Pergamon

Cement and Concrete Research, Vol. 26, No. 12, pp. 1809-1819, 1996

0008-8846/96 $15.00 + .00

PII S0008-8846(96)00178-0

ALKALI-SILICA REACTION AND PORE SOLUTION COMPOSITION IN MORTARS IN SEA WATER

Mitsunori Kawamura and Katsunobu Takeuchi
Department of Civil Engineering, Kanazawa University,
Kanazawa, Ishikawa 920, Japan

(Refereed)
(Received July 30, 1996; in final form October 9, 1996)

ABSTRACT

The promotion of expansion of mortars containing a reactive aggregate in 1N NaCl solution at 38°C was attributed to a rise of OH^- ion concentration in the pore solution in the mortars. However, it is ambiguous whether the promotion of expansion of mortars in sea water at a room temperature can be explained in the same way as in NaCl solution at an elevated temperature. This study aims at pursuing the expansion behavior of mortars containing a reactive aggregate relating it to their pore solution composition and the extent of alkali-silica reaction occurring within reactive grains. The alkali-silica reaction in mortars in sea water and 0.51N NaCl solution at 20°C appears to progress differently from that in mortars in 1N NaCl solution at an elevated temperature of 38°C. The promotion of expansion of mortars in sea water at 20°C was found to be responsible for an effect of Cl^- ions on the alkali-silica reaction at early stages of immersion. Only when OH^- ion concentration in the pore solution was relatively high, NaCl and sea water could accelerate the alkali-silica reaction in mortars at 20°C. *Copyright © 1996 Elsevier Science Ltd*

Introduction

It has been pointed out by some workers that the expansion of mortar and concrete containing reactive aggregate was promoted in sea water and NaCl solution (1, 2, 3). However, it has been also reported that the expansion of mortars containing Pyrex glass was accelerated in 1N NaCl solution at 40°C, but that not in the same solution at 20°C (4). The expansion behavior of mortar and concrete containing reactive aggregate in sea water appears to greatly vary with the mix proportion, the alkali content of cement, and the temperature and concentration of solution. It has been evidenced that Cl^- ions play a significant role in the alkali-silica reaction (5, 6). Considerably steep gradients of Cl^- and OH^- ion concentration exist within mortar and concrete specimens during immersion in sea water and NaCl solution (7). Thus, the expansion behavior of mortar and concrete in sea water must depend on the shape and size of specimens as well. It may be difficult to attain to a conclusive conclusion on effects of sea water on the alkali-silica reaction in concrete only from the apparent expansion behavior of mortar under various combinations of factors listed above.

The present authors revealed that the promotion of expansion of reactive aggregate-bearing mortars in 1N NaCl solution at an elevated temperature of 38°C was responsible for a rise of OH^- ion concentration in the pore solution (6). Some results showing that a part of expansion of mortars with relatively large amounts of added NaOH in the solution was caused by the formation of ettringite, were also obtained (8). However, it still remains ambiguous whether effects of sea water on the expansion of concrete containing reactive aggregate at an ordinary temperature can be explained in the same manner as in 1N NaCl solution at 38°C.

Relating the expansion behavior of reactive aggregate-bearing mortar in sea water to the changes in the pore solution composition and the microhardness within reactive grains in the mortar may shed light on the mechanisms of effects of sea water on the alkali-silica expansion in concrete.

In this study, the expansion test for mortars containing the Blue Circle calcined flint in a moist environment, an artificial sea water, 0.51N NaCl solution and distilled water at 20°C was carried out. Mechanisms of expansion of the mortars in sea water at 20°C were discussed pursuing time-dependent changes in the pore solution composition, microhardness within reactive grains, and ettringite and calcium hydroxide content in the mortars.

Experimental

Materials. A high alkali ordinary Portland cement, the chemical composition of which is given in Table 1, was used. The reactive aggregate used was the calcined flint (C.F.) which was supplied by Blue Circle Industries PLC. The size of the reactive aggregate ranges from 2.35 mm to 1.00 mm. As detailed by Lumley (9), the reactive aggregate consists of about 96% tetragonal cistobalite and its mean crystallite size is approximately 60 nm. The potential reactivity of C.F. determined according to ASTM Chemical Test, C289 is presented in Table 2. The density and absorption of the reactive aggregate were 2.29 and 1.79%, respectively. The Japanese standard sand used as a non-reactive aggregate mainly consists of quartz.

