ ions after the rapid reduction during the period of 4 to 12 hours which appears to be in response to the changes in OH$^-$ ion concentration and expansion of the mortars. In Fig. 4, SO$_4^{2-}$ ion concentrations for all the mortars are plotted against time for contrasting differences in the behavior of SO$_4^{2-}$ ion between different mortars. In the NaCl-bearing mortars with Beltane opal, a rapid reduction in SO$_4^{2-}$ ion concentration occurred for the period between 24 and 72 hours. For the same period, the OH$^-$ ion concentration rapidly decreased (Fig. 2).

On the other hand, as shown in Fig. 4, a relatively high SO$_4^{2-}$ ion concentration after the first rapid reduction in NaCl-bearing mortars with the calcined flint lasted for far longer periods than in the mortars with Beltane opal, followed by the second reduction in SO$_4^{2-}$ ion concentration for the period between 72 and 336 hours. Similar changes in SO$_4^{2-}$ ion concentration were also found in the NaCl-free mortars containing reactive aggregate, although overall SO$_4^{2-}$ ion concentrations were considerably lower than the NaCl-bearing mortars. At any rate, as shown in Fig. 4, the second reduction in SO$_4^{2-}$ ion concentration occurred only in the mortars containing reactive aggregate.

As shown in Figs. 1, 2 and 3, the reduction of OH$^-$ ion concentration in mortars with reactive aggregate from the level for the reactive aggregate-free mortar had started before the second reduction in SO$_4^{2-}$ ion concentration occurred. The second reduction in SO$_4^{2-}$ ion concentration is supposed to be associated with incorporation of SO$_4^{2-}$ ions into alkali-silica gels and/or other reaction products, e.g. ettringite. As shown in Figs. 2 and 4, in the mortars containing Beltane opal, the reduction in OH$^-$ ion and SO$_4^{2-}$ ion concentration, and a rapid expansion (Fig. 6) simultaneously occurred for the period between 24 and 72 hours. Therefore, it is impossible to infer what phenomena were associated with the second dissipation of SO$_4^{2-}$ ions from the results for the mortars containing Beltane opal.

A comparison between OH^- ion concentrations in NaCl-bearing mortars with and without the calcined flint (Figs. 1 and 3) indicates that, after at least 24 hours, OH^- ions were consumed by the alkali silica reaction. However, little change in SO_4^{2-} ion concentration was found during the active progress of the chemical reaction process in the alkali silica reaction in the mortars. It is conjectured from these results that SO_4^{2-} ions were not incorporated into alkali-silica gels. A number of cracks which were caused by the expansion occurring after the chemical reaction process of the alkali silica reaction progressed to some extent, may be available for the formation of secondary ettringite. In fact, Diamond and Ong (5, 6) have evidenced the deposition of secondary ettringite in cracks caused by the alkali silica reaction in steam cured mortars.

Fig. 5 shows differences in Cl^- ion concentration between mortars with and without reactive aggregate. During the first 6 hours, the Cl^- ion concentration in mortars with reactive aggregate was a little lower than in mortar without reactive aggregate. After that, the Cl^- ion concentration in mortars with reactive aggregate did not so rapidly decrease as in mortar without reactive aggregate. In our previous study (2), far more Cl^- ions were dissipated from the pore solution in the reactive aggregate-containing mortar than in the reactive aggregate-free mortar for the period of 12 to 24 hours. However, as shown in Fig. 5, the Cl^- ion concentration in the reactive aggregate-containing mortar was even a little higher than in the reactive aggregate-free mortar for the same period. This discrepancy may be due to differences in the composition of a high alkali cement used and in the grading of reactive aggregate. These differences were also reflected in a great difference in expansion between Beltane opal-containing mortars used in our present and previous study. In the previous study (2), at 3 days, expansions for the mortar with NaCl were approximately five times as high as those for the NaCl-free mortar. However, as described in the following, in this study, the addition of NaCl even reduced the expansion at 7 days by about 10%.

