

## INFLUENCES OF THE ALKALI-SILICA REACTION ON THE CORROSION OF STEEL REINFORCEMENT IN CONCRETE

Mitsunori Kawamura\*, Kunio Takemoto\*\*  
and Makoto Ichise

\* Dept. of Civil Engineering, Kanazawa University,  
Kanazawa, Ishikawa 920, Japan

\*\* Dept. of Civil Engineering, Ishikawa Technical  
College, Tsubata, Ishikawa 929-03, Japan

### 1. Introduction

The major factors influencing the chloride-induced corrosion of embedded steel reinforcement in concrete are (i) the relative concentrations of aggressive chloride ion and inhibitive hydroxyl ions in the pore solution, and (ii) the ionic mobility of chloride (1). The importance of solid  $\text{Ca}(\text{OH})_2$  formed near the surface of embedded steel bars in their passivation in concrete was also emphasized by Page (2). On the other hand, it has been recognized that  $\text{OH}^-$  ions in pore solution are consumed by the alkali-silica reaction in concrete with a reactive aggregate. Furthermore, recently, it was revealed that relatively large amounts of  $\text{Cl}^-$  ions in pore solution were taken up by the alkali-silica reaction in concrete (3). Only from the point of view of the relationship between the  $\text{Cl}^-/\text{OH}^-$  ratio in pore solution and the corrosion of steel reinforcement in concrete, the effects of the alkali-silica reaction on pore solution composition suggest that the reactions certainly influence the chloride-induced corrosion of steel reinforcement in concrete.

It has been pointed out that alkali-silica sols produced within reacting aggregate grains chemically attack the C-S-H gel and  $\text{Ca}(\text{OH})_2$  around the reacting grains (4). Presumably,  $\text{Ca}(\text{OH})_2$  phase formed around reactive aggregate grains might be corroded by the alkali-silica reaction product. The corrosive nature of the alkali-silica reaction to  $\text{Ca}(\text{OH})_2$  phase around reactive aggregate grains also suggests that the alkali-silica reaction plays a role in the corrosion of steel reinforcement in concrete through dissolution of the  $\text{Ca}(\text{OH})_2$  film around steel bars in concrete. Namely, the alkali-silica reactions might influence the protective nature of concrete for the depassivation of steel reinforcement even if effects of the cracking due to the alkali-silica reaction on the corrosion of steel reinforcement in concrete are not taken into consideration. This study aims at revealing the influence of the alkali-silica reaction on the corrosion of embedded steel reinforcement in the concrete contaminated with sodium chloride.

### 2. Experimental

#### 2.1 Materials

The cement used was ordinary Portland cement with the equivalent  $\text{Na}_2\text{O}$  of 0.93 percent. The Beltane opal aggregate with the size range of 1.2 mm to 0.6 mm was used as a reactive aggregate. A non-reactive aggregate of Toyoura standard siliceous sand was also used. The compositions of the cement used are

TABLE 1

Chemical Analyses of a Cement(%)

CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	Ign Loss
64.0	21.8	5.0	3.2	2.1	1.6	0.59	0.51	0.5

given in Table 1.

2.2 Procedure

2.2.1 Expression of pore solution and expansion test

Mortars were prepared with a total

aggregate : cement ratio of 2.0 and a water : cement ratio of 0.5. 3% of the total aggregate was

replaced by the reactive aggregate. Sodium chloride was pre-dissolved in the mix water of mortar specimens in amounts corresponding to the chloride ion addition levels of 0.25, 0.5, 1.0 and 2.0% of the weight of cement.

Mortar cylinders,  $\phi 5.6$  cm x 10 cm, for pore solution expression were stored in sealed vinyl sacks in a fog box at 38° C. After predetermined periods of curing, pore solutions were extracted from the mortar specimens by the high-pressure apparatus. Chloride ion concentrations were determined by coulometric titration. The extracted solutions were also analysed for hydroxyl ion concentration by titration against hydrochloric acid to the phenolphthalein end point.

Mortar prisms, 40 x 40 x 160 mm, were stored in a fog box at 38° C. The length changes of prisms were measured according to JIS A 530 - 1986 test.

