CONCRETE LIBRARY OF JSCE NO. 26, DECEMBER 1995

# MECHANISMS OF THE INFLUENCE OF EXTERNALLY SUPPLIED NaCl ON THE EXPANSION OF MORTAR CONTAINING REACTIVE AGGREGATE

(Translation from Proceedings of JSCE, No.502/V-25, November 1994)

Mitsunori KAWAMURA Katsunobu TAKEUCHI Ayanori SUGIYAMA

This study aims at revealing the mechanisms by which externally supplied NaCl influences the expansion of mortar due to the alkali-silica reaction. In reactive aggregate-bearing mortars with relatively low alkali contents, the promotion of their expansion in 1N NaCl solution at 38° C was promoted by a rise in $OH^-$ ion concentration in the pore solution. This increase in $OH^-$ ion concentration in the pore solution was responsible for the intrusion of $Cl^-$ ions into mortar. In reactive aggregate-bearing mortars with a relatively large amount of added NaOH, at least a part of the unusually large mortar expansion was caused by the delayed formation of ettringite during immersion in NaCl solution.

*Keywords: alkali-silica reaction, NaCl, ettringite,* $OH^-$ *ion,* $SO_4^{2-}$ *ion*

---

Mitsunori Kawamura is a professor in the Department of Civil Engineering at Kanazawa University. He has been active in cement and concrete research for 30 years. His research interests include the alkali-silica reaction, concrete durability, and the microstructure of cement-based materials. He is a member of the JSCE.

Katsunobu Takeuchi is a civil engineer in the Technical Research Laboratory of Magara Construction Co. Ltd. in Kanazawa in Japan. He obtained his D. Eng. from Kanazawa University in 1995. He is a member of the JSCE.

Ayanori Sugiyama is with the Research Institute of Nihon Cement Co. Ltd.. He obtained his M.S. Degree from Kanazawa University in 1992.

## 1. Introduction

Certain attention has been paid to acceleration of the alkali-silica reaction due to NaCl incorporated during the production of concrete and the effects of externally supplied NaCl on hardened concrete. The addition of NaCl to concrete during production certainly accelerates expansion due to the alkali-silica reaction [1] - [5]. It has been proposed that this acceleration of the alkali-silica reaction by NaCl is responsible for a rise in $OH^-$ ion concentration in the pore solution due to the formation of Friedel's salt [6]. However, experimental results suggesting that $Cl^-$ ions played an important role in the acceleration of the alkali-silica reaction have also been reported [7], [8].

Since sea water and NaCl used as a deicing agent affect the alkali-silica reaction in concrete, the mechanisms responsible for the expansion of reactive aggregate-bearing mortars immersed in NaCl solution are an important problem to be solved. As to the mechanisms causing the acceleration of the alkali-silica reaction in hardened mortar and concrete when NaCl is supplied from the outside, a proposal emphasizes the role of $Ca(OH)_2$ in the alkali-silica reaction [9] and another suggests that a part of the expansion of concrete containing reactive aggregate in a saline environment is due to the formation of an expansive Afm [10], [11]. Although the $OH^-$ ion concentration in the pore solution of mortars immersed in 1N NaCl solution fall to a very low level during the first two weeks, some opal-bearing mortars started expanding several months after immersion in an NaCl solution [12]. This delayed expansion and the accelerated expansion of mortars containing a reactive aggregate in NaCl solution seem difficult to explain on the basis of the established understanding that the alkali-silica reaction depends on the $OH^-$ ion concentration in the pore solution. Another unexpected result stems from SEM microscopic examinations of opal-bearing mortars immersed in NaCl solution for more than one year; large amounts of chloride-bearing ettringite were found in such mortars [13].

As to the relation between the alkali-silica reaction and the formation of ettringite in concrete, Regourd [14] concluded that a release of $OH^-$ ions accompanying the formation of ettringite can accelerate the alkali-silica reaction in concrete.

These various findings and proposals suggest that the intrusion of NaCl into hardened mortar or concrete containing a reactive aggregate affects the hydration products in the cement paste phase and/or the reaction products formed within reactive aggregate grains. Consequently, pursuing the changes in pore solution composition with time and changes in the reaction products formed within reactive aggregate grains in mortars during immersion in NaCl solution might lead to elucidation of the mechanisms of expansion for mortars containing reactive aggregate.

In this study, the characteristics of alkali-silica reaction progress within reactive aggregate grains in mortars submerged in NaCl solution are revealed by a combination of microhardness measurements and EDXA analysis. The mechanisms causing increased expansion in mortars containing a reactive aggregate in NaCl solution are discussed in terms of the results of analyzing pore solutions and chemical composition within the reactive aggregate grains. Furthermore, the relation between the expansion and the formation of ettringite in mortars containing reactive aggregate in 1N NaCl solution at the elevated temperature of 38° C is discussed by comparing experimental results for mortar made with powdered clinker and no gypsum with those for ordinary Portland cement mortar.

## 2. Experimental Outline

### 2.1 Materials

The reactive aggregate used was calcined flint (C.F.) which was supplied by Blue Circle Industries PLC. This reactive aggregate has a size fraction of 2.35 mm to 1.00 mm and is mostly pure cristobalite [14], as shown in an X-ray diffraction diagram (Fig. 1). In addition to the approximately 96% tetragonal cristobalite, there is about 2% quartz and 2% tridymite. The mean crystallite size is approximately 60 nm [14]. The density and absorption of the calcined flint grains are 2.29% and 1.79%, respectively. The mean porosity of the C.F. grains is about 4.75% [14]. Japanese standard sand, which mainly consists of quartz, was used as the non-reactive aggregate. The potential alkali reactivity of the reactive aggregate, determined according to ASTM Chemical Test C289, is given in Table 1. The equivalent $Na_2O$ percentages of ordinary high and low alkali Portland cements are 0.97% and 0.48%, respectively; that of the clinker used is 0.67%. The chemical compositions of the cements and clinker are given in Table 2.

