

Corrosion analysis and monitoring of the environmental factors for the deterioration of chromium-bearing reinforcing steel in mortar

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Abstract To understand environmental factors, Cl ion concentration and pH were monitored by inserting microelectrodes into artificial pores in the mortar. The corrosion behavior of reinforcing steels containing chromium were investigated with carbon steel (SM) by electrochemical impedance spectroscopy (EIS). From the EIS, the corrosion resistance of the Cr-bearing reinforcing steel was visibly higher than the SM reinforcing steel. Simultaneously, the Cl ion concentration in the mortar was obtained using Ag/AgCl microelectrodes, showing that this behavior is generally controlled by diffusion. Similarly, the pH in the mortar was obtained using W/WOx microelectrodes. With a 20-mm cover thickness, pH was limited to approximately pH 11, but with a 10-mm cover thickness, pH continued to decrease to around pH 9.5. Solutions were prepared simulating the condition in the pores in mortar and were used in EIS measurements. The charge transfer resistance, R_{ct} , in the simulated solutions showed good correspondence with that in the actual mortar. This is attributed to the fact that the corrosion of reinforcing steel was controlled by the solution conditions (mainly Cl concentration and pH) in mortar. Moreover, it was found that, as compared with SM, Cr-bearing steel could keep the passive film in severe condition, and have long incubation time until the passive film was destroyed.

Keywords Monitoring · Mortar · Cr-bearing reinforcing steel · Chloride · Electrochemical impedance spectroscopy · Microelectrode

Introduction

Deterioration of concrete structures has become a serious social problem in recent years, but in many cases, this deterioration is caused by corrosion of the reinforcing steel. As the deterioration due to salt damage is particularly severe, the total content of chlorides in freshly mixed concrete has been set at 0.3 kg/m³ or less. However, in Japan, corrosion deterioration due to salt damage is still a problem due to high levels of airborne sea salt and the use of road salt in cold regions to prevent freezing in wintertime. Salt damage of concrete reinforcing steel takes the form of corrosion due to destruction of the passivation film on the steel by chloride ions, and thus, has an important relationship with the concentration of chloride ions. As means of measuring chloride contents, the technique of crushing mortar and measuring the chloride content of the powder has long been used. However, in actual mortar, chlorides include fixed compounds such as Friedel's salt ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$) and chlorides which exist in the form of chloride ions in liquid solution in the pores in the mortar. A direct measurement of the free chloride ions in the pores of the mortar is essential, as these free chloride ion is the form which is directly related to corrosion of reinforcing steel. Recently, there have been attempts to measure the concentration of chloride ions using various types of sensors, and the penetration behavior of chloride ions in mortar has also been studied [1–18]. On the other hand, electrochemical techniques are used in analysis of corrosion of reinforcing steel in mortar. Electrochemical impedance spectroscopy (EIS) has attracted attention in this connection in recent years [19–29].

Concrete structures are essentially a type of composite material in which the composition, structure, manufacturing conditions, environmental conditions, and other factors are

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different in each case. Therefore, in detailed investigations, it is important to monitor the environment and corrosion for individual cases. As mentioned above, attempts have been made to monitor the environment and corrosion respectively in recent years, but there are virtually few examples of analysis of corrosion behavior based on simultaneous monitoring of the environment and reinforcing steel in mortar. In order to monitor the environment in mortar in this research, holes were made in the mortar by embedding extremely thin bamboo strips in the mortar during the initial period of hardening, and then withdrawing the strips after the mortar had hardened. As a result, it was possible to measure the chloride ion concentration and pH in the mortar by inserting microelectrodes into these artificial pores.

Moreover, research and development in the area of monitoring the deterioration of concrete structures cannot stand alone in order to solve corrosion-related problems. It is important to investigate new reinforcing rebars that are more corrosion resistant than carbon steel in mortar. Despite its excellent corrosion resistance, stainless steel has not been widely used due to its high cost. Hence, recently, various Cr-bearing steel were developed for reinforcing steel. The high performance of Cr-bearing reinforcing steel against the corrosion is reported [30–32]. However, there are few reports which show detail corrosion behavior of these Cr-bearing steels in concrete structures.

In this study, corrosion behavior of two types of Cr-bearing steels and carbon steel were monitored by EIS, and changes in environmental factors were obtained by microelectrodes. Solutions were prepared periodically simulating the solutions found in the holes in the mortar, as determined by the environmental measurements, and the corrosion behavior of the various reinforcing steels was investigated by comparing the EIS behavior of reinforcing steel in the simulated solutions and the EIS behavior of the steel in the actual mortar.