Expansion Test. Mortar bars, 25.3 by 25.3 by 285.5 mm, were prepared at a total aggregate:cement ratio of 0.75 and a water:cement ratio of 0.4. The mortars with various alkali:C.F. ratios of 0.01, 0.015, 0.03, 0.05, 0.08 and 0.15 were produced by changing the replacement level of total aggregate by C.F.. They were cured in a container maintained at 20°C and > 95% R.H. for 56 days, and then immersed in sea water, 0.51N NaCl solution and distilled water at 20°C. The composition of sea water is given in Table 3. A number of mortar bars were immersed in a far larger amount of solution than the total volume of mortar bars. Whenever the Cl^- ion concentration in a solution changed by 5%, the original solution was replaced by the new solution to maintain its concentration at a prescribed level. Measurements of length changes of mortar bars with time were initiated immediately after demoulding. The value of expansion was the average of two measurements.

TABLE 1

Chemical Composition of Cement (%)

Ig.loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	P_2O_3	MnO
0.7	21.1	4.9	3.1	65.1	1.4	2.0	0.50	0.72	0.28	0.10	0.05

TABLE 2

Reactivity of Calcined Flint

Rc (mmol/l)	Sc (mmol/l)
70	1063

Microhardness Test. Mortar bars with an alkali:C.F. ratio of 0.05 for the expansion test were cut into cubic blocks of 20 by 25 by 25 mm one day after casting. The 25 by 25 mm faces of each block were coated with a silicon resin type sealant for various ions to be allowed to diffuse into the mortar blocks only from the 20 by 25 mm faces. These mortar blocks were stored under the same curing regime as in the expansion test. The silicon resin coating on the two faces was removed at a prescribed time after the initiation of immersion, and then one of the faces was polished on the rotor using a set of SiC polishing paper.

The microhardness measurements tester with a Vickers indenter was used to measure the microhardness within a reacting aggregate grain along the longest radius at intervals of about 10 µm or 20 mm. Two grains with a diameter of about 2 mm appearing in the area within 5 µm deep from a surface of mortar blocks were selected for microhardness measurements. The value of micohardness was the average of measurements for two grains.

Pore Solution Expression. Pore solutions were extracted from ϕ 40 by 100 mm cylinders made with the same mortar with an alkali:C.F. ratio of 0.05 as used in the expansion test by the high pressure apparatus (10). The OH^- ion concentration was determined by titration against hydrochloric acid to the phenolphthalein end point. The Na^+, K^+ and Ca^{2+} ion concentrations were determined by atomic absorption, the OH^- ion concentrations by titration with HCl, and Cl^- ion concentrations by ion chromatography. The balance in concentration between cations and anions was good.

Differential Thermal Analysis. Mortar samples cut off from portions within 5 mm deep from the exposed surfaces of specimens were used in the differential thermal analysis. The heating rate and the amount of sample were 10 °C/min and 25 mg, respectively. The content of ettringite in mortars was obtained by the use of a hydrated clinker as the reference material according to the method proposed by Odler and Abdul-Maula (11). The chemical composition of the clinker used is given in Table 4. The relative content of ettringite and $Ca(OH)_2$ in mortars (Figs. 7 and 8) was evaluated by the ratio of the area covered by an endothermic peak for a mortar to that for the 28 days old standard sand mortar in a moist environment.

Results and Discussion

Expansion Behavior of Mortars. Fig. 1 (a), (b), (c) and (d) shows expansion curves of mortars in a moist environment (> 95% R.H.), sea water, 0.51N NaCl solution and distilled

TABLE 3

Composition of Sea Water (g/l)

Cl	Na	SO_4	Mg	K	Ca	HCO_3	Br	BO_3
19.13	10.75	1.89	1.37	0.38	0.32	0.08	0.06	0.04

TABLE 4

Chemical Composition of Clinker (%)