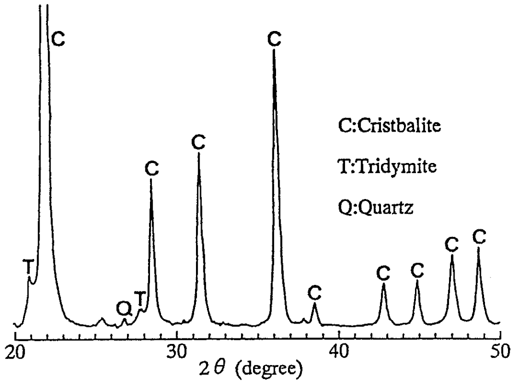

Fig. 1 X-ray Diffraction Pattern of Calcined Flint

Table 1 Alkali reactivity of the reactive aggregate (ASTM C289)

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

Table 2 Chemical compositions of cements and clinker

| | High alkali cement | Low alkali cement | Clinker |
|---|---|---|---|
| In. loss | 0.7 | 1.3 | 0.1 |
| Insol. | 0.1 | 0.2 | 0.0 |
| $SiO_2$ | 21.1 | 21.9 | 22.5 |
| $Al_2O_3$ | 4.9 | 5.5 | 5.7 |
| $Fe_2O_3$ | 3.1 | 2.9 | 3.0 |
| CaO | 65.1 | 63.1 | 65.4 |
| MgO | 1.4 | 1.7 | 1.6 |
| $SO_3$ | 2.0 | 2.3 | 0.2 |
| $Na_2O$ | 0.50 | 0.29 | 0.34 |
| $K_2O$ | 0.72 | 0.29 | 0.50 |
| $TiO_2$ | 0.28 | 0.35 | 0.32 |
| $P_2O_5$ | 0.10 | 0.05 | 0.14 |
| MnO | 0.05 | 0.17 | 0.10 |
| $Na_2Oeq.$ | 0.97 | 0.48 | 0.67 |

## 2.2 Microhardness Test

### a) Mortar Mix Proportions

A mortar with an alkali/reactive aggregate ratio of 0.05 was selected for microhardness tests from a series of mortars with various alkali/reactive aggregate ratios. The expansion behavior of these mortars in NaCl solution has been investigated by the present authors [15], [16]. The mortar actually used for the microhardness test corresponded to the one which was obtained by excluding the non-reactive aggregate from a mortar for the expansion test. Such a mortar containing only the reactive aggregate was prepared at a water/cement ratio of 0.4 and a reactive aggregate/cement ratio of 0.194.

### b) Preparation of Mortar Pieces

Cubic blocks of 2.0 by 2.5 by 2.5 cm were cut from a mortar bar of 2.5 by 2.5 by 25.8 cm obtained by demoulding one day after casting. The 2.5 by 2.5 faces of each block were coated with a silicon resin sealant so as to allow $Na^+$ and $Cl^-$ ions to intrude into the mortar block from a solution only from the 2.0 by 2.5 cm faces. These mortar blocks were sealed in vinyl sacks and cured in a container maintained at 38° C and >95% R.H. for 28 days. They were then immersed in 1N NaCl solution for prescribed periods. The other series of mortars were stored for reference in the same container for prescribed periods. The silicon coating on the two faces was removed at a prescribed age, and then one of the faces was polished on a rotor using a set of SiC polishing papers.

### c) Measurement of Microhardness

A Vickers indenter was used to measure the microhardness within a reactive aggregate grain along the grain's longest radius at intervals of about 10 μm to 20 μm. Two grains with a diameter of about 2 mm appearing within about 5 mm of the periphery of the mortar block were selected for microhardness measurements. The value of microhardness at a given distance from the interface between the cement paste phase and the aggregate was taken to be the average of measurements on two grains.

## 2.3 EDXA Analysis

After the completion of microhardness measurements, the polished surfaces of mortar blocks were coated with gold after drying in a vacuum drying at room temperature. EDXA analysis was carried out at a number of spots corresponding to where microhardness had been measured, using a scanning electron microscope (Nihon Denshi Co. Ltd.) equipped with an EDAX International energy-dispersive X-ray analyzer. The acceleration voltage was 25 kV. The spectrums for Kα peaks of Na, K, Ca, Si, S, Cl, and Al were accumulated for count periods of 100 seconds . The count ratio of each element at a spot was the average of measurements for two grains in different samples. Count ratios of each element to Si at various spots within reactive grains in reference samples made by embedding calcined flint grains in an epoxy resin were also measured. The results for the reference samples are tabulated in Table 3. The average ratio for each element given in Table 2 is shown as the base line in Figs. 13 - 18.

Table 3 Count ratios for various elements within C.F. grains embedded in epoxy resin

| Distance from interface (μm) | (Na+K)/Si | Ca/Si | Al/Si | S/Si | Cl/Si |
|---|---|---|---|---|---|
| 50 | 0.030 | 0.020 | 0.031 | 0.040 | 0.026 |
| 100 | 0.035 | 0.022 | 0.025 | 0.033 | 0.030 |
| 150 | 0.030 | 0.019 | 0.033 | 0.031 | 0.022 |
| 200 | 0.025 | 0.019 | 0.026 | 0.032 | 0.024 |
| 250 | 0.034 | 0.022 | 0.028 | 0.035 | 0.024 |
| 300 | 0.031 | 0.018 | 0.032 | 0.034 | 0.020 |
| 350 | 0.035 | 0.022 | 0.035 | 0.037 | 0.027 |
| 400 | 0.030 | 0.019 | 0.030 | 0.032 | 0.023 |
| Mean | 0.031 | 0.020 | 0.030 | 0.034 | 0.025 |

## 2.4 Expansion Test

Two types of mortar made with an ordinary Portland cement and powdered clinker without gypsum were prepared for expansion tests. The mortar mix proportions were aggregate/cement = 0.75, water/cement = 0.4 and C.F./(non-reactive aggregate + C.F.) = 0.26. A series of mortars with relatively low alkali/C.F. ratios not greater than 0.05 were produced by diluting a high-alkali cement with a low-alkali cement. Alkali/C.F. ratios greater than 0.06 were adjusted by adding NaOH. Alkali/C.F. ratios greater than 0.04 in clinker mortars were raised to that of the corresponding Portland cement mortars by adding NaOH.

Mortar bars 2.5 by 2.5 by 28.5 cm were prepared with a total aggregate/cement ratio of 0.75, a 0.26 replacement ratio of reactive aggregate, and a water/cement ratio of 0.4. The alkali/reactive aggregate ratio was 0.05 in this mortar. The bars were cured in a container maintained at 38° C and >95% R.H. for 28 days, and then immersed in 1N NaCl solution. Reference specimens were stored at 38° C and >95% R.H. throughout the expansion tests. Measurements of length changes with time were initiated immediately after demoulding. Expansions were the average of measurements for two specimens.

## 2.5 Pore Solution Analysis

Pore solutions were expressed by high-pressure apparatus from ϕ5 by 10 cm mortar cylinders. Mix proportions were the same as of mortar samples used in the expansion tests. Mortar cylinders were cured in >95% R.H. atmosphere at 38° C for 28 days in an unsealed state, and then immersed in 1N NaCl solution for a prescribed period before the pore solutions were expressed. Pore solutions taken from mortar cylinders cured in a moist container at 38° C throughout the prescribed period were also analyzed. The extracted solutions were analyzed for $OH^-$ ion concentration by titration against hydrochloric acid to the phenolphthalein end point. Other ions such as $Cl^-$, $Na^+$, $K^+$, and $Ca^{2+}$ were also analyzed by standard methods. The cation concentrations were equally balanced with the anion concentration in the pore solutions.