Experimental method

Preparation of specimens

Specimens were prepared from ordinary Portland cement and mountain sand using a water/cement ratio of 0.5 by adding 3 mass% of NaCl to the mixing water. Specimens of the size shown in Fig. 1 were prepared by mixing the ingredients thoroughly and pouring the mixture into a mold. All sides except for the test surface were sealed, and reinforcing steel plates were embedded in the specimens. At the same time, extremely thin (diameter: 0.5 mm) bamboo strips were also embedded in the specimens, and holes for insertion of microelectrodes were created by withdrawing the strips after the mortar had hardened. After curing in

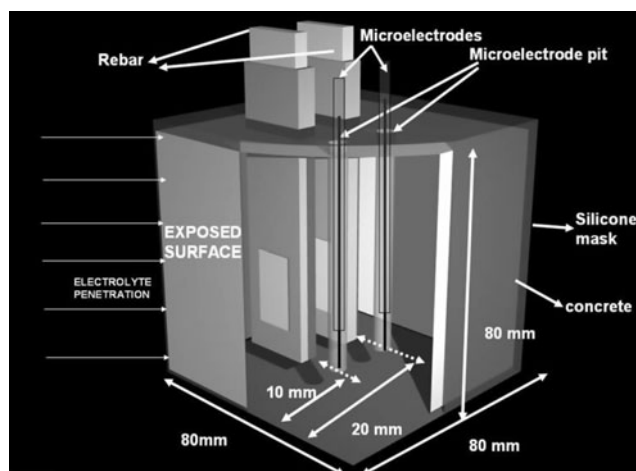


Fig. 1 Cross-sectional diagram of mortar block showing SM rebar and the microelectrode

water for 1 month, the specimens were sealed with a silicon sealant, leaving one surface of the specimen exposed as a test surface. The position of the steel plates was set so that the cover thickness from the test surface (i.e., thickness of the mortar above the plate) would be 10 mm or 20 mm. In the same manner, the artificial holes for insertion of the microelectrodes were set to at 5, 10, 20, 30, 40, and 50 mm from the surface. Three different types of reinforcing steels were studied in the present investigation. One of the steels was the conventionally used carbon steel (SM), and the other two were Cr-bearing steels. The chemical composition of all the three reinforcing steels is provided in Table 1.

Measurement conditions

As microelectrodes for use in environmental measurements, Ag/AgCl microelectrodes were prepared for chloride ion measurements. Using an Ag wire (diameter: 0.3 mm), the electrodes were made at 500 mV for 20 min in a 0.1 M HCl solution. For pH measurements, W/WOx electrodes were prepared using a W wire (diameter: 0.3 mm) by immersion for 18 h in a 10% HNO₃ solution. The calibration had previously taken on the Ag/AgCl electrode in saturated Ca(OH)₂, also, that on W/WOx electrode in high pH solutions.

Table 1 Designations and elemental composition of the reinforcing steels used in the present study

Elements (wt.%)					
Specimen	C	Si	Mn	Cr	Fe
SM	0.1	0.2	1.0	–	Bal.
Cr1	0.1	0.2	1.0	7.0	Bal.
Cr2	0.1	2.0	1.0	7.0	Bal.

For the corrosion test, the mortar specimens were immersed in a 0.5 M NaCl solution (room temperature: 25 °C), and EIS measurements of the reinforcing steel and measurements of the concentration of Cl ions and pH using the microelectrodes were made periodically. The entrance at the top of the microelectrode insertion holes was normally kept sealed, and was opened only during measurements. EIS measurements were made by the three electrode method using a Pt counter electrode and a saturated calomel electrode as the reference electrode. The EIS measurements were performed at a voltage of 10 mV and frequency range of 20 K to 2 mHz. The specimen area of the steel plate was 3 cm², and other parts were sealed.

Results and discussion

EIS behavior of reinforcing steel in mortar

The mortar specimens were immersed in a 0.5 M NaCl solution (room temperature: 25 °C), and EIS measurements of the various reinforcing steels of SM, Cr1, and Cr2 were performed periodically for a period up to a maximum of 203 days. Figures 2, 3, and 4 show the EIS results for the reinforcing steels (SM, Cr1, and Cr2) respectively, at a mortar cover thicknesses of 20 mm. The EIS results show a resistance component on the high frequency region on all days. Although this is solution resistance, based on the fact that the value is high, it is estimated to be the resistance of the solution in the holes in the mortar. On the low frequency region, Warburg impedance (*W*) due to diffusion by oxygen can be observed until day 35, but can no longer be seen thereafter. Furthermore, the impedance values in the

