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Corrosion behavior of reinforcing steel in concrete for nuclear facilities exposed in high chloride and low pH environment

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ABSTRACT

The Cl ion concentration and pH were monitored by inserting micro-electrodes into artificial pores in the mortar which was exposed in 0.5 mol/l chloride solution (pH 4.0). At the same time, the electrochemical behavior of the reinforcing steel was investigated by EIS. The Cl ion concentration in the mortar was obtained using Ag/AgCl micro-electrodes, showing that this behavior is generally controlled by diffusion. When the diffusion equation was used in this work, the diffusion coefficient (D_c) showed a high value of $D_c = 9.5 \times 10^{-5}\ \mathrm{mm^2/s}$. Similarly, the pH in the mortar was obtained using W/WO$_x$ micro-electrodes. With a 10 mm cover thickness, pH continued to decrease to pH 8.0, which was considered by penetration of H^+ ions from the surface. Based on the results of monitoring with the micro-electrodes, solutions simulating those in the pores in mortar were prepared and used in EIS measurements. The charge transfer resistance R_{ct} in the simulated solutions showed good correspondence with the impedance Z ($Z_{1mHz} - Z_{sol}$) 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.

1. Introduction

Deterioration of concrete structures in nuclear facilities has become a serious social problem in recent years, but in many cases, this deterioration is caused by corrosion of the reinforcing steel because they are located near the sea. Because deterioration due to salt damage is particularly severe, the total content of chlorides in freshly mixed concrete has been set at 0.3 kg/m^3 or less. However, corrosion deterioration due to salt damage is still a problem due to high levels of airborne sea salt. Moreover, recently, the acidic rain is a severe problem for the deterioration of concrete structure. Additionally, in the case of reprocessing plants, the steam of HNO_3 sometimes makes the environment acidic condition. Thus, it is very important to estimate the deterioration of reinforcing steel by corrosion for nuclear facilities.

In general, 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 a 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 ($3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$) and chlorides which exist in the form of chloride ions in liquid solution in the pores in the mortar. Because the form which is directly related to corrosion of reinforcing steel is the chloride ions in pores in the mortar, direct measurement of this type is important. 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 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. Moreover, there are few reports which examine the corrosion of reinforcing steel in mortar exposed in high chloride and low pH solution. 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 micro-electrodes into these artificial pores. Corrosion behavior was monitored by EIS, and changes in corrosion behavior accompanying environmental changes were obtained. Solutions were prepared periodically

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simulating the solutions found in the holes in the mortar, as determined by the environmental measurements, and the corrosion behavior of reinforcing steel 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.

2. Experimental method

2.1. Preparation of specimens

Specimens were prepared from ordinary Portland cement and mountain sand using a water/cement ratio of 0.5 by adding 0.5 mol/l 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 micro-electrodes were created by withdrawing the strips after the mortar had hardened. After curing in water for one 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 micro-electrodes were set to at 5, 10, 20, 30, 40, and 50 mm from the surface. The reinforcing steel was ordinary carbon steel of SM in Japan Industrial Standards (0.15C–0.2Si–1002E5Mn–Fe).

2.2. Measurement conditions

As micro-electrodes for use in environmental measurements, Ag/AgCl micro-electrodes were prepared for chloride ion measurements. Using an Ag wire (diameter: 0.3 mm), the electrodes were made at 500 mV for 2 h in a 0.1 M-HCl solution. For pH measurements, W/WO_x electrodes were prepared using a W wire (diameter: 0.3 mm) by immersion for 18 h in a 10%-HNO_3 solution. We had previously taken the calibration on the Ag/AgCl electrode in saturated $Ca(OH)_2$, also, that on W/WO_x electrode in high pH solutions.

For the corrosion test, the mortar specimens were immersed in a 0.5 M chloride solution (pH 4.0, 25 °C) and, as a comparison, in 0.5 M chloride solution (pH 6.0, 25 °C). The EIS measurements of the reinforcing steel and measurements of the concentration of Cl ions and pH using the micro-electrodes were made periodically. The solution was changed every week for preventing pH of the solution from increase by mortal. 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 3 electrode method using a Pt counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The counter and reference electrodes were set in the front of mortal block in a 0.5 M chloride solution (pH 4.0, 25 °C). The EIS measurement was performed at a voltage of 10 mV and frequency range of 20 K to 1 mHz. The specimen area of the steel plate was 3 cm^2, and other parts were sealed.