## 2.6 Determination of Ettringite Content in Mortar by DTA Analysis

As shown in Fig. 2(a), in the DTA curves obtained by using $Al_2O_3$ as a reference material, discrimination of the broad endothermic peak of C-S-H from that of ettringite around 110° C is impossible. However, the relative content of ettringite in mortar was determined by the use of a hydrated clinker as a reference material, according to the method proposed by Odler and Abdul-Maula [17] (Fig. 2(b)). The chemical composition of the clinker used is given in Table 1. The heating rate and the sample size in this analysis were 10° C/min. and 25 mg, respectively.

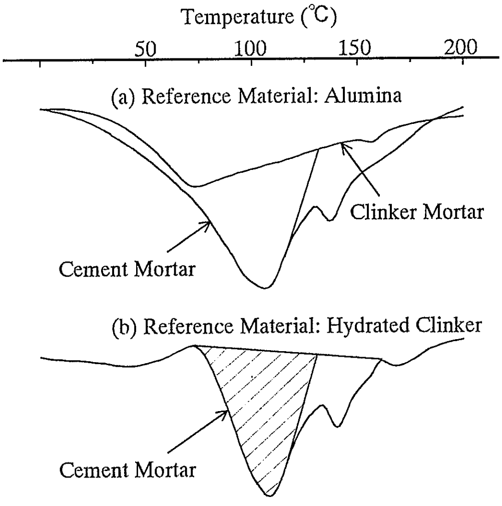

Fig. 2 DTA Curves for Cement and Clinker Mortars

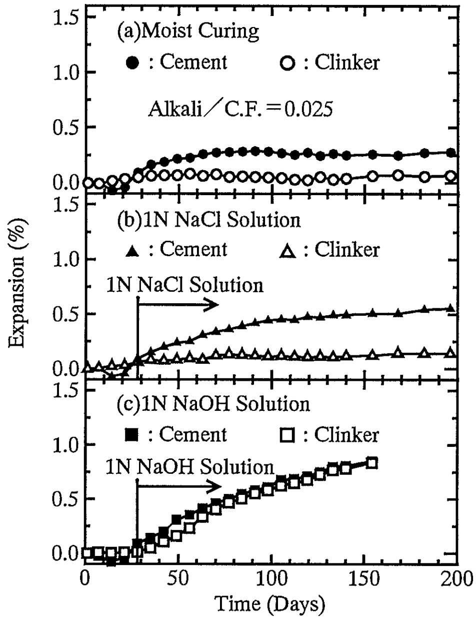

Fig. 3 Expansion Curves for Mortars with an Alkali/C.F. Ratio of 0.025

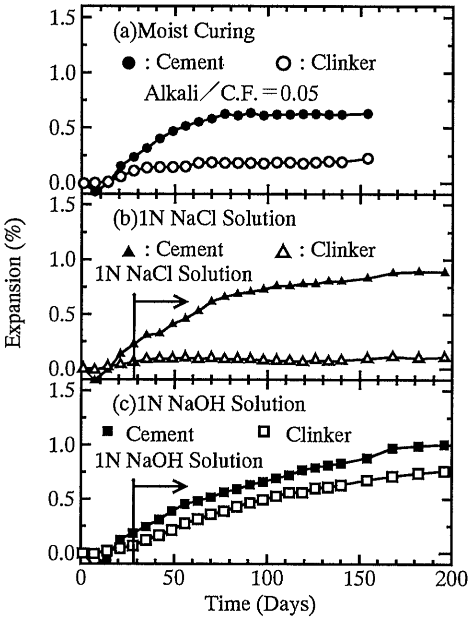

Fig. 4 Expansion Curves for Mortars with an Alkali/C.F. Ratio of 0.05

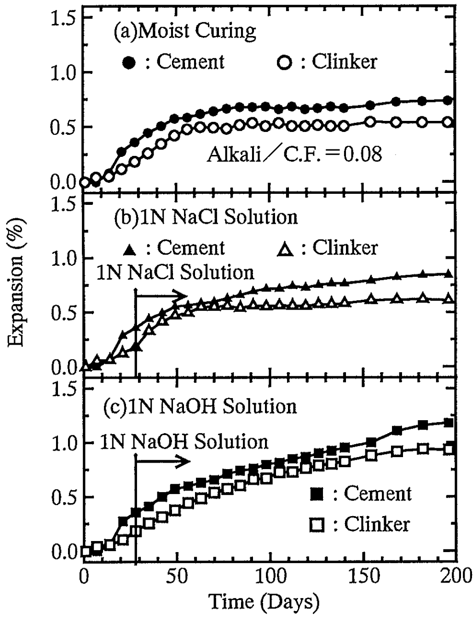

Fig. 5 Expansion Curves for Mortars with an Alkali/C.F. Ratio of 0.08

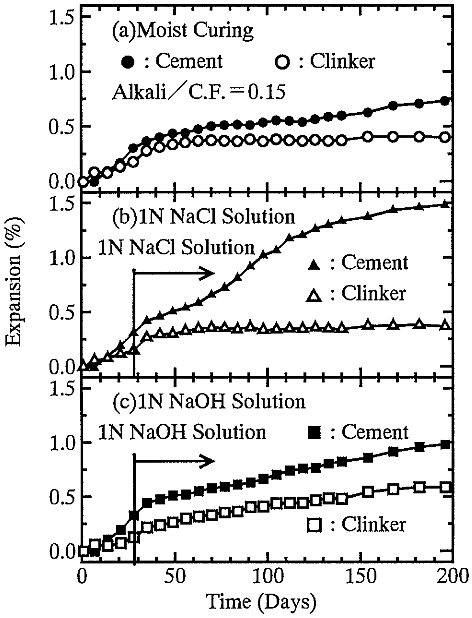

Fig. 6 Expansion Curves for Mortars with an Alkali/C.F. Ratio of 0.15

## 3. Results and Discussion

### 3.1 Mortar Expansion Behavior

Figures 3 - 6 show expansion curves for cement and clinker mortars containing reactive aggregate at an alkali/C.F. ratios of 0.025, 0.05, 0.08 and 0.15 under three different environmental conditions. In clinker mortars with the relatively low alkali/C.F. ratios of 0.025 and 0.05 immersed in NaCl solution and a moist environment (Figs. 3 and 4) expansion was not so great. However, the expansion in the case of clinker mortars in 1N NaOH solution increased proportionally with time. On the other hand, cement mortars expanded greatly at times beyond 14 days or 28 days under the three conditions.

Judging from the results that both cement and clinker mortar specimens in 1N NaOH solution expanded by almost the same degree (Fig. 3(c)) and that , at a given alkali/C.F. ratio, the $OH^-$ ion concentration in the pore solution of clinker mortars is lower than that in Portland cement mortars [15], the smaller expansions of clinker mortars than of cement mortars at alkali/C.F. ratios of 0.025 and 0.05 in NaCl solution and a moist environment might be responsible for their lower $OH^-$ ion concentrations in pore solutions.

