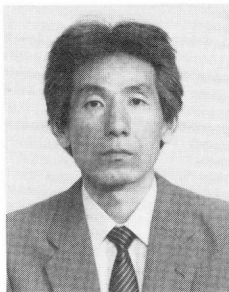


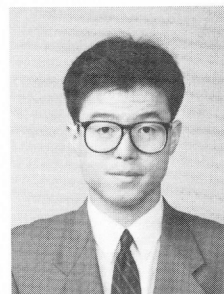
ALKALI-SILICA REACTION AND CORROSION OF STEEL REINFORCEMENT
IN MORTARS CONTAINING A REACTIVE AGGREGATE AND CHLORIDE
(Reprinted from Transaction of JSCE, No.451, V-17, 1992)



Mitsunori KAWAMURA



Kunio TAKEMOTO



Makoto ICHISE

SYNOPSIS

The relationships between pore solution composition and corrosion level - as experimentally evaluated by electrochemical measurements for a steel electrode embedded in mortar containing a reactive aggregate and a chloride - are discussed to reveal the influence of the alkali-silica reaction on the corrosion of steel reinforcement. The alkali-silica reaction is found to promote chloride-induced corrosion of steel bars embedded in mortars containing a reactive aggregate and a chloride. The extent of this promotion varies with the type of chloride. The relationship between corrosion level and Cl^-/OH^- ratio in the pore solution of CaCl_2 -bearing mortars is greatly different from that of NaCl -bearing mortars.

Keywords: chloride-induced corrosion, alkali-silica reaction, CaCl_2 , NaCl , pore solution composition, Cl^-/OH^- ratio, electrochemical measurements

M. Kawamura is a professor of civil engineering at Kanazawa University, Japan. He has been active in research into the durability of concrete, alkali-aggregate reaction, the use of additional cementitious materials in concrete making, and the microstructure of fiber-reinforced concrete.

K. Takemoto is an associate professor of civil engineering at Ishikawa National College of Technology, Japan. His research interest is concrete durability.

M. Ichise is a civil engineer at the Hokuriku Electric Power Co., Inc., Japan. He is a graduate student of civil engineering at Kanazawa University. He received his Master of Engineering degree in 1989.

1. INTRODUCTION

The major factors influencing chloride-induced corrosion of embedded steel reinforcement in concrete are the relative concentrations of aggressive chloride ions and inhibitive hydroxyl ions (the Cl^-/OH^- ratio) in the pore solution and the mobility of the corrosive substance (1). Thus, chloride-induced corrosion of embedded steel reinforcement in concrete may be enhanced by the presence of an alkali-reactive aggregate in the concrete because of the effect of the reactive aggregate on the Cl^-/OH^- ratio and the occurrence of extensive cracking due to the alkali-silica reaction.

It has been noted that the degree of chloride-induced corrosion of embedded steel reinforcement varies with the type of chloride. For example, although both NaCl and CaCl_2 are recognized as typical chlorides which cause chloride-induced corrosion in steel-reinforced concretes (1,2), steel bars in concretes containing CaCl_2 are more heavily corroded than those in concretes containing NaCl. On the other hand, it has been pointed out that NaCl and CaCl_2 promote the alkali-silica reaction (3,4) and that the alkali-silica expansion of mortars including NaCl is greater than that of mortars including CaCl_2 (5). Thus, since different chlorides have a different effect on the alkali-silica reaction and thus on the corrosion of steel reinforcement, the corrosion behavior of steel reinforcement in reactive aggregate-bearing concretes contaminated with CaCl_2 may be different from that in concretes contaminated with NaCl.

Considering the long-term usage of certain reinforced concretes containing an alkali reactive aggregate, the occurrence of the alkali-silica reaction itself may influence not only the durability of the concrete, but also the corrosion of steel reinforcement due to the cracks caused by the alkali-silica reaction (6). From the viewpoint of assessment and maintenance of concrete structures damaged by the alkali-silica reaction, it is necessary to understand the relationship between the alkali-silica reaction and corrosion of the steel reinforcement in concretes containing a reactive aggregate and chloride.

This study aims at revealing the effects of the alkali-silica reaction on embedded steel reinforcement in such concretes. The relationship between pore solution composition and corrosion level for mortars containing the reactive aggregate and a chloride as evaluated by electrochemical measurements on a steel electrode embedded is discussed. Differences in the effects of the alkali-silica reaction on steel reinforcement corrosion in mortars with the two different types of chloride are also discussed.