As far as the results obtained in this study are concerned, the presence of reactive aggregate a little raised Cl^- ion concentration. However, in the previous study (2), a large amount of Cl^- ions were taken up from the pore solution in the presence of reactive aggregate. The composition of the high alkali cement and the grading of Beltane opal used in the studies were different from each other. Such differences appear to greatly influence the behavior of various ions at

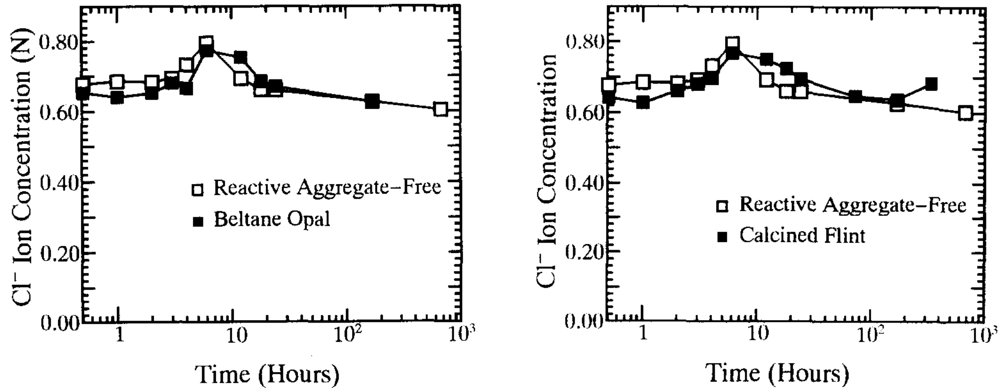

FIG. 5.

Changes of Cl^- ion concentration with time for Beltane opal ((a))-and the Calcined flint ((b))-containing mortars.

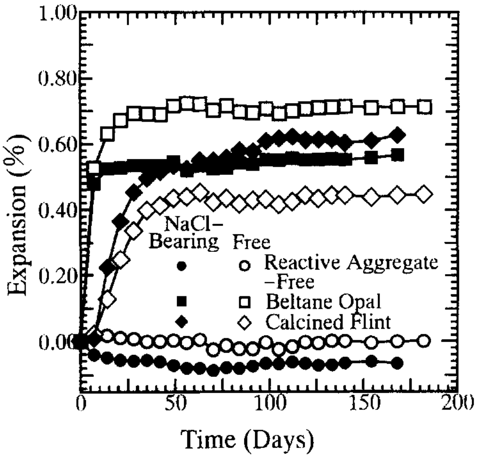

FIG. 6
Expansion curves for various mortars.

early stages of cement hydration in reactive aggregate-containing mortar with a large amount of NaCl.

Relationship Between Behavior of Various Ions and Expansion. Fig. 6 shows expansion curves for mortars containing Beltane opal and the calcined flint. As shown in this figure, the addition of NaCl reduced expansion for the mortar containing Beltane opal. Presumably, the alkali content in the mortar with NaCl might be over the pessimum in this reactive aggregate-containing mortar system, as conjectured from a little increase in OH^- ion concentration in the pore solution by the addition of NaCl (Figs. 1 and 2). Thus, it is impossible to relate the effects of the addition of NaCl on the behavior of various ions in the pore solution to expansion for the mortar containing Beltane opal.

However, expansion for the mortar containing the calcined flint was increased by the addition of NaCl from the early stage of expansion. Only in the mortar with NaCl, steadily increasing expansions were found even after about 50 days. The increase in expansion for the mortar in later stages may be possibly related to the second reduction in SO_4^{2-} ion concentration at later than 7 day (168 hours) (Fig. 4).

It is umambiguous that an increase in OH^- ion concentration due to the addition of NaCl promotes the alkali silica reaction (1). Furthermore, the Cl^- ion itself certainly accelerates the alkali silica reaction (3, 7). The second reduction in SO_4^{2-} ion concentration in the pore solution at later than a certain time, suggesting the formation of secondary ettringite in the alkali silica reaction-induced cracks, should be also taken into consideration in the mechanisms of an increase in expansion for the mortar with added NaCl.

Conclusions

(1) Considerably higher SO_4^{2-} ion concentrations were maintained in NaCl-bearing mortars than in NaCl-free mortars, when a high alkali cement was used.

(2) A rapid reduction of SO_4^{2-} ion concentration in the pore solution occurred between 4 and 12 hours in all the mortars. After that, however, the second reduction in SO_4^{2-} ion concentration occurred only in the mortars containing reactive aggregate.
(3) The second reduction in SO_4^{2-} ion concentration appears not to be associated with the formation of alkali-silica gels.
(4) The composition of cement, and the grading and reactivity of aggregate seems to influence the behavior of various ions in the pore solution in mortar containing reactive aggregate and NaCl at early ages.
(5) The suggestion that ettringite was being formed at the time of the second dissipation of SO_4^{2-} from pore solution, was obtained. The formation of ettringite in mortars containing reactive aggregate and NaCl should be taken into consideration in the mechanisms of an increase in expansion for the mortar with added NaCl.

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