Figures 5 and 6 show that the expansion behavior of mortars with alkali/C.F. ratios of 0.08 and 0.15 is considerably different from that of mortars with a relatively low alkali/C.F. ratio. Both cement and clinker mortars with a relatively high alkali/C.F. ratio under all three environmental conditions started actively expanding after 14 days. As a whole, clinker mortars exhibited less expansion than cement mortars. However, the shapes of the expansion curves for clinker and cement mortars are similar, except that mortars with an alkali/C.F. ratio of 0.15 in NaCl solution expanded in a peculiar manner. As shown in Fig. 6, clinker mortar with an alkali/C.F. ratio of 0.15 expanded to some extent for up to about one month after immersion in NaCl solution but, thereafter showed little expansion. However, the expansion of cement mortar with an alkali/C.F. ratio of 0.15 in NaCl solution increased proportionally with time after immersion, resulting in a final expansion about three times greater than the corresponding clinker mortar. At an alkali/C.F. ratio of 0.08, little difference in expansion behavior between cement and clinker mortars stored in the three different conditions was found. The cement mortar with an alkali/C.F. ratio of 0.15 showed extremely great expansion as compared to the corresponding clinker mortar in the NaCl solution (Fig. 6(b)).

Figure 7 shows expansion curves for mortars with various alkali/C.F. ratios immersed in 1N NaCl solution at 38° C. The shape of the expansion curves for mortar with alkali/C.F. ratios of 0.15 and 0.20 is found to be greatly different from that of other mortars. In these cases, expansion appears to actively resume around one month after immersion. These results suggest that expansion of mortar with a large amount of added NaOH is caused by other mechanisms in addition to the alkali-silica reaction.

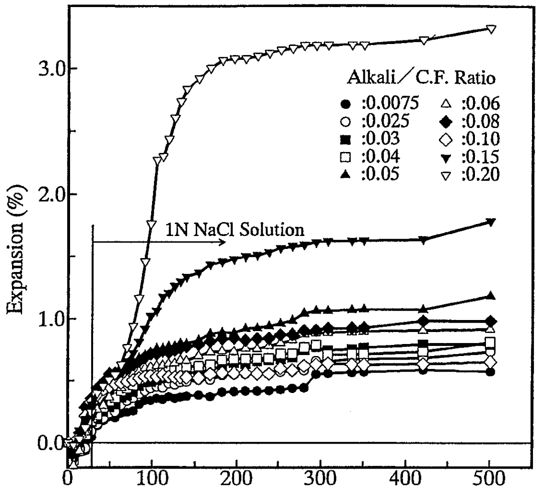

Fig. 7 Expansion Curves for Mortars with Various Alkali/C.F. Ratios

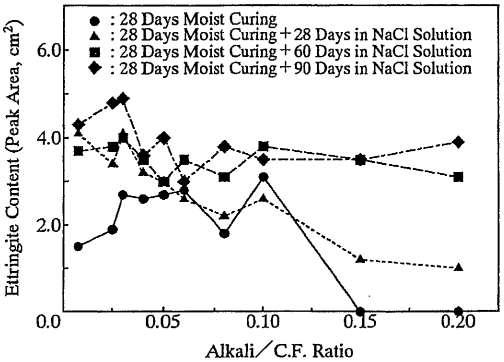

Fig. 8 Ettringite Content in C.F.-bearing Mortars

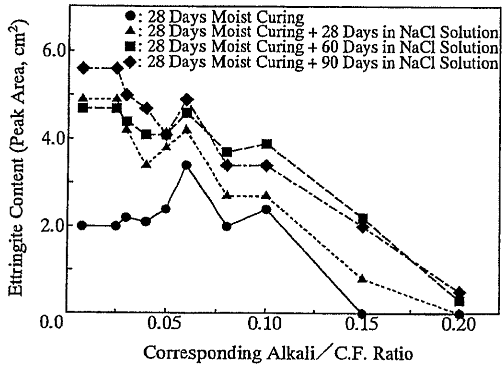

Fig. 9 Ettringite Content in Mortars without Reactive Aggregate

## 3.2 Relationship Between Ettringite Content and Expansion

Figures 8 and 9 show the relations between alkali/C.F. ratio and ettringite content in mortar with and without reactive aggregate immersed in 1N NaCl solution for various periods. It is clear that the amounts of ettringite produced in reactive aggregate mortar with an alkali/C.F. ratio of less than 0.10 during the first 28 days of moist curing are not different from those in corresponding reactive aggregate-free mortars. However, at alkali/C.F. ratios of 0.15 and 2.0, little ettringite was formed within the mortar during the first 28 days of moist curing. Considerable amounts of NaOH were added to the mortar to increase the alkali/C.F. ratio. The absence of ettringite in these mortar samples appears to be related to the extremely high OH$^-$ ion concentration in the pore solution [18].

The amounts of ettringite produced in the mortars both with and without reactive aggregate immersed in NaCl solution increased with time, as shown in Figs. 8 and 9. The rate of increase with time varied with the alkali/C.F. ratio. The presence of reactive aggregate also influenced the rate of increase in the amount of ettringite. At an alkali/C.F. ratio of less than 0.06, the amount of ettringite produced in reactive aggregate-free mortars during immersion in NaCl solution were greater than in mortars containing reactive aggregate. At an alkali/C.F. ratio of 0.08 and 0.10, little difference in the amounts of ettringite was found between mortars with and without reactive aggregate. However, conspicuous differences in the ettringite content between mortars with and without reactive aggregate were found at alkali/C.F. ratios of 0.15 and 0.20. In particular, as shown in Figs. 8 and 9, rapid production of ettringite with time in mortar containing reactive aggregate contrasted with the formation of only a little ettringite in reactive aggregate-free mortars during periods of immersion in NaCl solution.

## 3.3 Microhardness Within Calcined Flint Grains in Mortar

Figure 10 shows plots microhardness within reactive aggregate grains in mortars cured in a moist environment maintained at 38° C. Only slight reductions in microhardness from the level of the original calcined flint grains were found in whole grains in a three-day-old mortar. However, the microhardness in areas extending from the interface to about 120 μm fell significantly in the period from 3 to 7 days. From 7 to 14 days, further reductions in microhardness in areas up to about 120 μm away from the interface were accompanied by enlargement of the softened area up to about 200 μm. However, portions up to about 100 μm from the interface showed considerably higher microhardness in 28-day-old samples than in 14-days-old ones, while the microhardness of areas from about 100 μm to 170 μm continued to decrease even after 14 days and the softened area extended to about 250 μm away from the interface at the age of 28 days.

Figure 11 shows microhardness distribution curves within reactive aggregate grains in the reference mortar specimens cured in a moist environment the prescribed periods. The figure shows that the microhardness in areas from about 100 μm to 200 μm away from the interface still increased after 28 days, but in areas from 200 μm to 350 μm it decreased up to the age of 70 days. This indicates that, in mortars continuously cured in a moist environment, the alkali-silica reaction progresses inwards within reactive aggregate grains up to 70 days.