2. EXPERIMENTAL

2.1 Materials

The composition of the cement used in the experiments is given in Table 1; its Na_2O equivalent is 0.93% by weight of cement. Beltane opal aggregate with a size range of 0.6 mm to 1.2 mm was used as the reactive aggregate. A non-reactive aggregate, Toyoura standard siliceous sand, was also used. The two types of chloride used were NaCl and CaCl_2 . The steel reinforcement embedded in the mortar specimens for electrochemical measurements was a polished mild steel round bar 10 mm in diameter and 150 mm in length.

Table 1 Chemical composition of cement (%)

CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	MgO	Na ₂ O	K ₂ O	Ig. Loss
64.0	21.8	5.0	3.2	2.1	1.6	0.59	0.51	0.5

2.2 Mix Proportion of Mortars

Mortars were prepared with a total aggregate to cement ratio of 2.0 and a water to cement ratio of 0.5. The Beltane opal content in the aggregate was 3% by weight of aggregate, which was the pessimum content in these experiments. Chlorides were pre-dissolved in the mixing water in amounts corresponding to chloride ion addition levels of 0.25, 0.5, 1.0, and 2.0% of the weight of cement.

2.3 Procedure

2.3.1 Expansion test

Mortar prisms of size 40 x 40 x 160 mm were stored in a vapor container at 38°C. The length change of the prisms was measured according to the JIS A 1125 test procedure.

2.3.2 Expression of pore solution

Mortar cylinders of size ϕ 5.6 x 10 cm were stored in sealed vinyl sacks in a vapor container at 38°C. After the prescribed curing periods, pore solution was extracted from the specimens under high pressure (maximum 400 MPa) in a high-pressure apparatus. Chloride ion concentrations were determined by coulometric titration. The extracted solution was also analyzed for hydroxyl ion concentration against hydrochloric acid to the phenolphthalein end point. Concentrations were adjusted for the initial water content of the mix by measuring the non-evaporable water content according to the method for determining a cement's ignition loss (7).

2.3.3 Electrochemical measurements of the corrosion rate of embedded steel bars and evaluation of the corroded surface area

The mortar specimens containing a mild steel bar and a stainless steel electrode are schematically illustrated in Fig.1. The corrosion level of the steel bar was determined by measurements of half-cell potential and polarization resistance. A saturated calomel electrode (SCE) was used for the reference potential. In polarization resistance measurements, a potential scan ranging over 20 mV to either side of the rest potential was applied at 1 mV/sec, and potential (ΔE) versus current (ΔI) curves were recorded. The polarization resistance, $\Delta E/\Delta I$, was calculated from the slope of the measured polarization curve. Electrochemical measurements were carried out on specimens which had been left in a vapor container maintained at 38°C. Measurements were made daily on duplicate specimens until about one month, and thereafter every two days. In order to estimate the corrosion level of the embedded steel bars, corroded areas of steel bars removed from mortar specimens at the age of six months were sketched, and the corrosion area ratio (defined as the percentage of corroded area to total surface area of the steel bar) was calculated.

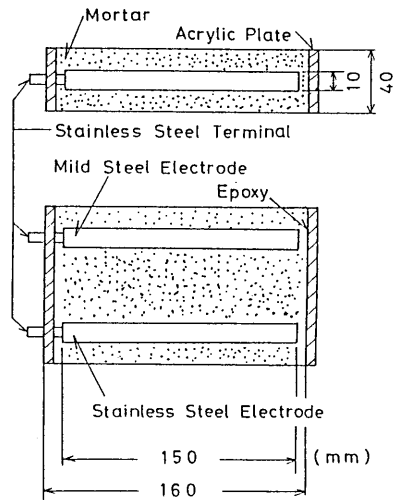
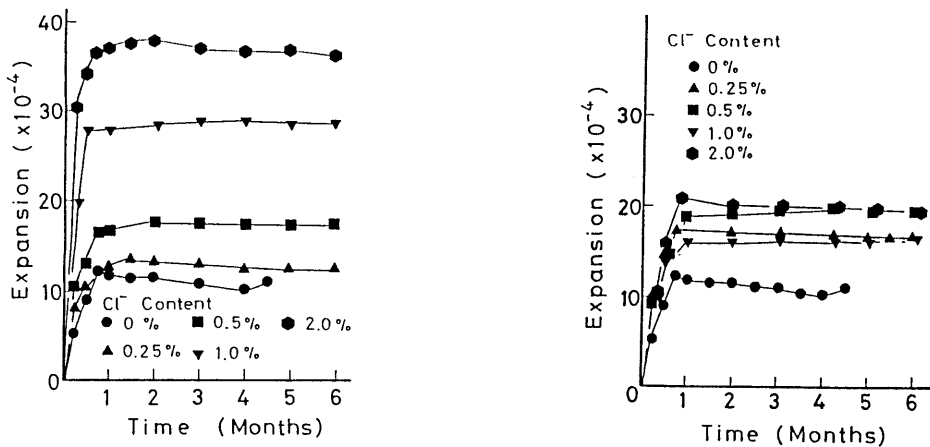