Ig.loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	P_2O_3	MnO
0.1	22.5	5.7	3.0	65.4	1.6	0.2	0.34	0.50	0.32	0.14	0.10

water at 20°C, respectively. It is found from these expansion curves that the mortars showed the largest expansion at the alkali:C.F. ratio of 0.015 in all the storage conditions. As shown in Fig. 1 (a), the expansion of mortars in a moist environment proportionally increased with time, while mortars in sea water and NaCl solution rapidly expanded during the first month of immersion, followed by the cease of expansion or the slow expansion. Especially, the expansion of mortars with an alkali:C.F. ratio of 0.015 and 0.03 in sea water and NaCl solution for early stages of immersion were rapid. However, as shown in Fig. 1 (d), the expansions of mortars in distilled water are found to be smaller than in other environmental conditions. At any rate, some of the mortars in the saline solutions far rapidly expanded than

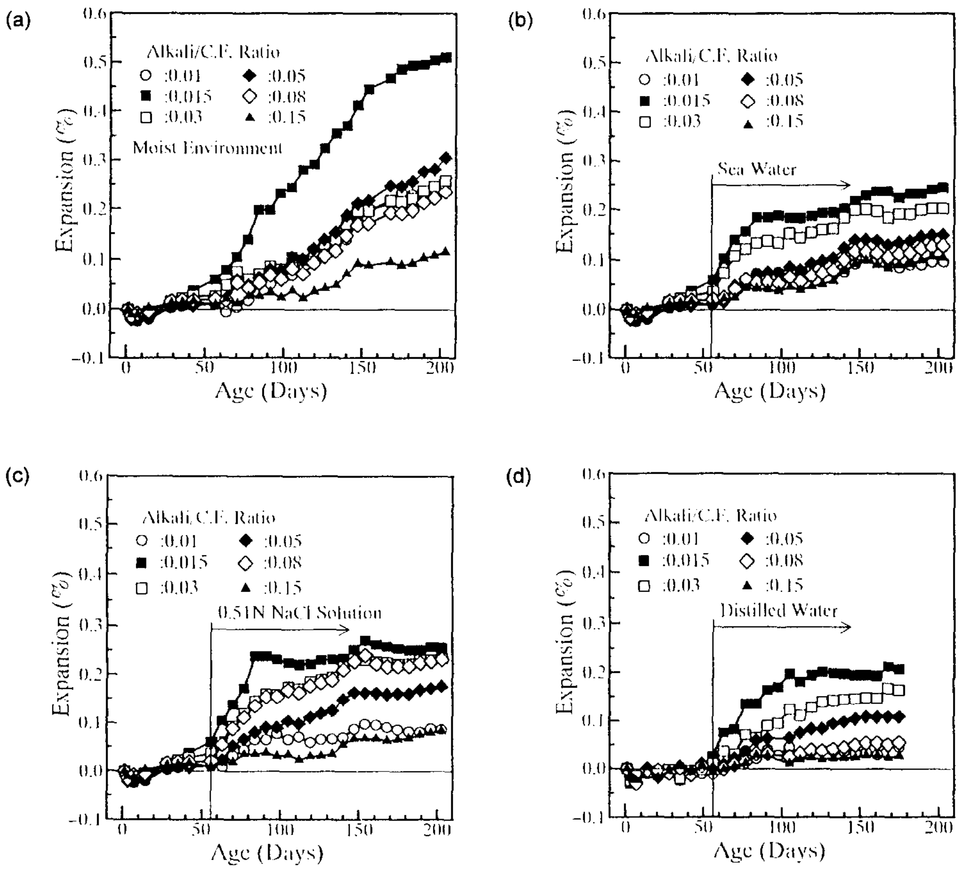

FIG. 1.

Expansion curves of C.F.-bearing mortars; (a) in moist environment, (b) in sea water, (c) in 0.51N NaCl solution (d) in distilled water.

those in a moist environment and distilled water for early stages of immersion. The differences in expansion between the mortars with an alkali: C.F. ratio of 0.03 in a moist environment and the saline solutions were conspicuous. As a result of the linear increase in expansion with time in mortars in a moist environment, the ultimate expansions of mortars in a moist environment were greater than those of mortars in the saline solutions. The expansion of mortars containing C.F. is certainly promoted both in sea water and 0.51N NaCl solution at 20°C in early stages of immersion.