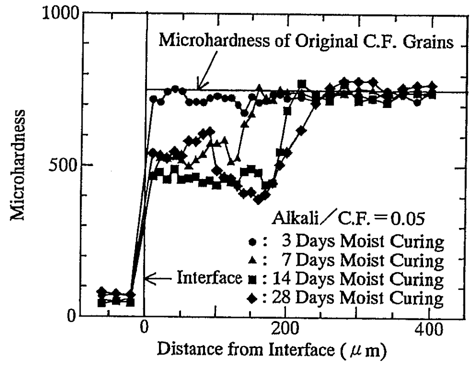

Fig. 10 Microhardness within C.F. Grains in Mortars in a Moist Environment

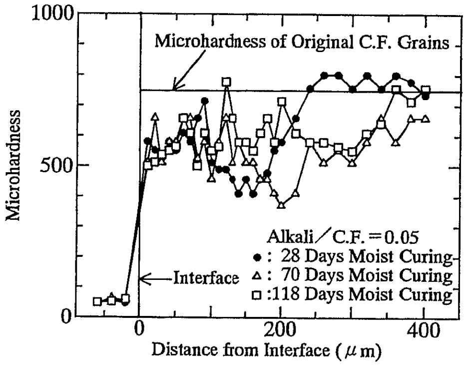

Fig. 11 Microhardness within C.F. Grains in Mortars in a Moist Environment

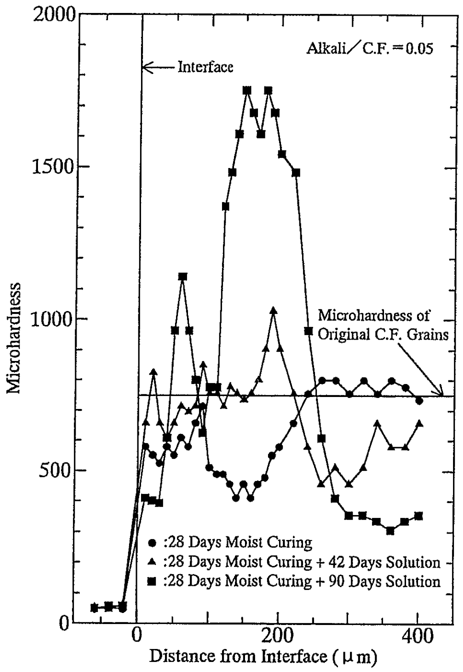

Fig. 12 Microhardness within C.F. Grains in Mortars Immersed in NaCl Solution after 28 Days of Moist Curing

Figure 12 shows changes in microhardness distribution within reactive grains in mortar immersed in 1N NaCl solution after curing in a moist environment at 38° C for 28 days. A comparison of the microhardness distributions resulting from curing under two different conditions for the same period (Figs. 11 and 12), two peculiarities can be noted.

(1) The microhardness in areas about 100 μm to 200 μm away from the interface, which had the lowest microhardness after 28 days of moist curing, increased rapidly with time during immersion in 1N NaCl solution. An extremely hard reaction product was formed with a microhardness of greater than that of Pyrex glass.

(2) The microhardness in areas deeper than about 250 μm from the interface of mortar immersed in NaCl solution, which fell little during the first 28 days of moist curing, decreased more with time in NaCl solution than in a moist environment.
These results indicate that the alkali-silica reaction in deeper areas of C.F. grains in mortars kept in NaCl solution progresses more actively than in mortar stored in a moist environment.

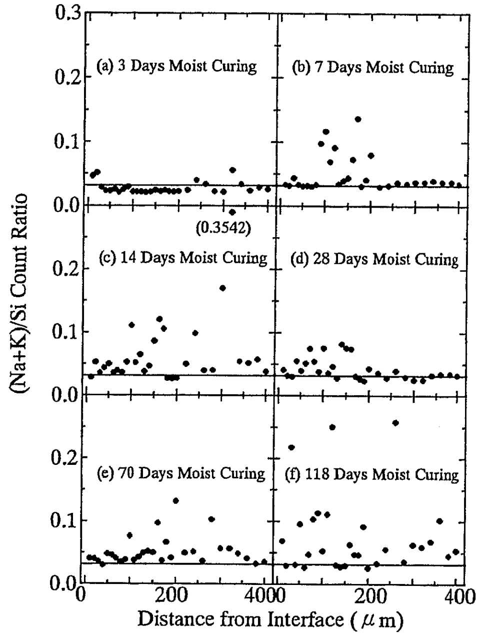

Fig. 13 (Na+K)/Si Count Ratios within C.F. Grains in Mortars in a Moist Environment

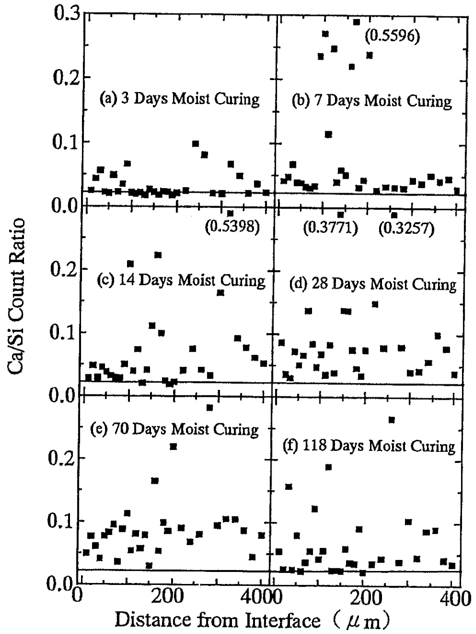

Fig. 14 Ca/Si Count Ratios within C.F. Grains in Mortars in a Moist Environment

## 3.4 Composition of Calcined Flint Grains in Mortar

Figure 13 shows (Na+K)/Si count ratios measured by EDXA analyses carried out at a number of spots within C.F. grains in mortar cured in a moist environment. Little evidence of alkalis was found within C.F. grains at the age of 3 days. Thereafter, the intrusion of alkalis into C.F. grains progressed with time, and they reached a depth of about 400 μm at the age of 118 days. The existence of several spots with higher (Na+K)/Si counts ratios in 14-day-old mortar than in 28-days-old samples may reflect variations in reactivity between individual C.F. grains. Ca/Si count ratios obtained for mortar cured in a moist environment are given in Fig. 14. $Ca^{2+}$ ions are found to intrude into C.F. grains just as alkalis do.

Figures 15 and 16 show, respectively, plots of (Na+K)/Si and Ca/Si count ratios obtained by EDXA analysis at various spots within reactive aggregate grains in mortar immersed in NaCl solution for 42 days and 90 days after 28 days of moist curing at 38° C. There are a number of spots with a relatively high (Na+K)/Si and Ca/Si count ratios in areas 100 μm to 250 μm away from the interface 42 days after immersion in NaCl solution. During the period from 42 days to 90 days in NaCl solution, the range of spots with relatively high (Na+K)/Si and Ca/Si count ratios widened to about 400 μm. Chatterji et al. [19] have already found that the Ca concentration within reactive grains in mortar in a saturated NaCl solution is greater than in mortar in water. Particularly, as shown in Fig. 8(b), Ca/Si ratios at some spots in areas ranging from about 70 μm to 200 μm away from the interface in reactive grains in mortars immersed in NaCl solution for 90 days are conspicuously high.

