

ROLE OF GYPSUM IN EXPANSION OF MORTARS CONTAINING REACTIVE AGGREGATE IN NaCl SOLUTION

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ABSTRACT

Some experimental results obtained by the authors show that clarifying a role of gypsum in Portland cement may lead to better understanding of the mechanisms of the expansion of mortar containing reactive aggregate in NaCl solution. The major objective of this study is to discuss a role of gypsum in cement in the expansion of mortars in NaCl solution at an elevated temperature of 38 °C. It was found that mortars with gypsum more rapidly expanded immediately after immersion in NaCl solution than gypsum-free ones. OH⁻ ion concentrations in pore solutions in mortars made with a clinker and 3% gypsum were higher than in mortars made with a gypsum-free clinker. The presence of ettringite and/or monosulfate certainly play a role in the increase of expansions of mortars in NaCl solution by raising OH⁻ ion concentration in the pore solution. However, a part of expansions of mortars with gypsum is possibly caused by the formation of ettringite during immersion in NaCl solution.

Keyword: alkali-silica reaction, ettringite, clinker, gypsum, NaCl, OH⁻

INTRODUCTION

Several explanations have been given on the expansion of mortars containing a reactive aggregate in NaCl solution. Some workers suggested that at least a part of expansion of concrete due to the alkali-silica reaction under a saline environment was responsible for the formation of an expansive chlorosulphoaluminate complex (Grattan-Bellew 1983), (Davies and Oberholster 1989). The present authors revealed that the promotion of expansion of reactive aggregate-bearing mortars in NaCl solution at an elevated temperature of 38 °C was attributable to a rise of OH⁻ ion concentration in the pore solution in the mortars brought about by the intrusion of NaCl (Kawamura et al. 1995). Another indication that a part of expansion of some mortars with relatively large amounts of added NaOH during the immersion in 1 N NaCl solution at 38 °C was caused by the formation of ettringite in the mortars was obtained (Kawamura et al. 1995). On the other hand, it might be certain that chloride ions play an important role in the acceleration of the alkali-silica reaction in mortars in NaCl solution at 20 °C (Helmuth and Stark 1992), (Kawamura and Takeuchi 1995). However, it still remains ambiguous whether the formation of ettringite in mortars is related to their expansions in NaCl solution.

Comparison in changes of the pore solution composition and solid phases between mortars made with a clinker with and without gypsum in NaCl solution will possibly lead to the elucidation of a role of gypsum in the ASR expansion of mortars in the solution. Some evidences on the role of chloride ions in the alkali-silica reaction can be also explicitly obtained from such experimental approaches. In this paper, a role of gypsum in Portland cement as well as chloride ions in expansion of mortars in NaCl solution at an elevated temperature of 38 °C is discussed on the basis of the expansion behavior, the pore solution composition and the formation of ettringite in clinker mortars with and without gypsum.

OUTLINE OF EXPERIMENTS

Materials

The reactive aggregate used was a calcined flint (C.F.) produced in Blue Circle Industries PLC, in England. The Japanese standard sand was also used as a non-reactive aggregate. The chemical composition of a clinker is presented in Table 1. Its alkali content was 0.71% as the equivalent Na₂O percentage. The gypsum used was the first class reagent of CaSO₄ 2H₂O.

Table 1 Chemical compositions of clinker (%)

Ig. loss	Insol.	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	MnO
0.1	0.1	21.9	5.6	2.8	65.5	1.9	0.5	0.30	0.63	0.39	0.14	0.09

Mix proportion of mortars

Mortars with C.F. : (standard sand + C.F.) ratios of 0.1, 0.2, 0.3, 0.4 and 0.5 were prepared maintaining (standard sand + C.F.) : clinker ratio and water : clinker ratio 0.75 and 0.5, respectively. Half of the mortar specimens were made with a clinker containing 3% gypsum by mass.

Expansion test

After 28 days curing of mortar bars of 2.5 by 2.5 by 285.5 mm in a moist container maintained at 38 °C and >95% R.H., they were immersed in 1N NaCl solution. The other series of mortar bars were stored in the container throughout expansion tests.