2.2.2 Electrochemical measurements of

corrosion rate of embedded steel The mortar specimens containing a mild steel electrode and a counter stainless steel electrode were schematically illustrated in Fig. 1. Corrosion intensities of the steel electrodes were determined by polarisation resistance measurements. A potential scan, 20 mV either side of the rest potential was applied at 1 mV/sec., and the potential ( $\Delta E$ )-current ( $\Delta I$ )

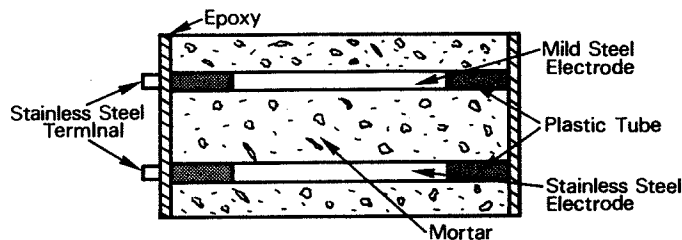


Fig. 1 Schematic Diagram of the Specimens for electrochemical measurements.

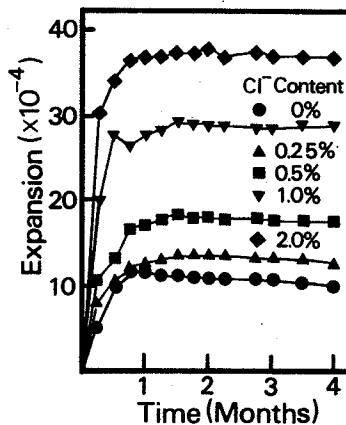


Fig. 2 Expansion Curves for Mortars Containing Various Amounts of NaCl.

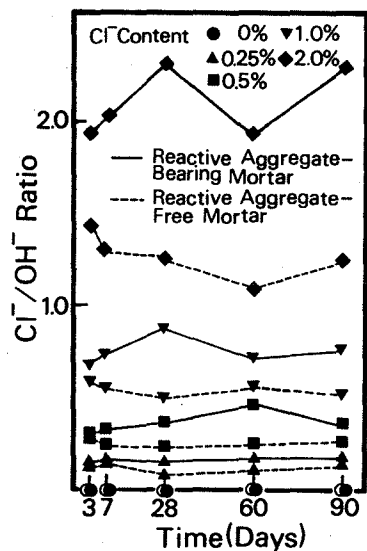


Fig. 3  $\text{Cl}^-/\text{OH}^-$  Ratio in Pore Solutions Expresses from Mortars with and without Reactive Aggregate at Various Ages.

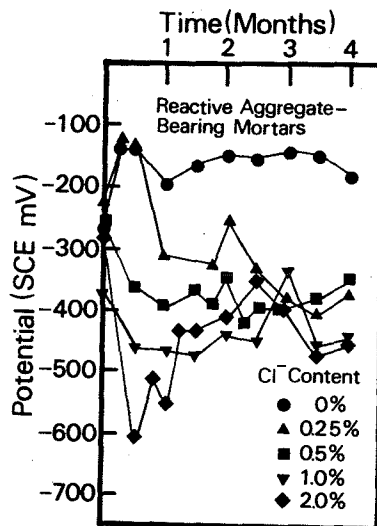


Fig. 4 Corrosion Potential of Mild Steel Electrodes in Mortars with Various Original  $\text{Cl}^-$  Contents and a Reactive Aggregate.

curves were recorded. The polarization resistance,  $\Delta E/\Delta I$ , was calculated from the slope of the measured polarization curve. The electrochemical measurements were made on the specimens which had been placed in a fog box maintained at  $38^\circ\text{C}$ . Measurements were made on duplicate specimens daily until about one month, and after that every two days.

### 3. Results and Discussion

#### 3.1 Expansion of Mortars Containing Beltane Opal

Expansion curves for mortars containing Beltane opal in which a mild steel and a counter stainless steel electrode are embedded, are given in Fig. 2. All mortars prepared at various treatment levels of NaCl expanded rapidly, and their expansions terminated by about one month. Although expansions of all mortars exceeded 0.1% after about one month, cracks were megascopically found only in the mortar specimens prepared at the treatment level of 2%  $\text{Cl}^-$  at the age of about one month.