Most of the spots with extremely high microhardness are found to fall within areas in which many spots with high Ca/Si count ratios were found.

Figures 17 and 18 shows S/Si count ratios within C.F. grains in mortar immersed in NaCl solution after 28 days of moist curing and continuously stored under a moist condition, respectively. A comparison indicates that S/Si count ratios for mortar immersed in NaCl solution for 90 days were extremely high at some spots within the areas with extremely high microhardness (Fig. 12).

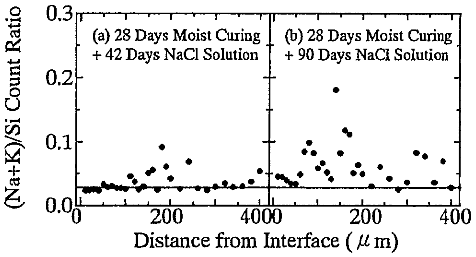

Fig. 15 (Na+K)/Si Count Ratios within C.F. Grains in Mortars Immersed in NaCl Solution after 28 Days Moist Curing

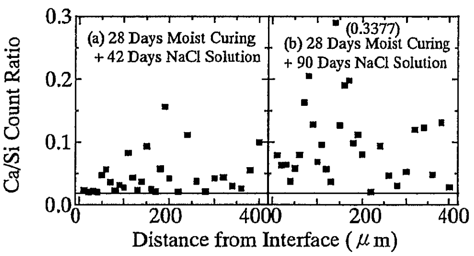

Fig. 16 Ca/Si Count Ratios within C.F. Grains in Mortars Immersed in NaCl Solution after 28 Days Moist Curing

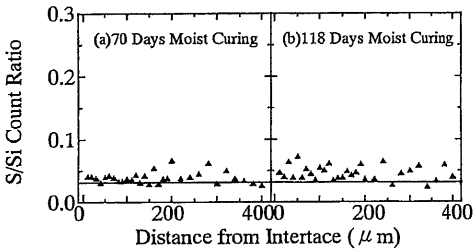

Fig. 17 S/Si Count Ratios within C.F. Grains in Mortars in a Moist Environment

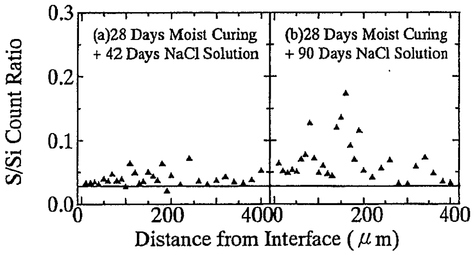

Fig. 18 S/Si Count Ratios within C.F. Grains in Mortars Immersed in NaCl Solution after 28 Days Moist Curing

## 3.5 Pore Solution Composition

### a) $OH^-$ Ion Concentration

Changes in $OH^-$ ion concentration with time in pore solution expressed from mortars with and without reactive aggregate immersed in NaCl solution after curing in a moist environment at 38° C for 28 days are given in Fig. 19. The results for pore solutions in reference mortar cured in a moist environment throughout the prescribed periods are also plotted. The $OH^-$ ion concentration in the pore solutions of mortar both with and without reactive aggregate fell to a low level due to the alkali-silica reaction and leaching of $OH^-$ ions from the mortar cylinders by the end of 28 days of moist curing. The $OH^-$ ion concentration in the pore solution of mortar without reactive aggregate proportionally decreased with time during continuous curing in a moist environment; however, in mortars with reactive aggregate little change in $OH^-$ ion concentration was found before the gradual decrease began at 14 days. On the contrary, the $OH^-$ ion concentration in the pore solution of mortar with reactive aggregate in NaCl solution increased considerably and, in mortars without reactive aggregate, increased slightly during the first 14 days. Thereafter, the $OH^-$ ion concentration in mortar without reactive aggregate decreased rapidly with time, but, in mortars with reactive aggregate, it decreased moderately during the period from 14 to 60 days; this was followed by a small increase. At any rate, it should be noted that in mortar containing the calcined flint immersed in NaCl solution, comparatively high $OH^-$ ion concentrations ranging from about 0.3 to 0.4 N were maintained up to at least 90 days.

These comparisons of changes of $OH^-$ ion concentrations with time in the pore solution between mortar immersed in NaCl solution and mortar stored in a moist environment indicate that $OH^-$ ions diffuse out from mortar specimens during immersion in NaCl solution and that considerable amounts of $OH^-$ ions are released into the pore solution within these samples (Fig. 19). In particular, the amounts of $OH^-$ ions released into the pore solution in mortar containing reactive aggregate during immersion in NaCl solution are much greater than in mortar without reactive aggregate.

X-ray diffraction analysis showed considerable amounts of Friedel's salt in mortar with and without reactive aggregate when it had been immersed in NaCl solution for periods longer than 28 days [15]. Chloride supplied from the surrounding solution is assumed to react with the tricalcium sulfoaluminate phase in the mortar to produce Friedel's salt [20]. Increases in the amount of ettringite both in mortars with and without reactive aggregate during immersion in NaCl solution were confirmed by quantitative DTA analysis (Figs. 8 and 9). Amounts of Friedel's salt and ettringite produced in mortar with reactive aggregate were not very different from those in reactive aggregate-free mortars. At any rate, the mechanisms responsible for the release of greater amounts of $OH^-$ ions in mortar with reactive aggregate than in mortar with only a non-reactive aggregate seem to be related to the presence of alkali-silica reaction products and the intrusion of the chloride into them.

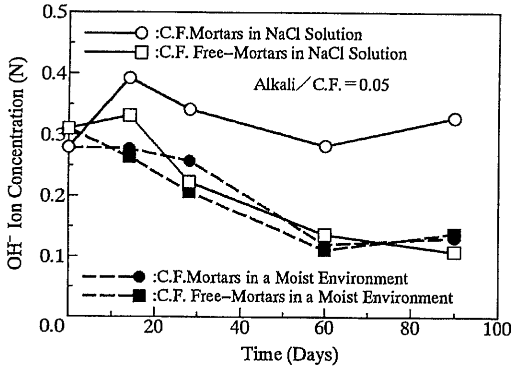

Fig. 19 Changes in $OH^-$ Ion Concentration with Time in Pore Solutions of Mortars Immersed in NaCl Solution and in a Moist Environment