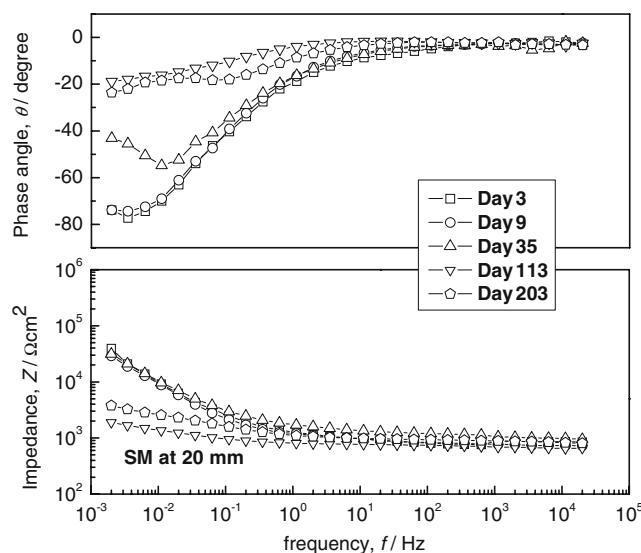


Fig. 2 EIS spectra of the SM rebar in mortar block at 20 mm from the surface

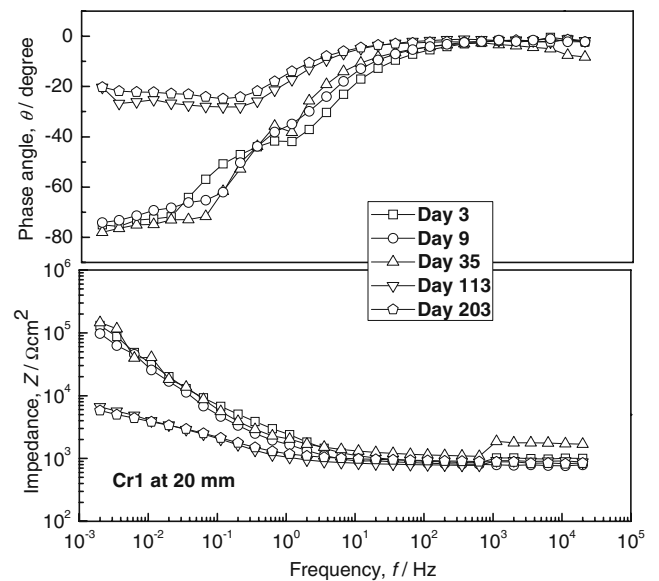


Fig. 3 EIS spectra of the Cr1 rebar in mortar block at 20 mm from the surface

low frequency region tend to decrease after day 35, indicating a nonuniform surface condition on the electrode. Based on this fact, an equivalent circuit like that shown in Fig. 5 is considered to exist due to the introduction of constant phase element (CPE) impedance. In other words, it is estimated that the corrosion of the reinforcing steel in the mortar displays the behavior of an equivalent circuit comprising the solution resistance in the mortar (*R_{sol}*), CPE impedance (*Z_{cpe}*), Warburg impedance (*W*), and charge transfer resistance (*R_{ct}*).

Figure 6 shows the change in the values in the impedance spectra in Figs. 2, 3, and 4 at 2 mHz. The Cr-bearing reinforcing steels, i.e., Cr1 and Cr2 show relatively high resistance compared to SM reinforcing steel, through-

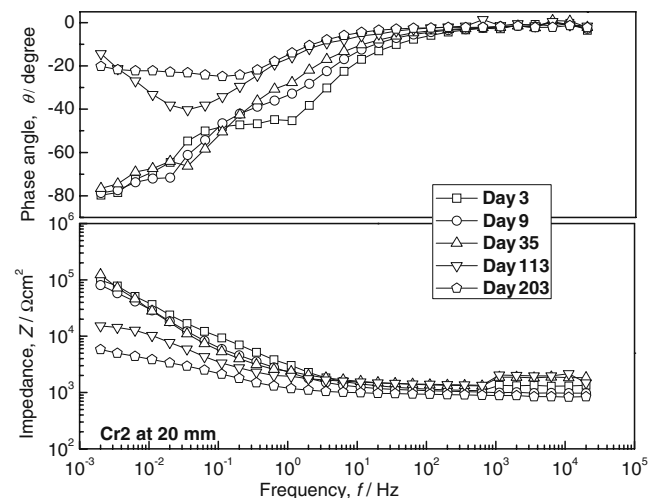
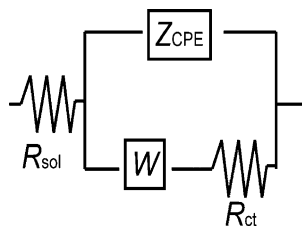