Microhardness within C.F. Grains in Mortars. Fig. 2 (a), (b) and (c) show plots of the microhardness within C.F. grains in mortars with an alkali:C.F. ratio of 0.05 stored in a moist environment (> 95% R.H.), sea water and 0.51N NaCl solution, respectively. As shown in Fig. 2 (a), the microhardness in areas from the interface to about 100 μm in C.F. grains in mortars in a moist environment reduced to some extent at the age of 56 days. The softened areas within the C.F. grains steadily extended toward the interior with time, reaching about 200 μm, 300 μm and 400 μm away from the interface at the age of 84 days, 116 days and

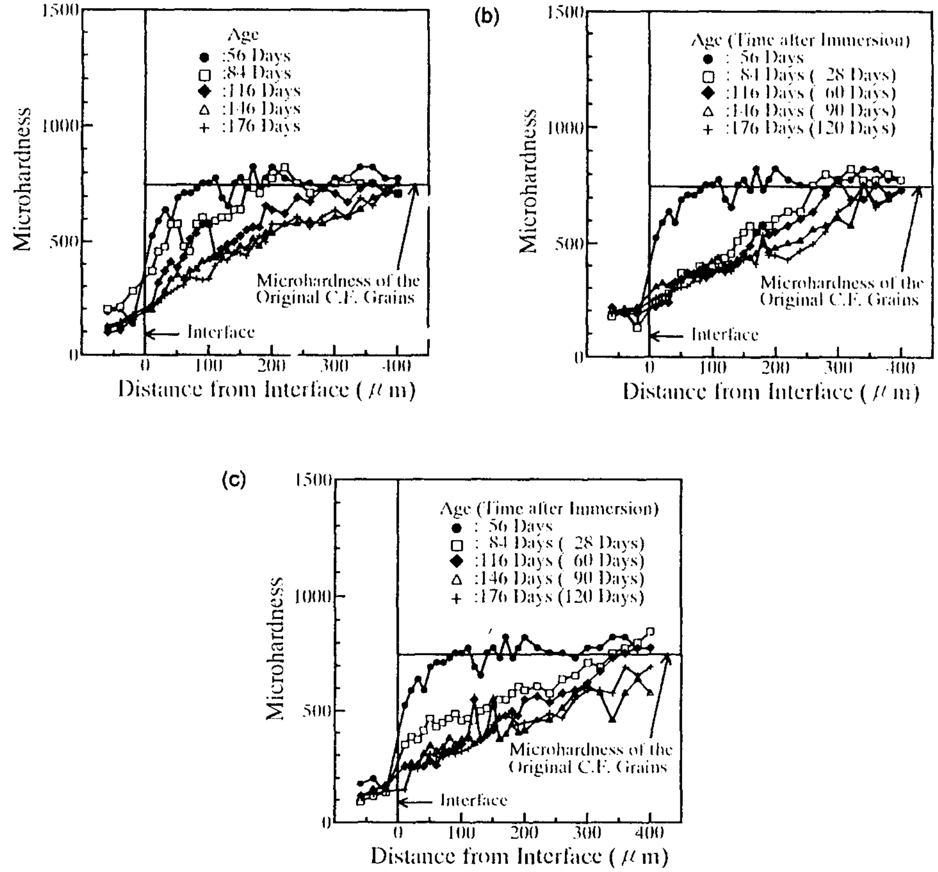

FIG. 2.

Microhardness within C.F. grains in mortars, (a) in moist environment, (b) in sea water, (c) in 0.51N NaCl solution.

146 days, respectively. On the other hand, plots of the microhardness in Fig. 2 (b) indicate that the areas up to about 250 mm away from the interface in C.F. grains in mortars immersed in sea water rapidly softened with time during the first 28 days and that thereafter the softened areas steadily progressed inward with time. Softening of C.F. grains in mortars immersed in 0.51N NaCl solution attained to about 300 μm for the first 28 days, the softened areas ranging to about 400 μm at 90 days after immersion. As indicated in Fig. 2 (b) and (c), substantial differences in the microhardness distributions in C.F. grains between mortars in sea water and 0.51N NaCl solution were not found. As a whole, softening of C.F. grains due to the alkali-silica reaction from the periphery to interior in mortars in sea water and NaCl solution more rapidly progressed than in mortars in a moist environment. The promotion of expansion in mortars in sea water and NaCl solution (Fig. 1 (b) and (c)) is found to correspond to the rapid progress of softening of C.F. grains due to the alkali-silica reaction in the mortars (Fig. 2 (b) and (c)).