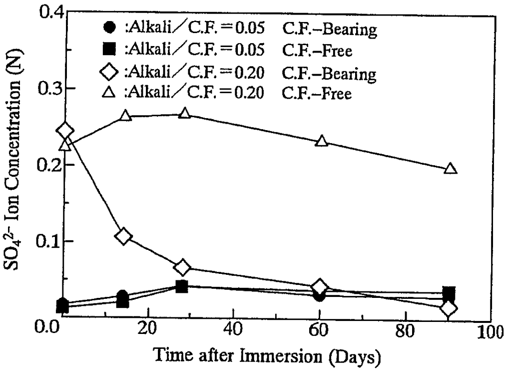

Fig. 20 Changes in $SO_4^{2-}$ Ion Concentration in Pore Solutions of Mortars with and without Calcined Flint

### b) $SO_4^{2-}$ Ion Concentration

Figure 20 shows changes in $SO_4^{2-}$ ion concentration with time in the pore solution of mortar samples containing reactive aggregate and no reactive aggregate with alkali/C.F. ratios of 0.05 and 0.20 during immersion in NaCl solution. The $SO_4^{2-}$ ion concentration in mortar with an alkali/C.F. ratio of 0.20 containing a relatively large amount of added NaOH is greatly different from that in samples with an alkali/C.F. ratio of 0.05. The $SO_4^{2-}$ ion concentration in the pore solution of mortar samples with an alkali/C.F. ratio of 0.05 was as low as about 0.02 N immediately before immersion in NaCl solution and this rose a little during the first 28 days of immersion. Changes in $SO_4^{2-}$ ion concentration with time in mortar without reactive aggregate were little different from those in the corresponding samples with reactive aggregate. On the contrary, at an alkali/C.F. ratio of 0.20, the $SO_4^{2-}$ ion concentrations in samples with and without reactive aggregate was extremely high upon immersion as compared with mortar with an alkali/C.F. ratio of 0.05.

As shown in Fig. 20, after immersion in NaCl solution, the behavior of $SO_4^{2-}$ ions in the pore solution of mortars with and without reactive aggregate was greatly different from each other. In mortar containing reactive aggregate immersed in NaCl solution, the $SO_4^{2-}$ ion concentration in the pore solution rapidly decreased with time, resulting in a slightly lower $SO_4^{2-}$ ion concentration than in mortar without reactive aggregate after 90 days of immersion. However, in mortar without reactive aggregate, the $SO_4^{2-}$ ion concentration increased slightly up to 28 days after immersion and, thereafter, slowly decreased with time. This behavior of $SO_4^{2-}$ ions in the pore solution, along with the observed increases in ettringite content in reactive aggregate mortar with time (Fig. 8), indicate that comparatively large amounts of ettringite are rapidly formed as $SO_4^{2-}$ dissipates from the pore solution in immersed mortar containing reactive aggregate.

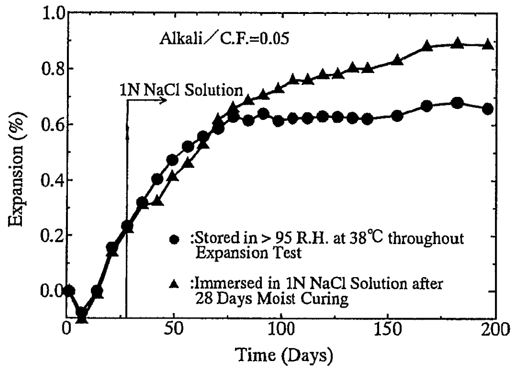

Fig. 21 Expansion Curves for Mortars Immersed in 1N NaCl Solution after 28 Days of Moist Environment throughout the Expansion Test

## 3.6 Expansion Mechanisms of Mortar Containing Reactive Aggregate in NaCl Solution

### a) Mortars with a Relatively Low Alkali/C.F. Ratio

Figure 21 shows expansion curves for mortar containing calcined flint and immersed in 1N NaCl solution after 28 days of moist curing with reference samples stored in a moist environment throughout the test. Expansion halted in the moist environment at about 75 days. However, in NaCl solution expansion continued steadily even after 75 days. This difference in expansion behavior between samples immersed in NaCl solution and stored in a moist environment corresponds well with the difference in microhardness in central portions of the reactive aggregate grains. As shown in Figs. 11 and 12, the microhardness falls more with time in central portions 250 μm to 400 μm away from the interface in reactive grains in mortar in NaCl solution than in a moist environment. This suggests that the alkali-silica reaction is more active in the reactive grains in NaCl solution than in a moist environment. Furthermore, the progress of the alkali-silica reaction in central portions of reactive grains during immersion in NaCl solution can be attributed to the maintenance of a relatively high level of $OH^-$ ion concentration of about 0.3 to 0.4 in pore solutions in the mortar cylinders (Fig. 19). Considering the threshold value of $OH^-$ ion concentration of 0.25 proposed by Diamond [21], an $OH^-$ ion concentration as high as about 0.3 N to 0.4 N is enough to maintain the progress of the alkali-silica reaction, even if the gradients of the $OH^-$ ion concentration within the mortar cylinder is taken into consideration.

The results of this study, thus allow us to deduce that increases in the expansion of mortar with a reactive aggregate in NaCl solution is caused by a rise in $OH^-$ ion concentration in the pore solution brought about by the intrusion of NaCl. Reaction product of the alkali-silica reaction and also $Cl^-$ ions certainly play an important role in raising the $OH^-$ ion concentration in the pore solution.

As previously mentioned, in mortar with an alkali/C.F. ratio of less than 0.10, there are significant differences in ettringite content depending on whether reactive aggregate is present (Figs. 8 and 9). Furthermore, at an alkali/C.F. ratio of less than 0.06, larger amounts of ettringite are produced in mortars without reactive aggregate than in those with reactive aggregate. These results indicate that the formation of ettringite in reactive aggregate mortars does not influence their expansion.

### b) Mortar with Added NaOH

Figure 22 shows expansion curves for samples with an alkali/C.F. ratio of 0.20 immersed in NaCl and NaOH solutions. Expansion in the NaCl solution was extraordinary as compared to that in NaOH solution. In samples in NaOH, a high $OH^-$ ion concentration must have been maintained throughout the expansion test. This great difference in expansion suggests that expansion in the mortar with a large amount of added NaOH in NaCl solution is due to the alkali-silica reaction as well as to other mechanisms. In Fig. 23, the ettringite content and measured expansion for mortar samples with an alkali/C.F. ratio of 0.20 are plotted against time during the immersion in NaCl solution to elucidate the correlation between expansion and ettringite content. These plots indicate that increases in expansion are approximately proportional to ettringite content. Taking account of this good correlation between expansion and ettringite content, and the reduction in $SO_4^{2-}$ ion concentration in the pore solutions in reactive aggregate mortars only (Fig. 20), it may be concluded that at least some of the extraordinary expansion of mortar with reactive aggregate containing a large amount of added NaOH in NaCl solution is attributable to the formation of ettringite within the mortar. Great differences in ettringite content between mortar samples with and without reactive aggregate at an alkali/C.F. ratio of 0.15 (Figs. 8 and 9) indicate that the formation of ettringite may also increase expansion.