Analysis of pore solution

Pore solutions were expressed by the high pressure apparatus (Barneyback and Diamond 1981) from ϕ 40 mm by 100 mm cylinders made with a cement clinker with and without gypsum at a C.F. : total aggregate ratio of 0.2. The pore solutions extracted from the reactive aggregate-free mortars made at a mix proportion corresponding to that of the above reactive aggregate-bearing mortars were also analyzed. The mortar cylinders were cured in a moist container at 38 °C for 28 days, and then immersed into 1N NaCl solution during periods of 14, 28, 60 and 90 days. The pore solutions were analyzed by standard methods.

Quantitative analysis of ettringite

A quantitative differential thermal analysis (DTA) (Odler and Abdul-Maula 1984) was made to obtain ettringite content in mortars immersed in NaCl solution. Mortar flakes were sampled from portions within the depth of 5 mm from the surfaces of mortar blocks. Dry powdered clinker samples obtained by grinding clinker mortars without gypsum placed in the same condition as the mortars containing 3% gypsum were used as a reference material. DTA curves were obtained at the heating rate of 10 °K/minute with 25 mg sample. Ettringite content in mortars was evaluated as the area covered by an endothermic peak at about 110 °C.

Measurements of microhardness

Mortar bars with an C.F. : total aggregate ratio of 0.2 for expansion tests were cut into cubic blocks of 20 by 25 by 25 mm one day after casting. The 25 by 25 by faces of each block were coated with a silicon resin type sealant to allow Na⁺ and Cl⁻ ions 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 tests. The silicon resin coating on the two faces was removed at a prescribed time after immersion in 1 N NaCl solution, and then one of the faces was polished on the rotor using a set of SiC polishing paper.

The microhardness measurements tester with Vickers indenter was used to measure the microhardness with a reacting aggregate grain along the longest radius at intervals of

about 10 to 20 μm . The load to be selected in measurements in samples immersed in NaCl solution for 60 days was 20g; 50g in samples immersed in 90 and 120 days. Two grains with a diameter of about 2 mm appearing in the areas within 5 mm deep from the surfaces of mortars blocks were selected for microhardness measurements. The value of microhardness was the average of measurements for two grains.

EDXA analysis

After the completion of microhardness measurements, polished surfaces of mortar blocks which had been dried in a vacuum drying oven at a room temperature, were coated with gold. EDXA analyses were made at a number of spots using scanning electron microscope Nihon Denshi Co. Ltd. equipped with the EDXA International energy-dispersive X-ray analyzer. The accelerating voltage was 25 kV. The spectrums for the $K\alpha$ peaks of Na, K, Ca, Si, S, Cl and Al were accumulated for period of 100 seconds of counting.

RESULTS AND DISCUSSION

Figs. 1, 2, 3 and 4 show expansion curves of reactive aggregate-bearing mortars with and without gypsum immersed in 1 N NaCl solution and stored in a moist environment at 38 °C. During the first 28 days moist curing, expansions of all of the mortars produced by the use of a clinker with gypsum are found to be considerably greater than those of the corresponding mortars made with the gypsum-free clinker. The results show that SO_4^{2-} ions functioned to increase the expansion of mortars due to the alkali-silica reaction during the moist curing at 38 °C. The addition of gypsum accelerates the hydration of C_3S (Bentur 1976). However, since OH^- ion concentration of the pore solutions in mortars with gypsum is almost the same as in gypsum-free mortars, as shown later (Fig. 5), the involvement of SO_4^{2-} ions in hydration of clinker minerals in the alkali reactive aggregate-bearing mortar system may bring about greater expansions in mortars with gypsum than in gypsum-free ones.

More significant differences in expansion behavior between mortars with and without gypsum were found in mortars immersed in NaCl solution, as shown in Fig. 2 and 4. Expansions of gypsum-free mortars with a C.F. : total aggregate ratio of 0.5 in NaCl solution were greater than in a moist environment (Fig. 1). However, only small differences in expansion between mortars stored in a moist environment and NaCl solution were found at other C.F. : total aggregate ratios. Greater expansions of gypsum-free mortars with a C.F. : total aggregate ratio of 0.5 in NaCl solution than in the moist environment indicates that Cl^- ions accelerated the alkali-silica reaction in mortars. A comparison between expansion curves in Fig. 2 and 4 shows that the expansion behavior of gypsum-bearing mortars was greatly different from that of gypsum-free ones in NaCl solution. All of the mortars with gypsum except the one with a C.F. : total aggregate ratio of 0.1 more rapidly expanded immediately after immersion in NaCl solution than gypsum-free ones, leading to considerably greater ultimate expansions of mortars with gypsum. However, at a C.F. : total aggregate ratio of 0.1, while the gypsum-free mortar did not expand at all, the gypsum-bearing mortar showed considerably great delayed expansions.