Fig. 4 EIS spectra of the Cr2 rebar in mortar block at 20 mm from the surface

Fig. 5 Equivalent circuit for the corrosion of the rebars in mortar block. R_{sol} solution resistance in mortar block, Z_{CPE} constant phase element, W Warburg impedance, R_{ct} charge transfer resistance)



out the period of immersion. With the cover thickness of 20 mm, all the spectra show high values in the initial period till day 35, due to Warburg impedance. However, from day 35, the values are generally attributable to R_{ct} , and after day 113, the values become constant. In case of SM reinforcing steel, the R_{ct} value stabilized at around $2,800 \Omega\text{cm}^2$. However, Cr1 and Cr2 reinforcing steels exhibited higher values of $6,600 \Omega\text{cm}^2$. Similarly, Fig. 7 shows the changes in impedance values at 2 mHz of the impedance spectra of various reinforcing steels in mortar with a cover thickness of 10 mm. The Cr-bearing reinforcing steels show higher resistance throughout the period of immersion compared to SM reinforcing steel. Although all the reinforcing steels show high values due to Warburg impedance during the initial period of immersion, their values decrease rapidly. A low value of $1,100 \Omega\text{cm}^2$ after day 113 was observed for SM reinforcing steel. Meanwhile, the values of Cr1 and Cr2 were observed to be higher at around $4,600 \Omega\text{cm}^2$ and $3,000 \Omega\text{cm}^2$, respectively. The values tend to remain constant thereafter until day 203 in all the reinforcing steel.

In comparison with the impedance results for the various reinforcing steel at a cover thickness of 20 mm in Fig. 6, it can be observed that the duration of the initial period Warburg impedance is extended by increasing the cover thickness. Furthermore, as R_{ct} is caused by the corrosion

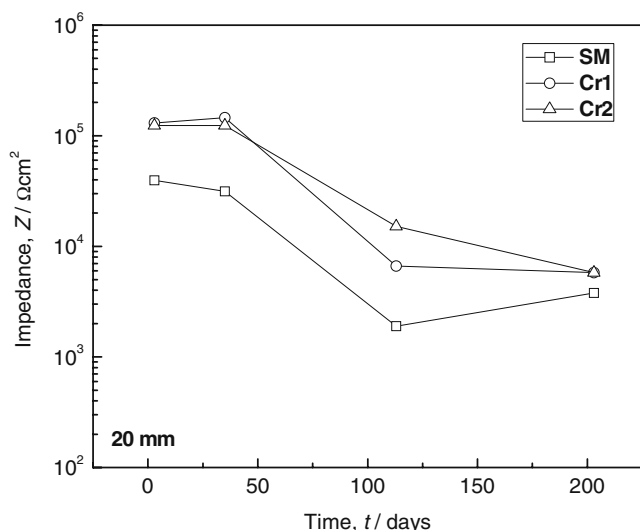


Fig. 6 Changes in impedance values at 2 mHz of the rebars in mortar block at 20 mm from the surface

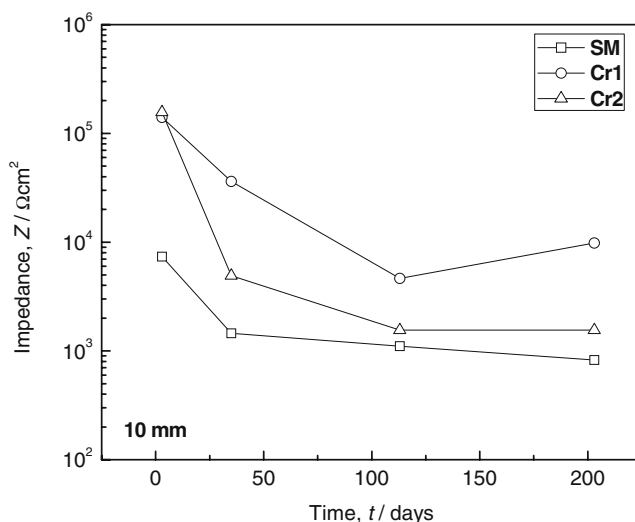


Fig. 7 Changes in impedance values at 2 mHz of the rebars in mortar block at 10 mm from the surface

reaction after a longer time, these results also suggest that corrosion is suppressed if the cover thickness is increased.

In this way, the Cr-bearing reinforcing steels show higher resistance of R_{ct} compared to SM reinforcing steel in the mortar. And from the comparison of Cr1 and Cr2, there is little difference between the EIS behavior of them. Thus, it was found that the adding of Cr was very effective to increase the corrosion resistance of steels, and Si was not so much in this case.

Measurement of changes in environmental factors in mortar

Simultaneous with the EIS measurements, the mortar specimens were immersed in a 0.5 M NaCl solution (room temperature: 25°C), and the changes in the environmental factors in the mortar during a period up to a maximum of 231 days were measured periodically using the micro-electrodes. We had earlier calibrated the Ag/AgCl micro-electrode in saturated $\text{Ca}(\text{OH})_2$ solution and the W/ WO_x microelectrode in high pH solutions. Figure 8 is a summary of the changes over time in the Cl ion concentration in the mortar relative to the distance from the surface (cover thickness). The Cl ion concentration was converted in units of molar from the voltage obtained with the Ag/AgCl microelectrodes, and thus shows the Cl ion concentration in the holes in the mortar. At the start of measurement (day 1), the concentration was no more than 0.05 M at a position 5 mm below the surface, and was zero at 10 mm and deeper. Based on this fact, the Cl ions contained in the 3 wt. % NaCl of the mixing water used when the mortar was prepared are thought to have been fixed in the form of salt. Until day 4, the ion concentration at the 5 mm position showed a low value of 0.1 M, but at day 7, this increased suddenly to 0.6 M. Moreover, also on day 7, the