Fig.1 Schematic diagram of a specimen for electrochemical measurements



(a) Mortars containing various amounts of NaCl

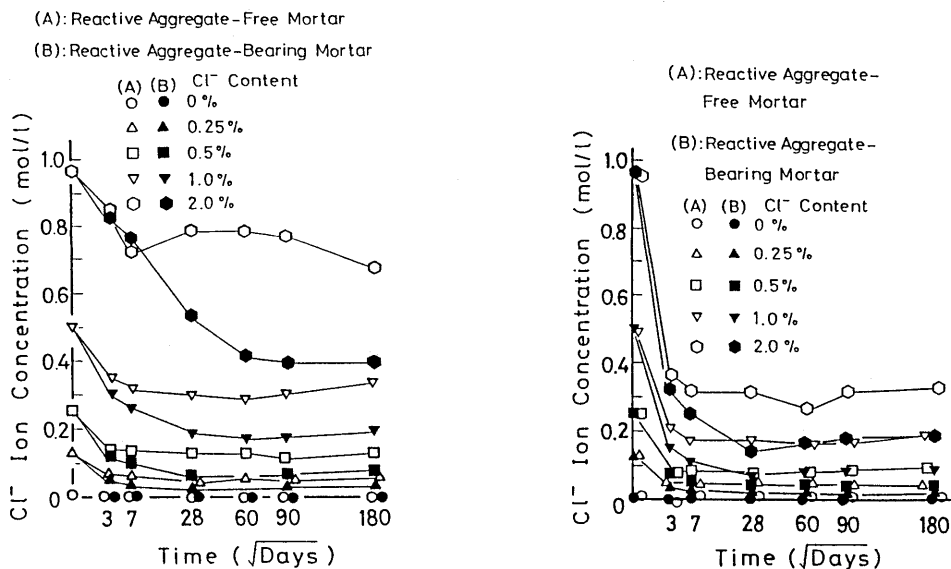
(b) Mortars containing various amounts of CaCl₂

Fig.2 Expansion curves for various mortars

3. RESULTS AND DISCUSSION

3.1 Expansion of Mortars Containing Beltane Opal and Various Amounts of Chloride

Expansion curves for the mortars containing Beltane opal are given in Fig.2. All mortars expanded rapidly, and most expansion had taken place by about one month. Expansion of all mortars containing chloride was greater than that of mortars



(a) Mortars containing various amounts of NaCl

(b) Mortars containing various amounts of CaCl_2

Fig.3 Cl^- ion concentration in pore solution of mortars with and without reactive aggregate at various ages

without chloride at all ages. The expansion of various mortars varied with the type and amount of chloride. Namely, mortars with NaCl expanded more with increasing NaCl, but differences in expansion between mortars containing various amounts of CaCl_2 were considerably smaller. At a Cl^- content of 1 and 2% by weight of cement, expansion of mortars containing CaCl_2 was considerably smaller than that of mortars with NaCl. It was found that the addition of NaCl and CaCl_2 in amounts up to 2% Cl^- increased the alkali-silica expansion of mortars containing Beltane opal and that the expansion increase resulting from the addition of NaCl was greater than that resulting from the addition of CaCl_2 at high chloride contents.

3.2 Cl^- and OH^- Concentrations in the Pore Solution of Mortars with Chloride

Figure 3 shows changes of Cl^- ion concentration in the pore solution of various mortars with time. As can be seen, the Cl^- ion concentration in the pore solution rapidly decreased with time until about one month, and thereafter changes in Cl^- ion concentration with time were small. However, the Cl^- ion concentration in the pore solution of mortars containing Beltane opal at a given Cl^- content was lower than that in the pore solution of Beltane opal-free mortars at the same Cl^- content. Differences in Cl^- ion concentration between mortars with and without Beltane opal increased with increasing Cl^- content.

The relationships between Cl^- ion concentration in the pore solution and the original Cl^- content are shown for various mortars in Fig.4. The Cl^- ion concentration in the pore solution increased proportionally with increasing Cl^- content in each case. The Cl^- ion concentration in the pore solution of mortars with CaCl_2 was lower than that in the pore solution of mortars with NaCl at a given Cl^- content in mortars, both with and without the reactive aggregate.