OH^- and SO_4^{2-} ion concentration in the pore solution

Fig. 5 presents changes in OH^- ion concentration with time in pore solutions for mortars with and without gypsum stored in a moist environment throughout prescribed periods and immersed in NaCl solution after 28 days moist curing. All the mortars showed rapid decreases in OH^- ion concentration immediately after immersion in NaCl solution. However, a higher level of OH^- ion concentration was maintained in mortars containing both gypsum and reactive aggregate than in other mortars after at least 14 days immersion in NaCl solution. These results show that some reactions releasing more OH^- ions have occurred only in ASR reacting mortars containing gypsum.

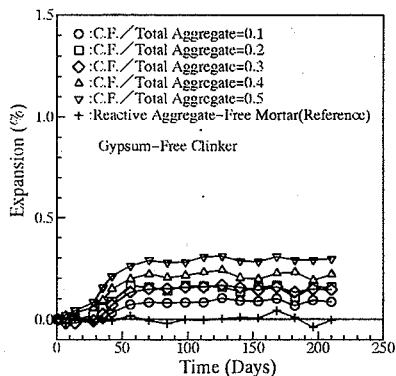


Fig. 1 Expansion curves for gypsum-free clinker mortars containing calcined flint in a moist environment at 38 °C.

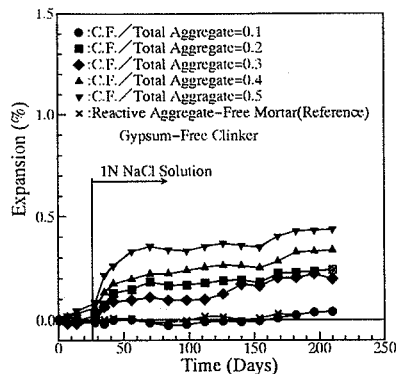


Fig. 2 Expansion curves for gypsum-free clinker mortars containing calcined flint in 1 N NaCl solution.

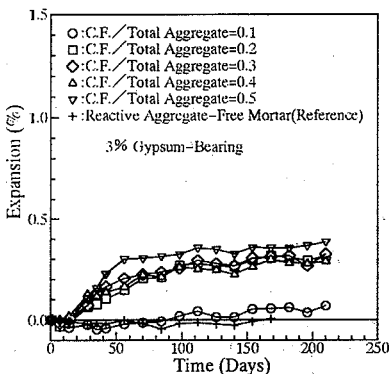


Fig. 3 Expansion curves for 3% gypsum-bearing clinker mortars containing calcined flint in a moist environment at 38 °C.

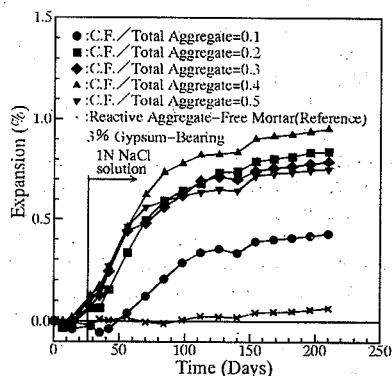


Fig. 4 Expansion curves for 3% gypsum-bearing clinker mortars containing calcined flint in 1 N NaCl solution.

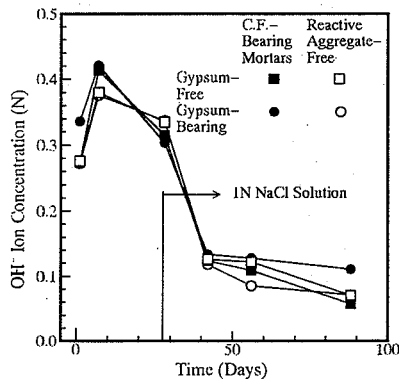


Fig. 5 Changes in OH^- ion concentrations with time in the pore solutions in various mortars.