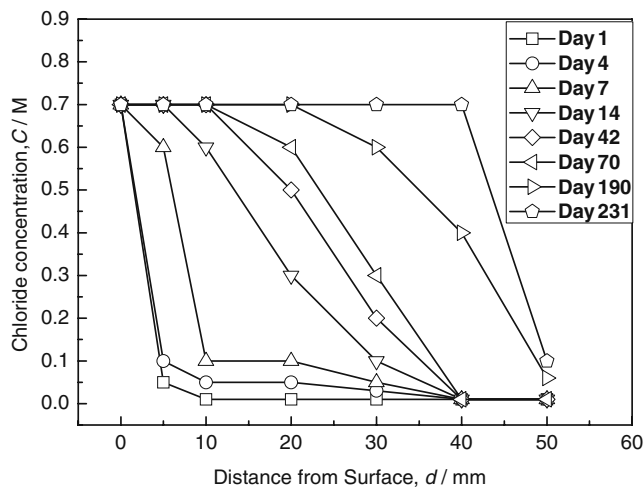


Fig. 8 Monitoring of chloride concentration using microelectrodes in the mortar block exposed to 0.5 M NaCl for 231 days

concentrations at 10 and 20 mm were 0.1 and 0.08 M, respectively, confirming penetration of Cl ions into the interior of the mortar. On day 14, the Cl ion concentration showed its largest value, 0.7 M, at the 5 mm position, and decreased with distance from the surface, being 0.6 M at 10 mm, 0.3 M at 20 mm, and 0.1 M at 30 mm. From this, it can be said that Cl ions had penetrated quite deep into the mortar by day 14, and the speed of Cl ion penetration was quite high.

Figure 9 shows the change over time in the pH in the mortar at distances (cover thicknesses) of 10 and 20 mm from the surface. Here, pH was converted from the voltage obtained with the W/WO_x microelectrodes, and shows the pH in the measurement holes in the mortar. Initially, at the position 20 mm from the surface, pH decreased from pH 12 to around pH 11, and was constant thereafter at pH 11. At the 10-mm position, pH also decreased over time from

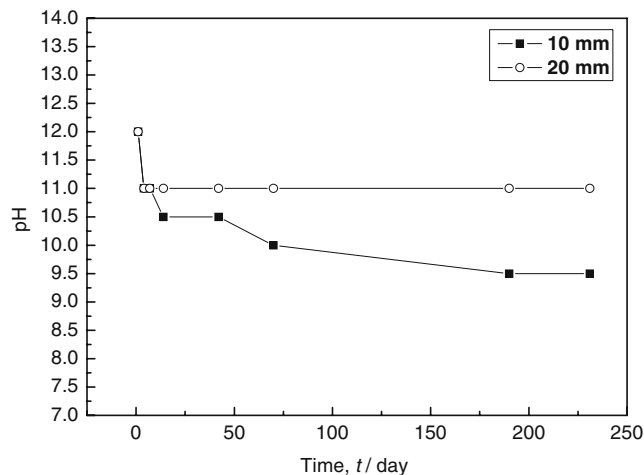


Fig. 9 Monitoring of pH using microelectrodes in the mortar block at 10 and 20 mm from the surface in 0.5 M NaCl solution

pH 12, but continued to decrease throughout the experiment. The 10-mm position being relatively close to the surface, the effect of neutralization by penetration of the immersion solution (3 wt.% NaCl, pH 6) from the surface is apparent. At the position more distant from the surface, i.e., the 20-mm position, it is thought that the decrease of pH was suppressed by the pH buffering property in the mortar.

Figure 10 shows the changes over time in the solution in the holes in the mortar at distances (cover thicknesses) of 10 and 20 mm from the surface. The Cl ion concentration increases continuously to a maximum of 0.7 M. In comparison with the 20-mm position, the Cl ion concentration at the 10-mm position shows a high value. At the 20-mm position, the pH decreases from the initial pH 12, but reaches pH 11 at day 35 and remains constant thereafter. At the 10-mm position, pH decreases continuously from the initial pH 12, reaching pH 9.4 by day 203. Based on this change in the pH, it can be thought that pH changes due to neutralization by penetration into the mortar of the immersion solution at the surface (in this research, 3 wt.% NaCl). These results also show the possibility of continuously monitoring the changes in solutions in holes in mortar using microelectrodes.