#### 3.2 $\text{Cl}^-/\text{OH}^-$ Ratio in Pore Solutions in Mortars Treated with NaCl

The  $\text{Cl}^-/\text{OH}^-$  ratios in pore solutions extracted from mortars with and without Beltane opal at various ages up to 90 days are presented in Fig. 3. The  $\text{Cl}^-/\text{OH}^-$  ratio in pore solutions changes a little with age in most mortars except that  $\text{Cl}^-/\text{OH}^-$  ratio in mortars with a NaCl content corresponding to 2.0%  $\text{Cl}^-$  by weight of cement changes with age to some extent. The  $\text{Cl}^-/\text{OH}^-$  ratio in pore solutions in which equilibrium was attained increases with increasing amounts of NaCl. Fig. 3 also indicates that the difference in  $\text{Cl}^-/\text{OH}^-$  ratio

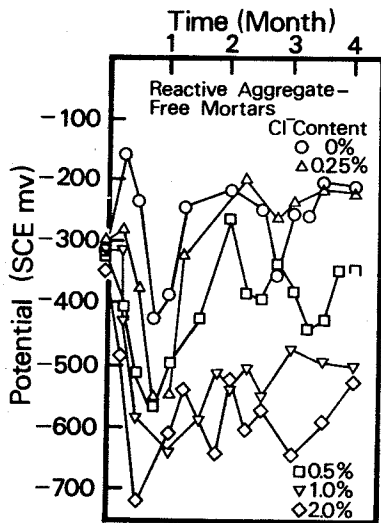


Fig. 5 Corrosion Potential of Mild Steel Electrodes in Reactive Aggregate-Free Mortars with Various Original  $\text{Cl}^-$  Contents

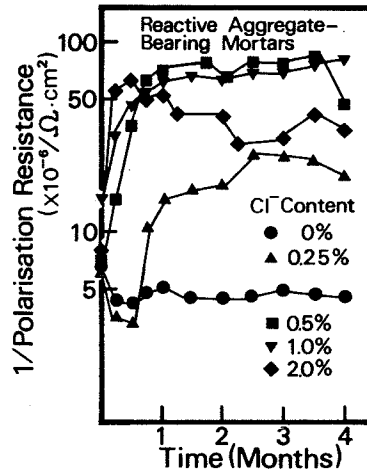


Fig. 6 Polarization Resistance of Mild Steel Electrodes in Reactive Aggregate-Bearing Mortars with Various Original  $\text{Cl}^-$  Contents.

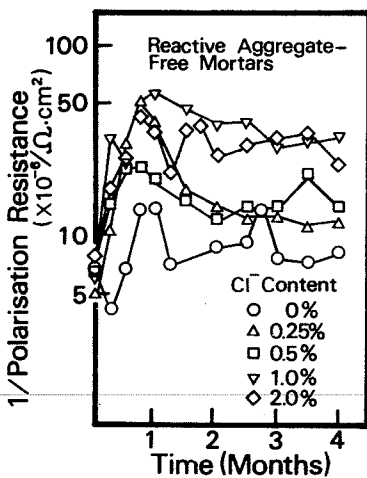


Fig. 7 Polarization Resistance of Mild Steel Electrodes in Reactive Aggregate-Free Mortars with Various Original  $\text{Cl}^-$  Contents.

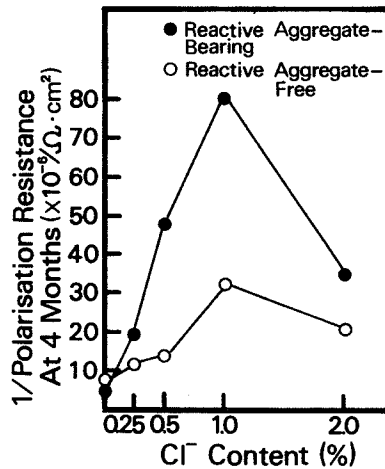


Fig. 8 Relationship between Polarization Resistance of Mild Steel Electrodes and Original Chloride Addition Levels in 4 months Old Mortars with and without a Reactive Aggregate.

between mortars with and without Beltane opal increases with increasing treatment level of NaCl. Since both  $\text{OH}^-$  and  $\text{Cl}^-$  ions are taken up from pore solutions by the alkali-silica reaction, the fact that  $\text{Cl}^-/\text{OH}^-$  ratios in pore solution in mortars with the reactive aggregate are always higher than those in the ones without the reactive aggregate (Fig. 3) demonstrates that more  $\text{OH}^-$  ions are consumed by the reactions than  $\text{Cl}^-$  ions after at least 3 days.