Pore Solution Composition and Expansion in Mortars. Time-dependent changes in OH^- ion concentration in the pore solution in mortars with an alkali:C.F. ratio of 0.05 in a moist environment, sea water, 0.51N NaCl solution and distilled water are given in Fig. 3. As shown in this figure, the OH^- ion concentration in the pore solution in mortars stored in a moist environment throughout the expansion test gradually decreased with time. A comparatively high level of OH^- ion concentration of about 0.5 N was maintained in the mortars even at the age of 176 days. However, the OH^- ion concentration in the pore solution in mortars immersed in sea water and NaCl solution rapidly decreased with time for the first 14 days. Thereafter, OH^- ions continued to slowly diffuse out from the mortar cylinders.

In Fig. 4, expansions of mortars stored in a moist environment, the saline solutions and distilled water are plotted against time in order to more exactly compare their expansion behavior. Comparison of expansion curves with the corresponding plots of OH^- ion concentration demonstrates that the proportionally increasing expansion of mortars in a moist environment with time is attributed to the maintenance of a relatively high OH^- ion concentration of the pore solution. Another indication that the cease of expansion of mortars in sea water and NaCl solution around 90 days after immersion is responsible for a great reduction in OH^- ion concentration below a threshold value, is obtained from Figs. 3 and 4. However, it is

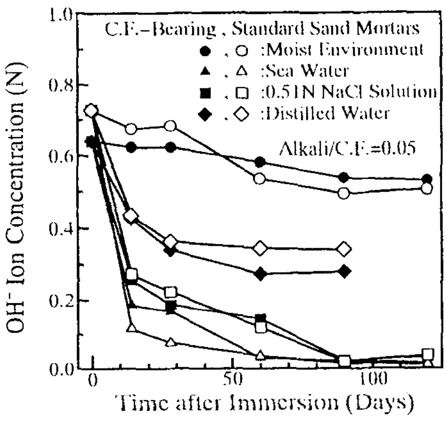

FIG. 3.
Change in OH^- ion concentration with time.

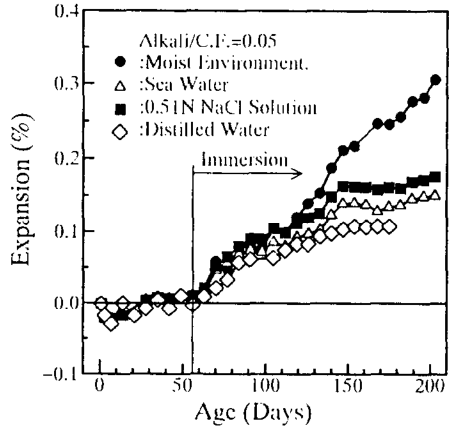

FIG. 4.
Expansion curves of C,F,-bearing mortars.

impossible to discuss any rigorous correspondence between the expansion behavior and the pore solution composition in the mortars because of the presence of gradients of OH^- and Cl^- ion concentration within mortar cylinders.

As shown in Fig. 4, there are little differences in expansion between the mortars stored in a moist environment and the saline solutions up to the age of 120 days. Fig. 1 also shows that, as a whole, mortars in a saline solution during the first one month more rapidly expanded than the corresponding mortars in a moist environment. Taking account of these results and the fact that the OH^- ion concentration in mortars in a moist environment was far greater than in mortars in a saline solution, the rapid expansion of mortars in a saline environment for early stages of immersion suggests that Cl^- ions play a significant role in accelerating the expansion of mortars due to the alkali-silica reaction above a threshold value of OH^- ion concentration. Furthermore, since the OH^- ion concentration in the pore solution in mortars in distilled water was considerably greater than in mortars in the saline solutions, smaller expansions in mortars in distilled water than in mortars in the saline solutions explicitly evidences an important role of Cl^- ions in the promotion of expansion in the saline solutions. The acceleration of the alkali-silica reaction within C.F. grains in mortars in a saline solution was also revealed by the microhardness measurements within C.F. grains (Fig. 2 (a), (b) and (c)).