EIS behavior of reinforcing steel in solution simulating pores in mortar

Solutions simulating the solution in pores in mortar, as obtained using the microelectrodes, were prepared, and the EIS behavior of reinforcing steels in those solutions was investigated. In the model solutions, only the Cl ion concentration and pH were simulated, and other ions were ignored. Figures 11, 12, and 13 show the EIS behavior of

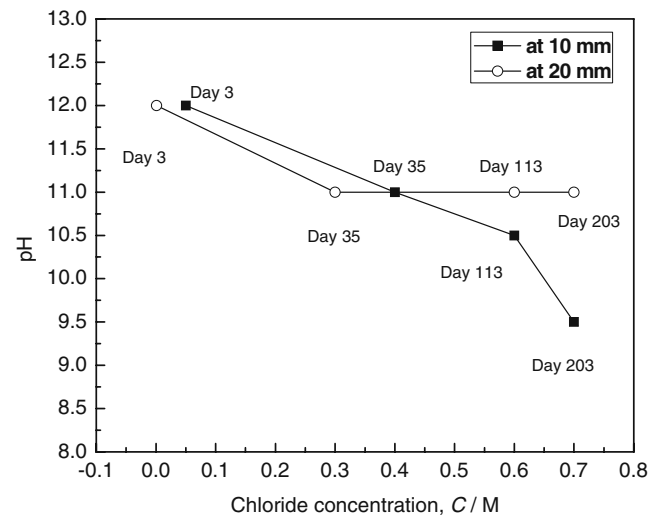


Fig. 10 Changes in the pH and chloride concentration in mortar block measured by microelectrodes

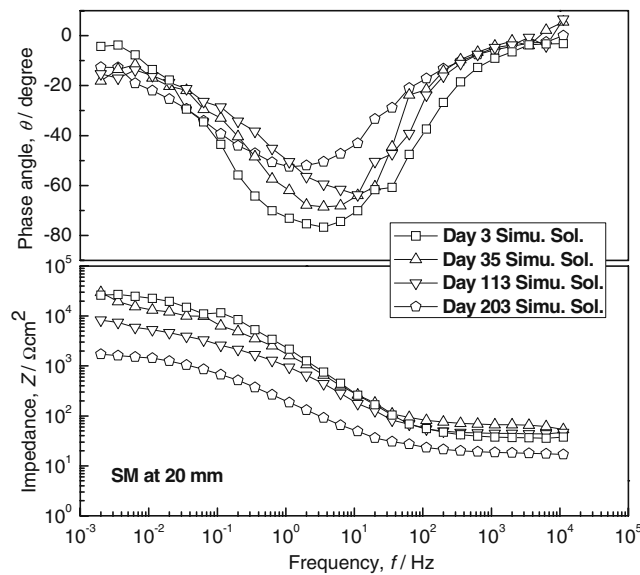


Fig. 11 Impedance spectra of SM in simulated solution of mortar block. Simulated conditions correspond to the actual result in Fig. 10 at 20 mm from the surface

reinforcing steels, SM, Cr1, and Cr2, respectively, in the solutions prepared to simulate the results of the solutions in the artificial pores in the mortar at a position 20 mm from the surface, after various elapsed times (days). In comparison with reinforcing steels in mortar, the following differences were found in the impedance spectra of the steels in these simulated solutions. Firstly, Warburg impedance did not appear. This is because there was no diffusion of ions like in mortar. Furthermore, in the intermediate frequency region, the spectra have a -1 slope and are not like that shown in actual mortar in

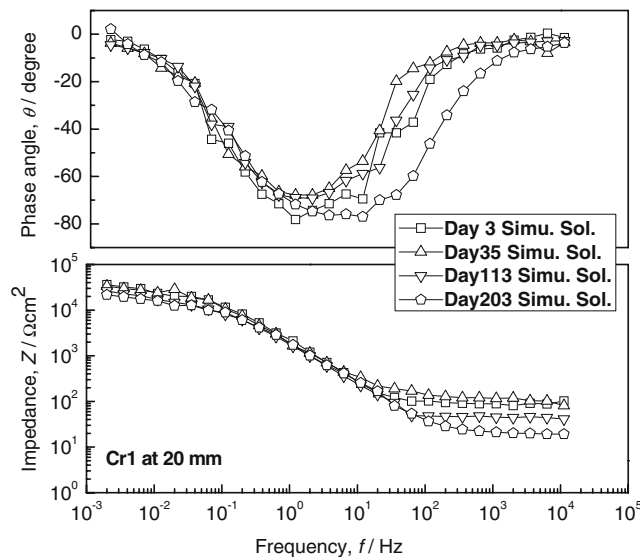


Fig. 12 Impedance spectra of Cr1 in simulated solution of mortar block. Simulated conditions correspond to the actual result in Fig. 10 at 20 mm from the surface