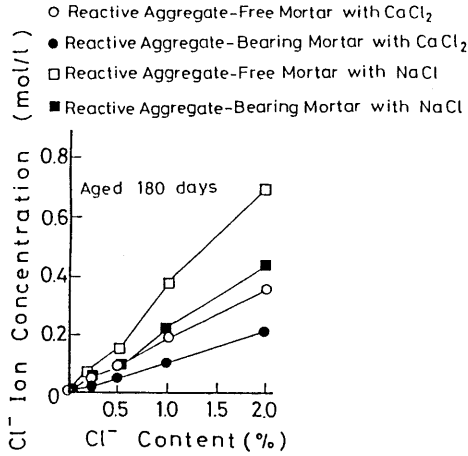
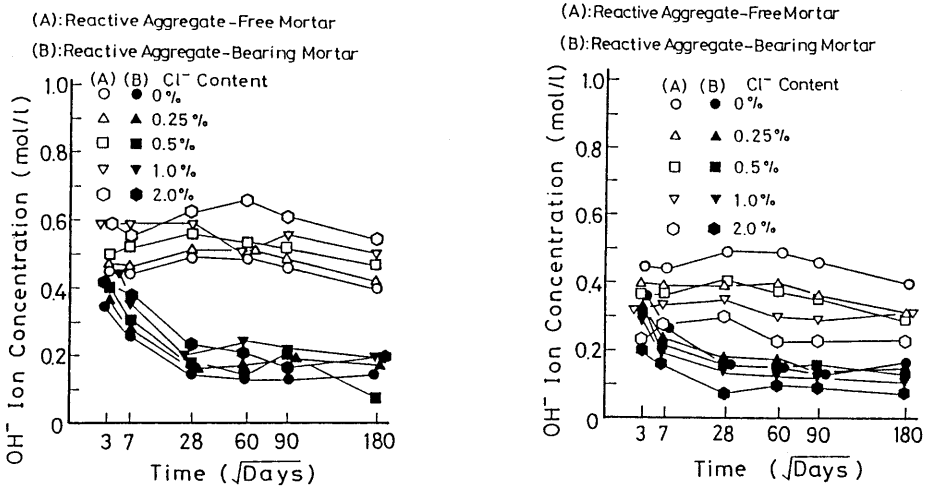


Fig. 4 Relationship between Cl^- ion concentration in pore solution and Cl^- content in various mortars

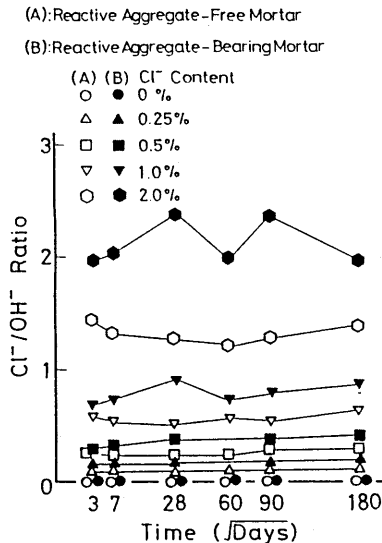


(a) Mortars containing various amounts of NaCl

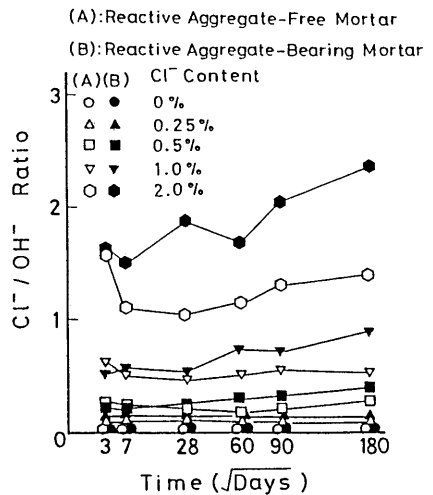
(b) Mortars containing various amounts of CaCl_2

Fig. 5 OH^- ion concentration in pore solution in mortars with and without the reactive aggregate at various ages

Figure 5 shows changes in OH^- ion concentration in the pore solution of various mortars with time. Large differences in time-dependent changes of OH^- ion concentration between mortars with and without Beltane opal were found. The OH^- ion concentration in mortars with Beltane opal was much lower than that in mortars without Beltane opal, especially after about 28 days of aging. Differences in OH^- ion concentration between NaCl-containing mortars with and without Beltane opal were