As indicated in Fig. 3, any rise in OH^- ion concentration in the pore solution in mortars in sea water and 0.51N NaCl solution at 20°C was not found during the early stages of immersion. However, in another experiment by the present authors (6), the OH^- ion concentration in the pore solution in mortars in 1N NaCl solution at 38°C considerably increased during the first 14 days. The maintenance of a higher OH^- ion concentration in the pore solution in mortars containing C.F. than in reactive aggregate-free mortars was not also found in sea water and 0.51N NaCl solution at 20°C, although found in mortars in 1N NaCl solution at 38°C (6). Such an extremely hard substance as produced within C.F. grains in mortars during the immersion in 1N NaCl solution at 38°C was not found in mortars in sea water and 0.51N NaCl solution at 20°C, as shown in Fig. 2 (b) and (c). The alkali-silica reaction in mortars in sea water and 0.51N NaCl solution at 20°C appears to progress differently from that in mortars in 1N NaCl solution at an elevated temperature of 38°C.

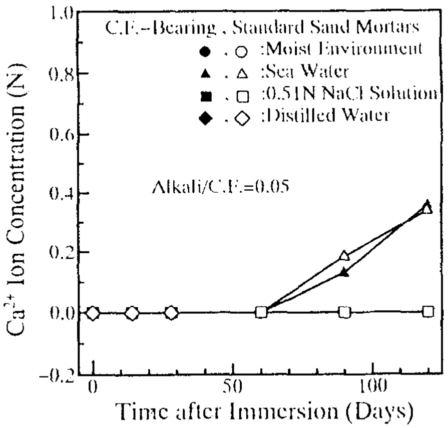

FIG. 5.
Change in Ca^{2+} ion concentration with time.

Figs. 5 and 6 show the changes in Ca^{2+} and Cl$^-$ ion concentration with time in the pore solution in mortars with an alkali:C.F. ratio of 0.05 in sea water and 0.51N NaCl solution, respectively. It is found from Fig. 5 that Ca^{2+} ion concentration in the pore solution in mortars with and without C.F. in sea water was so extremely low as in mortars in a moist environment and NaCl solution up to about 60 days after immersion, but that thereafter rapidly increased with time to a high level of about 0.4N at 120 days. As shown in Fig. 6, the Cl$^-$ ion concentration in the pore solution in mortars in 0.51N NaCl solution steadily increased with time, being in equilibrium with Cl$^-$ ion concentration of the surrounding solution around 90 days after immersion. On the contrary, the Cl$^-$ ion concentration in the pore solution in mortars in sea water reached the level corresponding to that of sea water at a certain time, followed by a further increase beyond the Cl$^-$ concentration of sea water for the period of 90 to 120 days. The initiation of a great increase in Ca^{2+} and Cl$^-$ ion concentration in the pore solution in mortars in sea water around 60 days after immersion may be responsible for the production of CaCl^2 in the mortars in the process of the formation of brucite (12). Such a

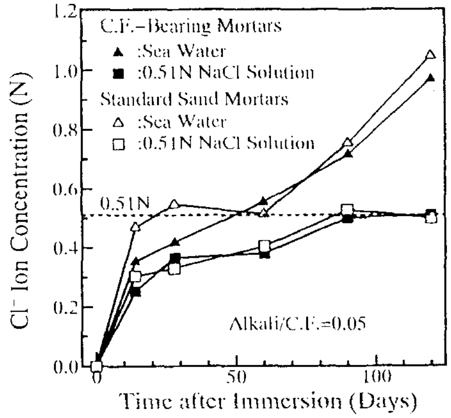

FIG. 6.
Change in Cl$^-$ ion concentration with time.