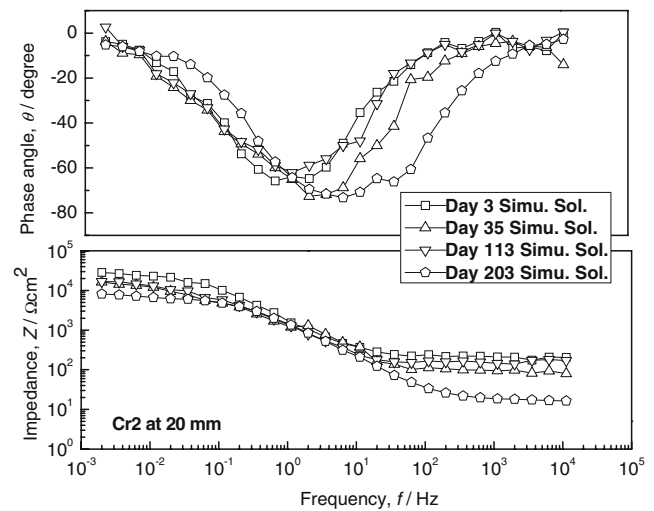


Fig. 13 Impedance spectra of Cr2 in simulated solution of mortar block. Simulated conditions correspond to the actual result in Fig. 10 at 20 mm from the surface

Figs. 2, 3, and 4. This indicates that the electrode reaction was uniform. Z_{cpe} shows the electric double layer capacitance (C_{dl}) of the electrode surface. The solution resistance (R_{sol}) becomes simply the resistance in each solution, and thus, is different from the solution resistance in the measurement holes in the mortar in Fig. 2. At the lowest frequency of 2 mHz, as the phase angle is almost zero, the impedance is thought to be showing the charge transfer resistance (R_{ct}). Although R_{ct} of SM is reducing as the day, however, R_{ct} of Cr1 and Cr2 are keeping the high value, which indicate that Cr1 and Cr2 keep the passive film even in the severe solution.

Figure 14 summarizes the impedance value ($Z_{2\text{ mHz}}$) at the 2 mHz from spectra in the simulated solutions in mortar. From the above, in the simulated solutions, the $Z_{2\text{ mHz}}$ value is considered to show the charge transport resistance (R_{ct}). In comparison with the results with actual mortar, the results with the simulated solutions follow a similar trend like the actual results at 10 mm. This shows that the state (Cl concentration, pH) in the solution in pores at 10 mm in mortar determines the corrosion reaction of reinforcing steels. Furthermore, $Z_{2\text{ mHz}}$ shows large values during the initial period, but after day 35, these become small values. Based on Fig. 9, the Cl concentration of 0.3 M and pH 11 at day 35 are considered to be threshold values for the solution in pores in mortar, and corrosion progresses rapidly under higher Cl concentrations and lower pH conditions. From this, it is considered that the passivation film on the reinforcing steel is destroyed, resulting in the high corrosion, when the Cl concentration and pH exceed the threshold conditions. Further, in both the cases, i.e., the simulated and actual solution in mortar, the Cr-bearing reinforcing steels show significantly high $Z_{2\text{ mHz}}$ compared to SM.