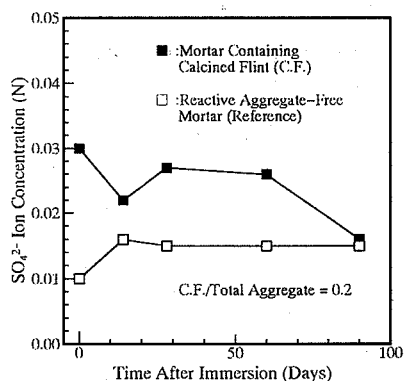


Fig. 6 Changes in SO_4^{2-} ion concentrations with time in pore solutions expressed from mortars with and without reactive aggregate.

Fig. 6 shows changes in SO_4^{2-} ion concentration with time in pore solutions extracted from gypsum-bearing mortars with and without reactive aggregate after immersion in NaCl solution. As shown in Fig. 6, at the end of 28 days curing in a moist environment, SO_4^{2-} ions in the pore solutions in reactive aggregate-bearing mortars are found to be considerably higher than in the corresponding reactive aggregate-free mortar. While SO_4^{2-} ion concentrations rose a little within two weeks after immersion in NaCl solution in reactive aggregate-free mortars, followed by leveling off, reactive aggregate-bearing mortars showed gradual decreases with time. From the differences in the changes in SO_4^{2-} ion concentration with time between mortars with and without reactive aggregate, it is presumed that SO_4^{2-} ions were taken up by the alkali-silica gel produced during immersion in NaCl solution. It has been certainly shown by the authors (Kawamura et al. 1995) that SO_4^{2-} ions intruded into reacting calcined flint grains in mortars immersed in NaCl solution. However, as shown later (Fig. 7), a little greater amount of ettringite was produced in mortars with calcined flint than in reactive aggregate-free ones. Therefore, an assumption that more SO_4^{2-} ions taken up from the pore solutions in mortars with reactive aggregate were used for the formation of ettringite, might be also possible.

Ettringite content in mortars

Fig. 7 presents measured ettringite contents in mortars containing calcined flint and reactive aggregate-free mortars stored in a moist environment and NaCl solution. It is found from the data in Fig. 7 that greater amount of ettringite were produced in reactive aggregate-bearing mortars than in reactive aggregate-free ones. Great changes in ettringite content with time were not found in mortars in a moist environment. In contrast, both mortars with and without reactive aggregate showed gradual increases with time over a period of 60 days. Furthermore, it was also found from Fig. 7 that differences in ettringite content between

mortars with and without reactive aggregate increased with time. Production of greater amounts of ettringite in mortars with reactive aggregate than the reference corresponds to reductions in SO_4^{2-} ion concentration with time in mortars with calcined flint (Fig. 6).

Alkalis and calcium concentration within calcined flint grains

Plots of $(\text{Na}+\text{K})/\text{Si}$ and Ca/Si count ratios within reacting calcined flint grains in mortars obtained by EDXA spot analyses are presented in Figs. 8 - 11. A base line is also drawn based on the values obtained for original calcined flint grains. The reactive aggregate is a synthetic cristobalite. However, the reactivity of individual grains may vary from grain to grain to some extent. As shown in Figs. 8 and 9, $(\text{Na}+\text{K})/\text{Si}$ count ratios at various spots within reactive aggregate grains appeared to depend on the reactivity of a grain incidentally selected for analysis as well as on the progress of the alkali-silica reaction. However, comparison in $(\text{Na}+\text{K})/\text{Si}$ count ratio between gypsum-free and -bearing mortars at the same age indicates that more alkalis ions were incorporated in reactive grains in gypsum-bearing mortars than in gypsum-free ones. More active progress of the alkali-silica reaction within reactive grains in gypsum-bearing mortars than in gypsum-free ones is not inconsistent with the maintenance of a little higher OH^- ion concentration in the pore solutions in the former than in the latter (Fig. 5).

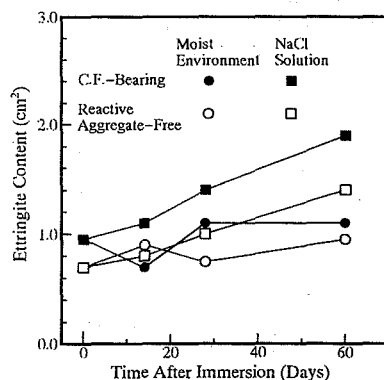


Fig. 7 Ettringite contents in mortars containing calcined flint and reactive aggregate-free mortars.