### 3.3 Corrosion Rate of Embedded Steel

Figs. 4 and 5 show the time-dependent changes of the corrosion potential of steel bars embedded in the mortar specimens with and without the reactive aggregate. As shown in Fig. 5, rapid reduction in corrosion potential of steel bars until about one month was followed by a recovery in the reactive aggregate-free mortars, and then their corrosion potential appears to be stabilized in all mortars. However, as shown in Fig. 5, the initial rapid reduction in the corrosion potential was not found in steel bars embedded in mortars with the reactive aggregate. The corrosion potential of steel bars in mortars without the reactive aggregate, after stabilized, decreases with increasing amounts of NaCl added, while differences in the corrosion potential between different  $\text{Cl}^-$  contents are not so great. The corrosion rate ( $I_R$ ) calculated from the polarization resistance of steel bars measured changed with time, as shown in Figs. 6 and 7. The values of  $I_R$  of steel bars embedded in NaCl-bearing mortars with the reactive aggregate increased rapidly until about one month, while  $I_R$  of steel bars in the NaCl-free ones little changed. The rapid increase in  $I_R$  of steel bars in mortars without the reactive aggregate until about one month was followed by the gradual decrease of  $I_R$  with time.

Fig. 8 shows the relationships between the original chloride ion addition level and the values of  $I_R$  at 4 months for mortars with and without the reactive aggregate. The values of  $I_R$  of steel bars embedded in mortars with the reactive aggregate at a given chloride ion addition level are found to be far greater than those in the corresponding reactive aggregate-free ones. As shown in Fig. 3, the measured  $\text{Cl}^-/\text{OH}^-$  ratios in pore solutions extracted from mortars with the reactive aggregate are greater than those in pore solutions in mortars without the reactive aggregate at a given chloride ion addition level. Therefore, it is deduced from these results that the rises in the value of  $I_R$  brought about by the incorporation of the reactive aggregate resulted partly from the increase in the  $\text{Cl}^-/\text{OH}^-$  ratio in pore solutions due to the occurrence of the alkali-silica reactions in the mortars. Another indication obtained from Fig. 8 is that there exists the original chloride ion addition level giving the maximum corrosion rate of steel bars embedded in both NaCl-bearing mortars with and without the reactive aggregate.

The value obtained by integrating the corrosion rate ( $I_R$ ) from zero to a certain time is regarded as a measure showing the total loss in metal due to the corrosion up to the time. The ratios of the total corrosion losses calculated at 4 months for steel bars in various mortars to that for steel bars in the reference mortar without the reactive aggregate and NaCl are plotted against the  $\text{Cl}^-/\text{OH}^-$  ratios in pore solutions at 3 months, as shown in Fig. 9. There also exists the maximum total corrosion loss at a certain  $\text{Cl}^-/\text{OH}^-$  ratio. It is found from Figs. 8 and 9 that the values of  $I_R$  and the relative corrosion loss ratios of steel bars in mortars with the reactive aggregate are far greater than those in the reactive aggregate-free mortars at a given  $\text{Cl}^-/\text{OH}^-$  ratio. This fact suggests that some changes in the microstructure of mortar phase due to the alkali-silica reactions influence the chloride induced corrosion of steel in mortars with the reactive aggregate.

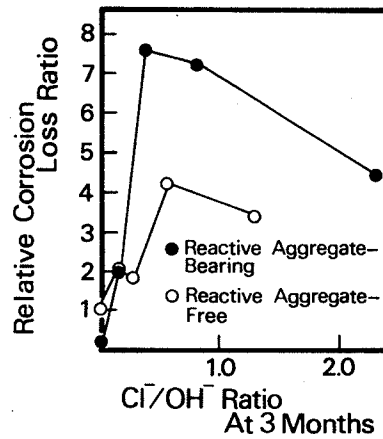


Fig. 9 Relative Corrosion Loss Ratio of Mild Steel Electrodes in Mortars at 4 Months for Various  $Cl^-/OH^-$  Ratios of Pore Solutions Expressed from 3 Months Old Mortars with and without a Reactive Aggregate.

#### 4. Conclusions

The addition of the reactive aggregate increased the corrosion rate of steel bars embedded in mortars with a reactive aggregate. The occurrence of the alkali-silica reactions in mortars contaminated with NaCl raised the  $Cl^-/OH^-$  ratio in pore solutions in the mortars. It was also confirmed that the alkali-silica reactions increased the corrosion rate of steel bars in the mortars even at a given  $Cl^-/OH^-$  ratio in pore solution. Therefore, it is deduced from these results that the increase of the corrosion rate of steel bars embedded in mortars containing the reactive aggregate is attributable to the increase in the  $Cl^-/OH^-$  ratio in pore solutions as well as to some changes of the micro-structure of mortar phase due to the alkali-silica reactions. It may be concluded that the alkali-silica reactions occurring in concretes contaminated with NaCl increases the risk of chloride induced corrosion of steel reinforcement.

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