(a) Mortars containing various amounts of NaCl

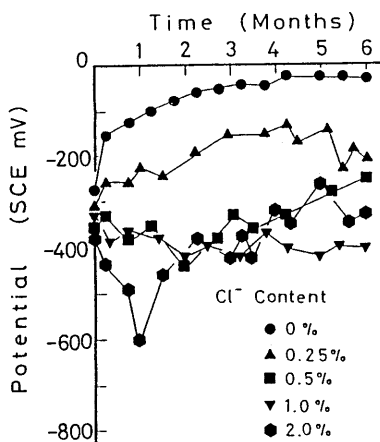


(b) Mortars containing various amounts of CaCl_2

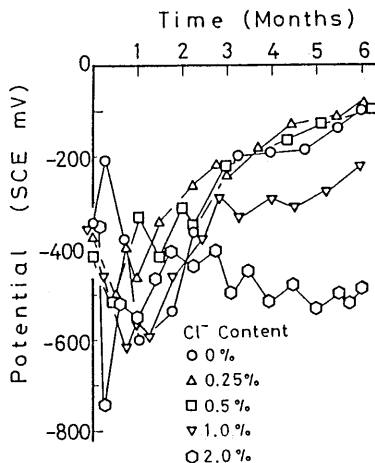
Fig.6 Cl^-/OH^- ratio in pore solution in mortars with and without the reactive aggregate at various ages

larger than those in CaCl_2 -containing mortars. The relationship between OH^- ion concentration in the pore solution and the original Cl^- content in various mortars was different for mortars with different types of chloride. The OH^- ion concentration in the pore solution increased with increasing NaCl, but the addition of CaCl_2 tended to depress OH^- ion concentration in the pore solution.

It has been pointed out by many researchers that there is a close correlation between Cl^-/OH^- ratio in the pore solution and the corrosion of embedded steel reinforcement (8,9,10). Cl^-/OH^- ratios in the pore solution of various mortars at various ages up to 180 days are given in Fig.6. As shown in Fig.6(a), the Cl^-/OH^- ratio in the pore solution changed only slightly with time in most mortars except that considerable change was seen in mortars with the highest NaCl content of 2.0% Cl^- . The Cl^-/OH^- ratio in pore solutions that had reached equilibrium increased with increasing NaCl. It was also found that the difference in Cl^-/OH^- ratio between mortars with and without Beltane opal increased with increasing NaCl treatment. On the other hand, the Cl^-/OH^- ratio in mortars with CaCl_2 changed in the same manner as that in mortars with NaCl, except that in mortars without Beltane opal the Cl^-/OH^- ratio decreased between 3 and 7 days and that the Cl^-/OH^- ratio in Beltane opal-bearing mortars with Cl^- contents of 0.5, 1.0, and 2.0% increased slightly with time (Fig.6(b)). Since both OH^- and Cl^- ions are taken up from the pore solution by the alkali-silica reaction (Fig.3 and 5), the fact that Cl^-/OH^- ratios in the pore solution of mortars with the reactive aggregate were almost always higher than in mortars without the reactive aggregate demonstrates that more OH^- ions than Cl^- ions are consumed by the reaction.

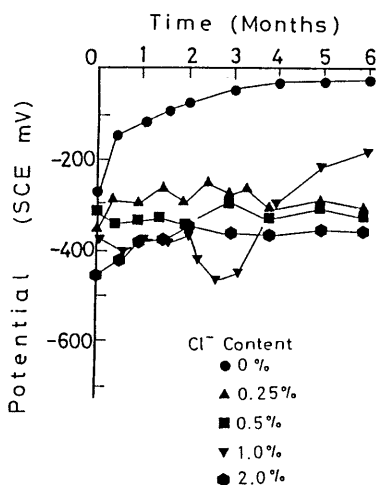


(a) Reactive aggregate-bearing mortars

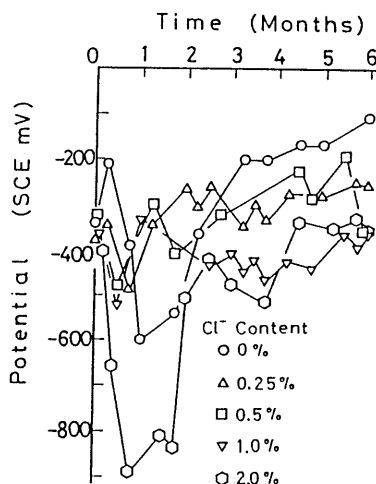


(b) Reactive aggregate-free mortars

Fig. 7 Corrosion potential of mild steel electrodes in mortars containing various amounts of NaCl



(a) Reactive aggregate-bearing mortars



(b) Reactive aggregate-free mortars

Fig. 8 Corrosion potential of mild steel electrodes in mortars containing various amounts of CaCl₂

3.3 Corrosion Level Evaluated by Electrochemical Measurements for a Steel Bar Embedded in Various Mortars

3.3.1 Corrosion potential of steel bars embedded in mortar

Figures 7 and 8 show the time-dependent changes in corrosion potential for mild steel bars embedded in mortars with NaCl and CaCl₂, respectively. There are considerable differences in the time-dependent changes in corrosion potential between

mortars with and without Beltane opal. In particular, differences in corrosion potential behavior of steel bars in mortar containing CaCl_2 with and without the reactive aggregate are found to be more significant than in mortars containing NaCl . The corrosion potential of steel bars embedded in all the reactive aggregate-free mortars decreased rapidly up to about one month, and then gradually increased toward an equilibrium level with repeated small rises and falls in potential. This repetitive rising and falling behavior is a result of alternating pitting of the steel surface by Cl^- ions and repassivation by OH^- ions supplied by the dissolution of $\text{Ca}(\text{OH})_2$ crystals (11). On the other hand, the corrosion potential of steel bars in chloride-bearing mortars with Beltane opal did not change as greatly as that in mortars without Beltane opal. The time-dependent changes of corrosion potential in mortars with Beltane opal which do not undergo small rises and falls, are probably responsible for the depression of OH^- ion concentration caused by the alkali-silica reaction (12).