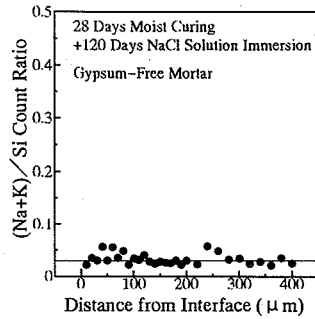
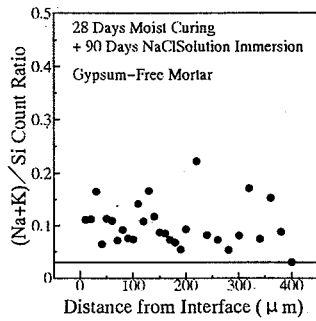


Fig. 8 (Na+K)/Si count ratios at various spots within calcined flint grains in gypsum-free clinker mortars.

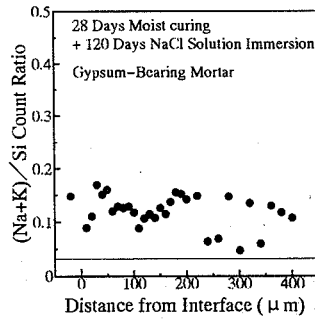
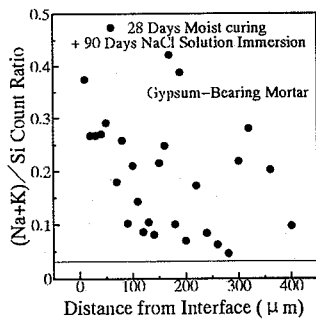


Fig. 9 (Na+K)/Si count ratios at various spots within calcined flint grains in gypsum-bearing clinker mortars.

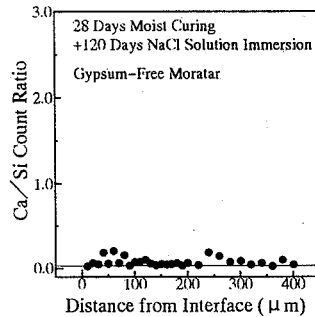
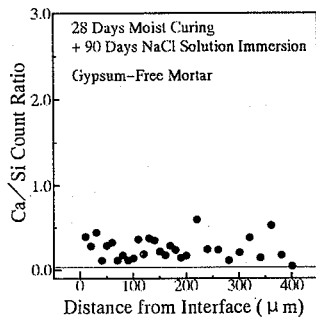


Fig. 10 Ca/Si count ratios at various spots within calcined flint grains in gypsum-free clinker mortars.

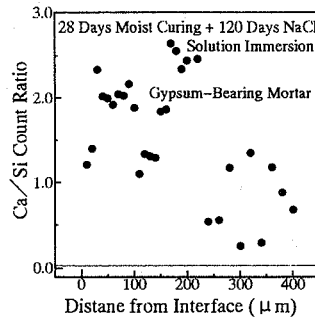
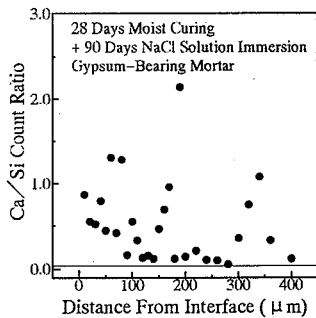


Fig. 11 Ca/Si count ratios at various spots within calcined flint grains in gypsum-bearing clinker mortars.

Figs. 10 and 11 show Ca/Si count ratios at a number of spots within reactive grains in gypsum-free and -bearing mortars, respectively. As shown in these figures, far greater amounts of Ca^{2+} ions intruded into reactive grains in mortars with gypsum than in mortars without gypsum during periods longer than 90 days after immersion in NaCl solution. As a whole, Ca/Si count ratios in reactive grains in these mortars were extremely high as compared with Ca/Si count ratios of less than about 0.56 obtained in another series of mortars produced with a high alkali cement with the equivalent Na_2O percentage of 0.97 by the present authors (Kawamura et al. 1995). Such extremely great differences in Ca/Si count ratios between these two mortars made with different cements may be due to a difference in alkali content of the cements used.