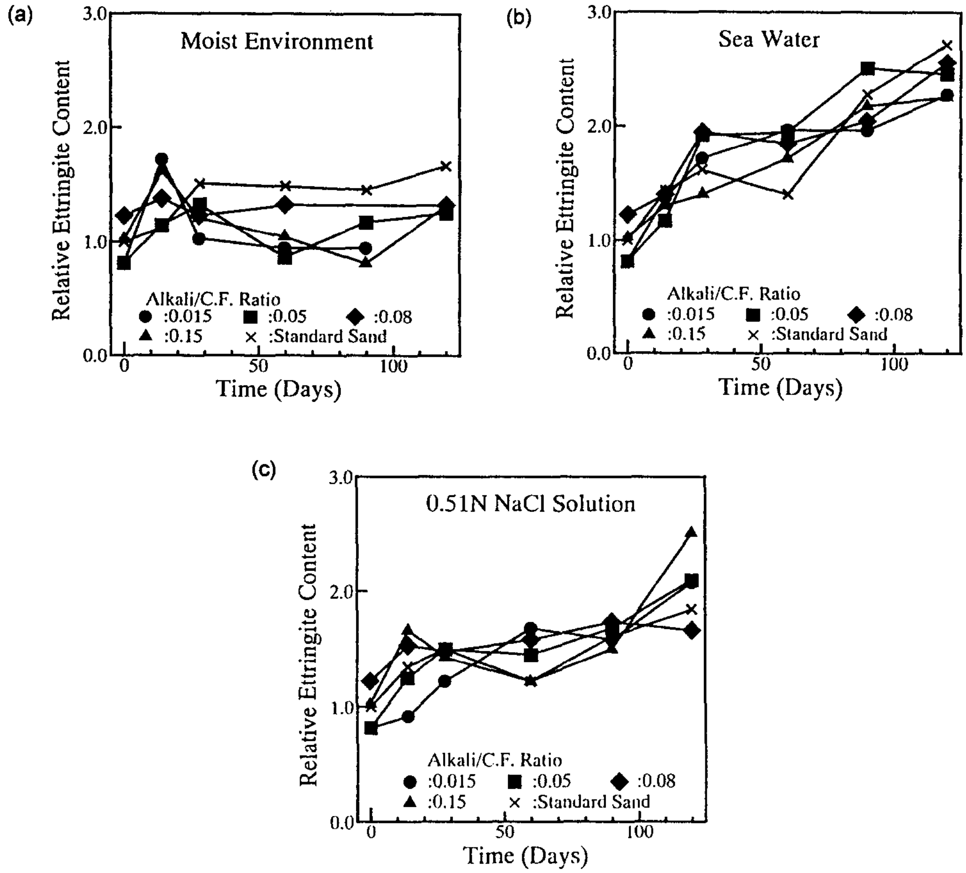

FIG. 7.

Change in ettringite content with time, (a) in moist environment, (b) in sea water, (c) in 0.51N NaCl solution.

delayed increase in Ca^{2+} and Cl$^-$ ion concentration in the pore solution in mortars immersed in sea water seems not to affect the expansion of mortars due to the alkali-silica reaction.

Ettringite and $Ca(OH)_2$ Content in Mortars. In Fig. 7, the relative ettringite contents in mortars stored under the three different environments are plotted against time after immersion. As shown in Fig. 7, the ettringite content in mortars in sea water and NaCl solution proportionally increased with time. However, little changes of the ettringite content with time were found in mortars in a moist environment. It is also found from Fig. 7 that the ettringite content in mortars in sea water was greater than in mortars in 0.51N NaCl solution as a whole. A deduction that ettringite produced within mortars in the saline solutions was not related to the expansion of mortars may be derived from the fact that the amounts of ettringite in mortars containing C.F. were not different from those in reactive aggregate-free mortars. It has been also evidenced that the formation of ettringite in C.F.-bearing mortars without added NaOH during the immersion in 1N NaCl solution at 38°C did not influence the expansion of mortars (8).

The changes in $Ca(OH)_2$ content in mortars with time during the storage of mortars in the three different environments are given in Fig. 8. The $Ca(OH)_2$ content in mortars in a moist environment and NaCl solution tended to increase with time, but in mortars in sea water to decrease with time, as shown in Fig. 8. Most of $Ca(OH)_2$ which dissipated in mortars in sea water, are supposed to be consumed by the formation of brucite and aragonite as stated previously (12). However, the dissipation of $Ca(OH)_2$ within mortars seems not to affect the expansion of mortars.