If the possibility of steel bar corrosion in mortar is evaluated on the basis of corrosion potential as measured according to ASTM C-876, steel bars embedded in NaCl -bearing mortars with and without Beltane opal can be expected to corrode when the Cl^- content is greater than 0.5% and 1.0%, respectively, and to corrode in all CaCl_2 -bearing mortars both with and without the reactive aggregate.

3.3.2 Corrosion rate of steel bars embedded in mortar

Figures 9 and 10 show the time-dependent changes in corrosion rate (the reciprocal of polarization resistance) for steel bars embedded in mortar with NaCl and CaCl_2 , respectively. The corrosion rate of steel bars embedded in mortar containing the reactive aggregate and a chloride increased rapidly until one or two months, and then stabilized. On the contrary, a rapid increase in the corrosion rate of steel bars embedded in mortars without Beltane opal was seen until about one month, followed by a gradual decrease with time. The corrosion rate of steel bars in chloride-free mortars was actually zero after half a month. These figures suggest that the corrosion rate of steel bars embedded in mortar is enhanced by the presence of a reactive aggregate and the addition of a chloride, but the relationship between

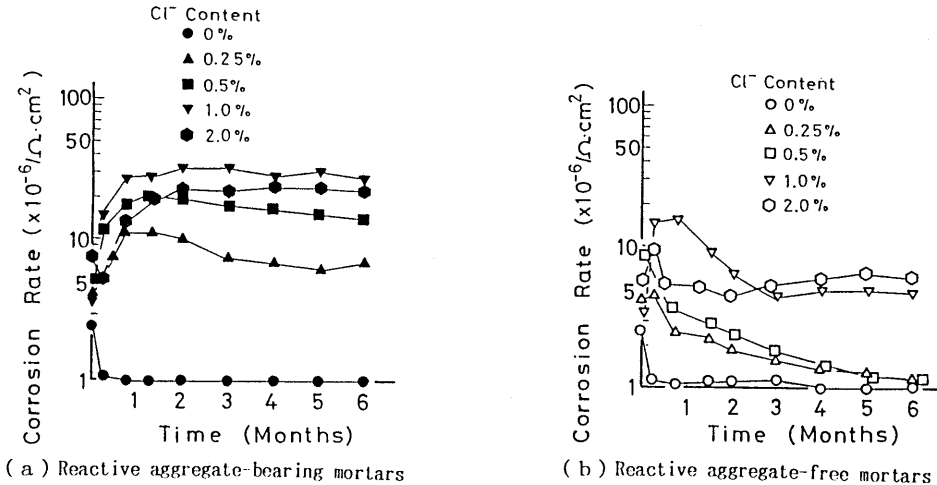


Fig. 9 Corrosion rate of mild steel electrodes in mortar containing various amounts of NaCl

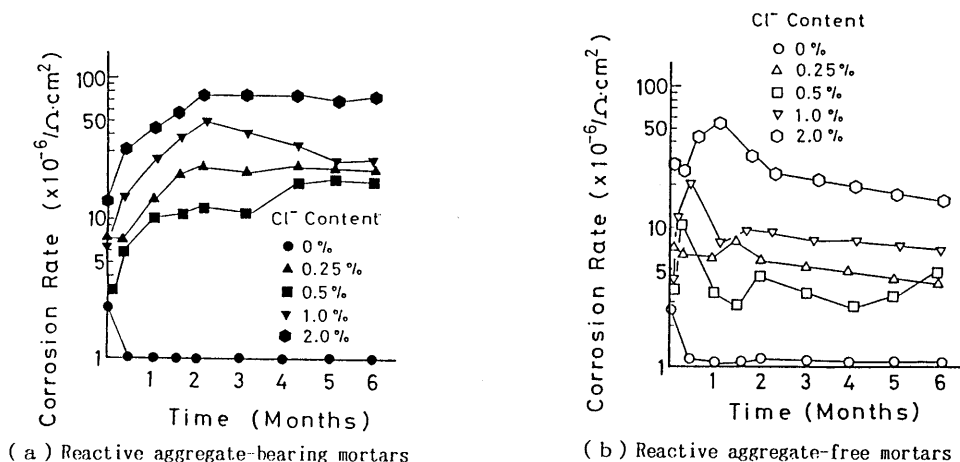


Fig. 10 Corrosion rate of mild steel electrodes in mortar containing various amounts of CaCl_2