Microhardness within calcined flint grains in mortars

Figs. 12 and 13 presents measured microhardness values within calcined flint grains in gypsum-free and -bearing mortars immersed in NaCl solution during prescribed periods after 28 days moist curing. It is found from these figures that areas up to about 170 μm away from the interface softened up to 60 days after immersion in NaCl solution both in gypsum-free and -bearing mortars. However, the immersion of mortars in NaCl solution for at least 90 days brought about great changes in microhardness within reacting calcined grains. Great increases in microhardness in the areas up to about 350 μm away from the interface were found both in mortars with and without gypsum immersed in NaCl solution during periods longer than 90 days. Especially, as shown in Fig. 13, the values of microhardness in the areas ranging from about 100 μm to 350 μm away from the interface in mortars immersed in NaCl solution during a period of 120 days were extremely high. The correspondence between great increases in microhardness and the intrusion of great amounts of Ca^{2+} ions in some areas within reacting grains was also found previously (Kawamura et al. 1995). The load of 50g selected in microhardness measurements in this study was greater than the load of 20g in the previous work (Kawamura et al. 1995). It should be noted that the value of microhardness varies with the load selected (Igarashi et al. 1996). However, the differences in the extent of progress of the alkali-silica reaction within reactive grains between mortars with and without gypsum found in the EDXA analysis data (Figs. 8 and 9) were not so explicitly reflected in the changes in microhardness distributions (Figs. 12 and 13).

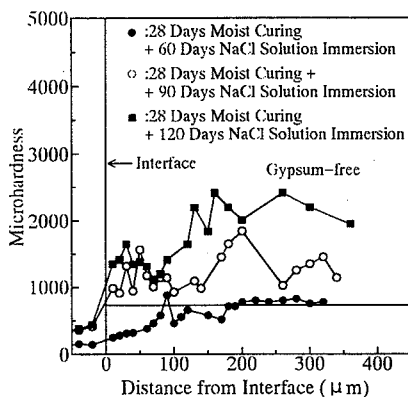


Fig. 12 Microhardness within calcined flint grains in gypsum-free mortars.

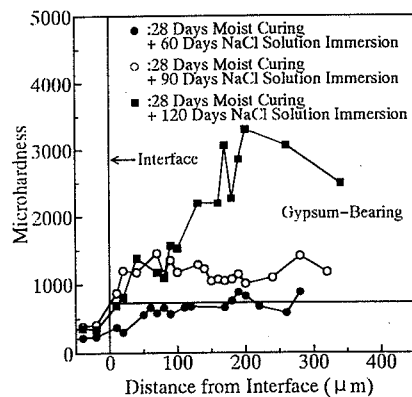


Fig. 13 Microhardness within calcined flint grains in gypsum-bearing mortars.

In our previous study (Kawamura et al. 1995), it was found that the presence of alkali-silica gel and the intrusion of Cl^- ions were prerequisite for a rise in OH^- ion concentration in the pore solutions in mortars in NaCl solution. From the results obtained in this study, it is evident that the presence of ettringite and/or monosulfate in mortars is also another factor essential to the increase in OH^- ion concentration in the pore solutions. It is obvious that more active progress of the alkali-silica reaction in mortars with gypsum than in gypsum-free ones in NaCl solution was due to the maintenance of higher OH^- ion concentrations in the mortars. However, since greater amounts of ettringite were produced in mortars with reactive aggregate than in the reference mortar in NaCl solution, a part of expansions of mortars with gypsum in NaCl solution was possibly caused by the formation of ettringite during immersion in NaCl solution.

CONCLUSIONS

- (1) Expansions of mortars made with gypsum were considerably greater than those of gypsum-free clinker in a moist curing at 38 °C.
- (2) Most mortars made with gypsum-bearing clinker more rapidly expanded immediately after immersion in NaCl solution than those of gypsum-free clinker mortars, leading to considerably greater ultimate expansions.
- (3) Greater amounts of ettringite were produced in mortars with reactive aggregate than in those without reactive aggregate.
- (4) The alkali-silica reaction in gypsum-bearing clinker mortars more actively progressed than in gypsum-free mortars.
- (5) More active progress of the alkali-silica reaction in mortars made with gypsum-bearing clinker is due to a higher OH^- ion concentration in the pore solution in the mortars in NaCl solution. However, a part of greater expansion of mortars with gypsum is possibly caused by the formation of ettringite during immersion in NaCl solution.

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