Effects of Sea Water on the Alkali-Silica Reaction. As shown in Fig. 3, OH ions rapidly diffused out from mortar cylinders. Naturally, as OH^- ions diffused out from mortar specimens in sea water, in portions of the specimens in which OH^- ion concentration is reduced to a threshold level, the alkali-silica reaction must have ceased. However, when an attention is paid to the OH^- ion concentrations and expansion of the corresponding mortars in Figs. 3 and 4, the expansion due to the alkali-silica reaction in the presence of Cl^- ions is found to prog-

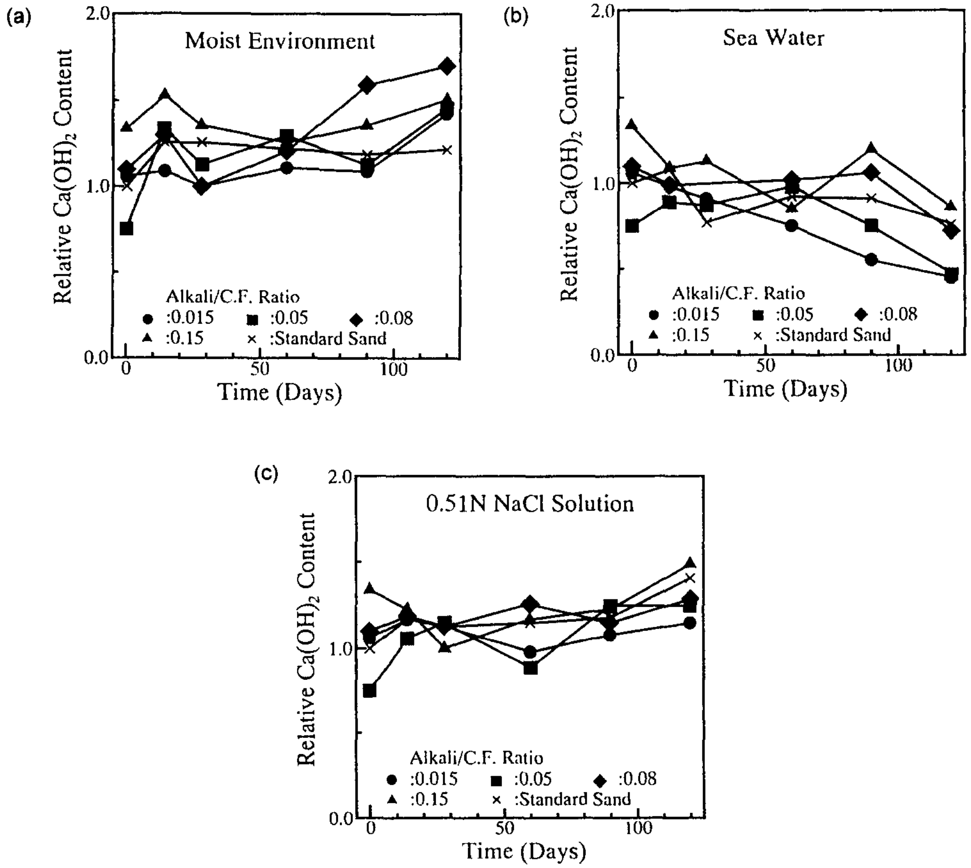

FIG. 8.

Change in $Ca(OH)_2$ content with time, (a) in moist environment, (b) in sea water, (c) in 0.51N NaCl solution.

ress even in an OH^- ion concentration low enough for the cease of the alkali-silica reaction in the absence of Cl^- ions. This fact does not contradict with a number of experimental results that the expansion of mortars and concretes in sea water and NaCl solution depends on various factors such as the shape and size of specimen, the alkali content of cement, mix proportions, and the temperature and concentration of solution.

Conclusions

(1) The expansion of mortars containing the calcined flint was promoted both in sea water and 0.51N NaCl solution only for early stages of immersion. The OH^- ion concentration of the pore solution in the mortars in the saline solutions rapidly reduced during the first 14 days, leading to the cease of expansion.

(2) Softening of the reactive aggregate grains due to the alkali-silica reaction from the periphery to interior in mortars in sea water and NaCl solution more rapidly progressed than in mortars in a moist environment.

(3) Expansion of mortars containing reactive aggregate in the saline solutions depends on the OH^- ion concentration of pore solution. Cl^- ions seem to accelerate the alkali-silica reaction as far as an OH^- ion concentration above a threshold value is maintained.

(4) Ettringite produced in mortars during the immersion in sea water is not related to the expansion of the mortars.

(5) The reduction in $Ca(OH)_2$ content in mortars during the immersion in sea water appears not to affect the expansion of mortars due to the alkali-silica reaction.

(6) The Cl^- ion concentration in the pore solution in mortars with and without the reactive aggregate in sea water was beyond the Cl^- ion concentration of the surrounding sea water for the period of 90 to 120 days after immersion.

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