- Reactive Aggregate-Free Mortar with CaCl_2
- Reactive Aggregate-Bearing Mortar with CaCl_2
- Reactive Aggregate-Free Mortar with NaCl
- Reactive Aggregate-Bearing Mortar with NaCl

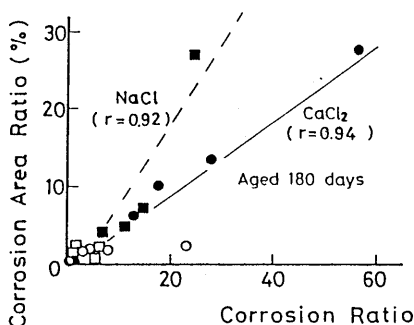


Fig. 11 Correlation between corrosion area ratio and corrosion ratio of mild steel electrodes in various mortars

corrosion rate and Cl^- content are different in mortars with different types of chloride.

The value obtained by integrating the corrosion rate from time zero to a certain age is regarded as a measure of the total loss of metal due to corrosion up to that time (13). The corrosion ratio, which is defined as the ratio of total corrosion loss for steel bars in a particular mortar to that for steel bars in a standard mortar without chloride and reactive aggregate at six months, is plotted against the corrosion area ratio for corresponding specimens in Fig.11. There is a good correlation between corrosion ratio and corrosion area ratio in mortars with both NaCl and CaCl_2 .

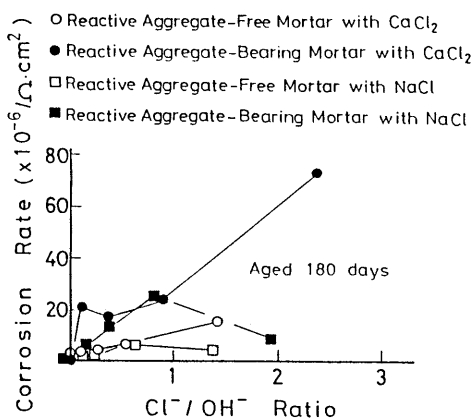


Fig. 12 Relationship between corrosion rate of mild steel electrodes and Cl^-/OH^- ratio in the pore solution of corresponding mortars

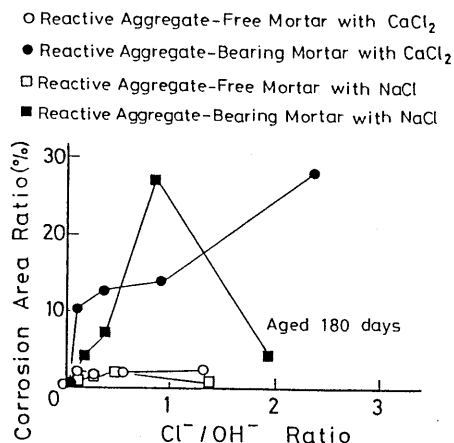


Fig. 13 Relationship between corrosion area ratio of mild steel electrodes and Cl^-/OH^- ratio in the pore solution of corresponding mortars

However, the relationship between these two parameters in mortars with NaCl is considerably different from that in mortars with CaCl_2 .

3.4 Relationship between the Cl^-/OH^- Ratio in the Pore Solution and the Corrosion Level of Steel Bars Embedded in Various Mortars

Figure 12 shows the relationship between corrosion rate of embedded steel bars and Cl^-/OH^- ratio in the pore solution of the corresponding mortar at six months. Plots of the corrosion area ratio of embedded steel bars against Cl^-/OH^- ratio in the pore solution of the corresponding mortar at six months are shown in Fig.13. The corrosion rate and corrosion area ratio at a given Cl^-/OH^- ratio in mortars with Beltane opal are found to be greater than in those without the reactive aggregate; this is independent of the type of chloride added. The corrosion rate and corrosion area ratio reach a maximum at a Cl^-/OH^- ratio of 1.0 in the mortar with NaCl . However, the corrosion rate and corrosion area ratio in mortars with CaCl_2 continue to increase with increasing Cl^-/OH^- ratio. It is thus concluded that the presence of the reactive aggregate greatly promotes the corrosion of steel bars embedded in mortars with a chloride. The effects of the alkali-silica reaction on chloride-induced corrosion depend on the type of chloride added. In particular, the relationship between corrosion level and Cl^-/OH^- ratio in the pore solution of CaCl_2 -bearing mortars is very different from that in NaCl -bearing mortars.