As described above, some of the extreme expansion of mortar with relatively large amounts of added NaOH in 1N NaCl solution at an elevated temperature of 38° C appears to result from an additional mechanism related to ettringite formation. However, such mortars with an alkali/C.F. ratio of 0.15 or 0.20 produced by adding large amounts of NaOH fall outside the alkali-silica reaction system encountered in real concrete. The increase in expansion in mortar with no added NaOH and containing reactive aggregate in 1N NaCl solution at 38° C is mainly due to a rise in $OH^-$ ion concentration in the pore solution brought about by intrusion of NaCl. However, under conditions of 0.51N NaCl solution, which correspond to sea water at 20° C, no increase in $OH^-$ ion concentration in the pore solution occurs even in the presence of reactive aggregate [22].

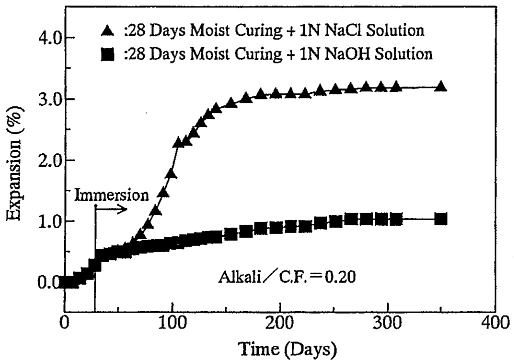

Fig. 22 Expansion Curves for Mortars with an Alkali/C.F. Ratio of 0.20

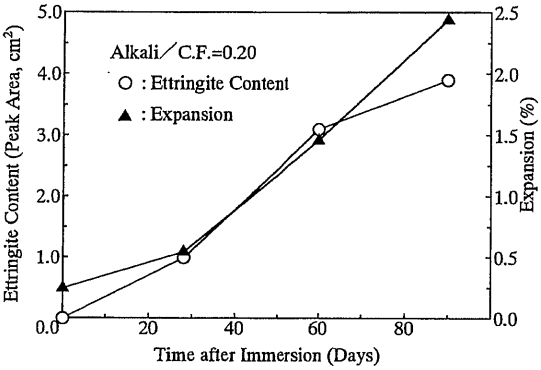

Fig. 23 Correlation between Ettringite Content and Expansion

## 4. Conclusions

The expansion behavior, composition of reaction products within reactive aggregate grains, and the behavior of various ions and ettringite formation in the cement paste phase of mortar samples were measured. The mechanisms of mortar expansion in NaCl solution at an elevated temperature of 38° C when the mortar contains reactive aggregate appear to differ according to the amount of NaOH added. The main results obtained in this work are as follows:

(1) The microhardness in the region about 100 μm to 200 μm from the interface increases dramatically with time after immersion in 1N NaCl solution, resulting in the production of an extremely hard substance.

(2) The increased expansion of mortar with a relatively low alkali/C.F. ratio in NaCl solution is attributable to progress of the alkali-silica reaction in central portions of reactive aggregate grains which causes a rise in $OH^-$ ion concentration in the pore solution.

(3) Both the alkali-silica reaction and $Cl^-$ ions play an important role in raising the $OH^-$ ion concentration in the pore solution.

(4) The $SO_4^{2-}$ ion concentration in mortar with a large amount of added NaOH is extremely high. Only in mortar containing reactive aggregate does the $SO_4^{2-}$ ion concentration in the pore solution decrease with time during the immersion in NaCl solution. At the same time, the ettringite content in the mortar increases with time.

(5) At least some of the extreme expansion of mortar containing reactive aggregate and a large amount of added NaOH is due to the formation of ettringite during immersion in NaCl solution.

## References

[1] Mehta, P.K.: Proc. intl. conf. on the effects of alkalis in cement and concrete, Purdue University, pp. 229 - 234, 1978
[2] Nakano, K., Kobayashi, S. et al.: Annual report of CAJ Vol. 38, Cement Association of Japan, pp. 106 - 109, 1984 (in Japanese)
[3] Chatterji, S.: Cement and Concrete Research, Vol. 8, pp. 647 - 650, 1978
[4] Nishibayashi, S.,et al.: Informative abstracts for JSCE annual meeting, V, pp. 428 - 429, 1987 (in Japanese)
[5] Kawamura, M., Takemoto, K., and Terashima, N.: Annual report of CAJ Vol. 42, Cement Association of Japan, pp. 327 - 330, 1988 (in Japanese)
[6] Nixon, P. J., Page, C.L. et al.: Advances in cement research, Vol. 1, No. 2, pp. 99 - 106, 1988
[7] Kawamura, M., and Ichise, M.: Cement and concrete research, Vol. 20, pp. 757 - 766, 1990
[8] Nagataki, S., Otsuki, N., et al.: Durability of building materials and components 6 , E & FN Spon Co. Ltd., pp. 363 - 372, 1993
[9] Chatterji, S.: Cement and concrete research, Vol. 9, pp. 185 - 188, 1979
[10] Grattan-Bellew, P.E.: Durability of building materials 1, pp. 363 - 376, 1983
[11] Davis, G., and Oberholster, R.E.: Proc. 8th intl. conf. on alkali-aggregate reaction, Kyoto, pp. 623 - 628, 1989
[12] Kawamura, M., Takemoto, K.: 6th intl. conf on alkalis in concrete, Copenhagen, pp. 167 - 172, 1983
[13] Kawamura, M. and Diamond, S.: in the course of preparation
[14] Lumly, J.S.: Proc. 8th intl. conf. on alkali-aggregate reaction, Kyoto, pp. 561 - 566, 1989
[15] Takeuchi, K., Kawamura, M. and Sugiyama, A.: Proc. the Japan Concrete Institute, Vol. 15, No. 1, pp. 917 - 922, 1993 (in Japanese)
[16] Kawamura, M., Igarashi, M., and Takeuchi, K.: Proc. 9th intl. conf. on alkali-aggregate reaction in concrete, London, pp. 529 - 536, 1992
[17] Odler, I., and Abdul-Maula, S.: Cement and concrete research, Vol. 14, pp. 133 - 141, 1984

[18] Spiering, G.A.C.M., and Stein, H.N.: Cement and concrete research, Vol. 6, pp. 265 - 272, and pp. 487 - 496, 1976

[19] Chatterji, S., Jensen, A.D., Thaulow, N., and Christen, P.: Cement and concrete research, Vol. 16, pp. 246 - 254, 1986

[20] Verbeck, G.J.: ACI special publication, SP-49, pp. 21 - 30, 1975

[21] Diamond, S. : Proc. 6th intl. conf. on alkalis in concrete, Copenhagen, pp. 155 - 166, 1983

[22] Kawamura, M., and Takeuchi, K.: Real world concrete, Proc. R.N. Swamy Symp., Milwaukee, ACI SP, pp. 235 - 250, 1995