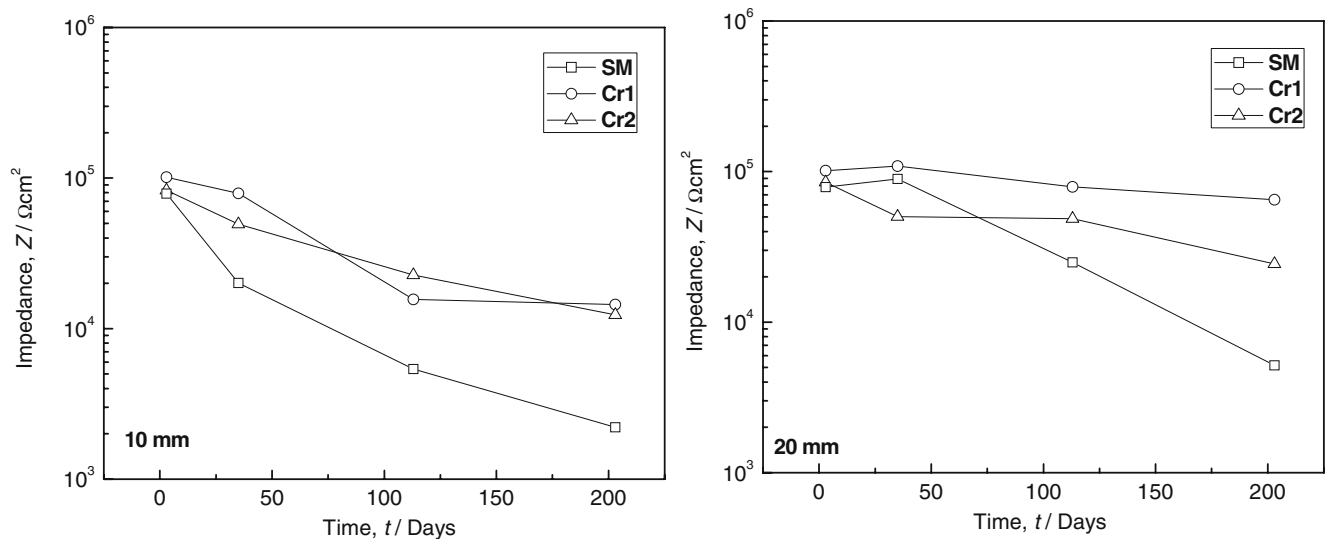


Fig. 14 Changes in impedance values at 2 mHz of the rebars in the simulated solution

Although the influence of Si in Cr2 is not completely shown, the influence of Cr is apparent in this study. Moreover, in the case of 20 mm, $Z_{2 \text{ mHz}}$ of Cr1 and Cr2 in simulated solution keep very high values of $Z_{2 \text{ mHz}}$ even after 200 days. On the other hand, $Z_{2 \text{ mHz}}$ of Cr1 and Cr2 in actual solution are reduced to low values after 200 days. These two facts are thought to indicate that Cr-bearing steel has the long incubation time even in the severe solution until the passive film is destroyed. In this way, it was found that Cr-bearing steel could keep the passive film in the severer condition, and have the long incubation time until the passive film was destroyed in the severest one. Thus, Cr-bearing steel is thought to have the high resistance in mortar because of these effects.

As described above, this research has demonstrated that it is possible to monitor the solution in pores in mortar, and further, that the EIS behavior in a simulated solution prepared using the results of such monitoring can convincingly explain the actual corrosion behavior in mortar. Moreover, it is found that these monitoring can precisely help to evaluate the performance of the reinforcing steels. In particular, this work has clarified the fact that, in addition to penetration of the immersion solution, phenomena including a decrease in pH and a rapid increase in the Cl ion concentration occur in the surface layer of mortar. Furthermore, the fact that the corrosion behavior of reinforcing steels changed according to these phenomena was also confirmed by EIS. Thus, the changes in the internal environmental factors in actual mortar are complex, and the importance of monitoring was recognized. As it is possible to gain an evaluation of the environmental condition by performing monitoring, the corrosion mechanism of reinforcing steels will be understood more detail in the future.

Conclusions

As internal environmental factors in mortar, the chloride ion concentration and pH were monitored by inserting micro-electrodes into the mortar. Simultaneously, the corrosion behavior of the reinforcing steel was also investigated by EIS. As a result, it was possible to determine the changes in corrosion behavior which accompany environmental changes. Based on the results of the environmental measurements, simulating solutions in the pores in the mortar were prepared, and the corrosion behavior of reinforcing steel was investigated by comparing the EIS behavior of steels in these solutions and that in actual mortar. By using these methods, Cr-bearing reinforcing steel was found to have high resistance against the corrosion as reinforcing steel compared to the carbon steel (SM).

1. In the EIS measurements of various reinforcing steels in mortar which was immersed in a 0.5 M NaCl solution, diffusion behavior was confirmed in the initial period, but diffusion by oxygen could no longer be observed after 35 day. The Cr-bearing reinforcing steels exhibited higher impedance behavior compared to the SM steel. Further, in comparison with a cover thickness of 10 mm, a 20-mm cover thickness showed a higher impedance behavior.
2. When the Cl ion concentration in the mortar was obtained using Ag/AgCl microelectrodes, the Cl ion concentration generally increased due to diffusion, but a rapid increase due to penetration of the immersion solution was confirmed in the vicinity of the surface. Similarly, when the pH in the mortar was obtained using W/WO_x microelectrodes, with a 20-mm cover

thickness, the pH was limited to approximately pH 11, but with a 10-mm cover thickness, the pH continued to decrease to around pH 9.5. The latter phenomenon was considered to be the result of neutralization by penetration of the immersion solution from the surface.

3. Based on the results of monitoring with the micro-electrodes, solutions simulating in the pores in the mortar were prepared, and EIS measurements of reinforcing steel were made using these solutions. The charge transfer resistance (R_{ct}) in the simulated solutions showed good correspondence with the impedance ($Z_{2 \text{ mHz}}$) in the low frequency region (2 mHz) in the actual mortar. This is attributed to the fact that the corrosion of reinforcing steel was controlled by the solution conditions (mainly Cl concentration and pH) in the pores in mortar. Furthermore, as compared with SM, Cr-bearing steel could keep the passive film in the severer condition, and have the long incubation time until the passive film was destroyed in severest one. Thus, Cr-bearing steel is thought to have the high resistance in mortar because of these effects.

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