The relatively large differences in chloride-induced corrosion of embedded steel bars with different types of added chloride and in mortars with and without the alkali-reactive aggregate may affect the Cl^-/OH^- ratio in the pore solution as well as certain other factors. The differences in corrosion level between mortars with NaCl and CaCl_2 may be explained by the considerable differences in the electrochemical properties of the corrosion system operating. These differences in electrochemical properties are a result of variations in the pore structure and pore solution composition of the mortars (2). Moreover, a few cracks in all the mortar samples used for electrochemical measurements could be detected macroscopically. This indicates that factors other than the occurrence of such macroscopic cracks due

to the alkali-silica reaction promote chloride-induced corrosion of the steel bars. Such factors are thought to be not only changes in the pore structure and the pore solution composition of the reactive aggregate-bearing mortar, but also the disappearance of $\text{Ca}(\text{OH})_2$ crystals around steel bars due to the alkali-silica reaction (12,14).

4. CONCLUSIONS

The alkali-silica reaction considerably accelerates the chloride-induced corrosion of steel bars embedded in mortar containing a reactive aggregate and a chloride. The extent of this promotion of corrosion varies with the type of chloride. In particular, the relationship between the corrosion level of embedded steel bars and Cl^-/OH^- ratio in the pore solution of reactive aggregate-bearing mortar with CaCl_2 is different from that in the mortars with NaCl . The promotion of chloride-induced corrosion of steel bars embedded in mortar containing a reactive aggregate may be also responsible for certain factors other than changes in the pore solution composition brought about by the alkali-silica reaction.

ACKNOWLEDGMENT

The authors are very grateful to Dr.T.Yonezawa of the Technical Research Laboratory at Takenaka Corporation, for his useful advice.

REFERENCES

- (1) C.L.Page, N.R.Short, and W.R.Holden, 'The influence of different cements on chloride-induced corrosion of reinforcing steel', Cement and Concrete Research, Vol.16, No.1, pp.79-86, 1986
- (2) C.M.Hansson, Th.Frølund, and J.B.Marukussen, 'The effect of chloride cation type on the corrosion of steel in concrete by chloride salts', Cement and Concrete Research, Vol.15, No.1, pp.65-73, 1985
- (3) T.E.Stanton, O.J.Porter, L.C.Meder, and A.Nicol, 'California experience with the expansion of concrete through reaction between cement and aggregate', Journal of the American Concrete Institute, Vol.13, No.3, pp.209-236, 1942
- (4) J.J.Shideler, 'Calcium chloride in concrete', Journal of the American Concrete Institute, Vol.23, No.7, pp.537-559, 1953
- (5) M.Kawamura, M.Ichise, and K.Takemoto, 'Effects of chlorides on alkali-silica reaction', Proc. of the Japan Concrete Institute, Vol.11, No.1, pp.65-70, 1989 (in Japanese)
- (6) Committee on ASR of Hanshin Expressway Public Corporation, 'Committee report on alkali-aggregate reaction', Hanshin Expressway Public Corporation, 1986 (in Japanese)
- (7) R.S.Barneyback, Jr. and S.Diamond, 'Expression and analysis of pore fluids from hardened cement pastes and mortars', Cement and Concrete Research, Vol.11, No.2, pp.279-285, 1981
- (8) D.A.Hausmann, 'Steel corrosion in concrete', Material Protection, Vol.6, No.19, pp.19-23, 1967
- (9) V.K.Gouda, 'Corrosion and corrosion inhibition of reinforcing steel- I: Immersed

in alkaline solution', British Corrosion Journal, Vol.5, pp.198-203, 1970

(10) S.Diamond, 'Chloride concentrations in concrete pore solutions resulting from calcium and sodium chloride admixtures', Cement and Concrete Research, Vol.8, No.2, pp.97-102, 1986

(11) T.Yonezawa, V.Ashworth, and R.P.M.Procter, 'Threshold chloride content for steel corrosion in concrete', Proc. of the Japan Concrete Institute, Vol.8, pp.141-144, 1986 (in Japanese)

(12) S.Diamond, 'Pore solution and alkali aggregate attack', Proc. of Symposium on Alkali-Aggregate Reaction - Preventive Measures, Reykjavic, Iceland, pp.165-181, 1975

(13) K.Okada, K.Kobayashi, T.Miyagawa, and S.Honda, 'Corrosion monitoring system of reinforcing steel using polarization resistance method', Proc. of the Japan Concrete Institute, Vol.5, pp.249-252, 1983 (in Japanese)

(14) C.L.Page, 'Mechanism of corrosion protection in reinforced concrete marine structures', Nature, Vol.258, No.5535, pp.514-515, 1975