3. Experimental results and discussion

3.1. EIS behavior of reinforcing steel in mortar

The mortar specimens were immersed in a 0.5 M chloride solution (pH 4.0, 25 °C) and EIS measurements of the carbon steel reinforcing plate (SM) were performed periodically for a period up to a maximum of 140 days. Figs. 2 and 3 shows the EIS results for the reinforcing steel (SM) at the respective positions from the surface, i.e., at mortar cover thicknesses of 10 mm and 20 mm. In Fig. 2, a resistance component on the high frequency region can be seen in the results 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. The impedance spectrum on the low frequency region assumes a crushed form after Day 14, indicating a non-uniform electrode reaction. Based on this fact, an equivalent circuit like that shown in Fig. 4 is considered to exist due to the introduction of CPE (Constant Phase Element) 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}). Although the impedance spectra does not show W actually, however, in the case of the equivalent circuit, W is

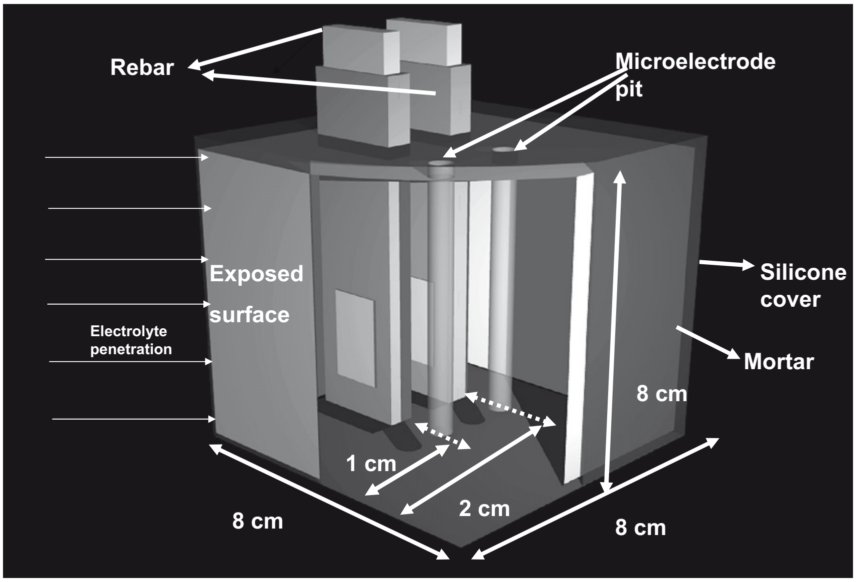

Fig. 1. Cross-sectional diagram of mortar block showing SM rebar and the microelectrode.

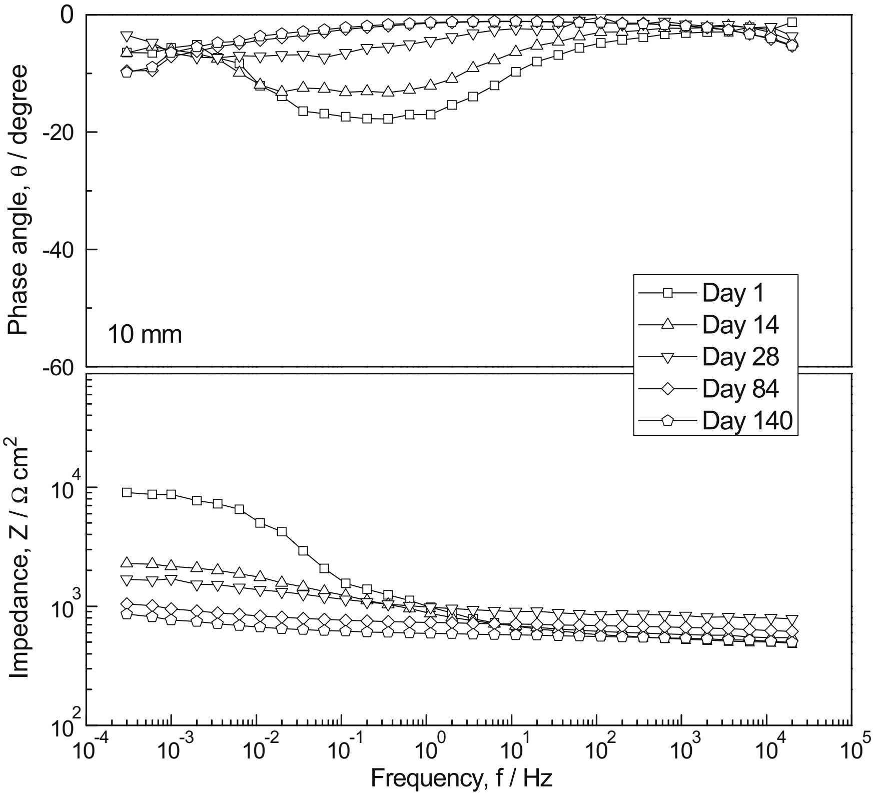

Fig. 2. EIS spectra of the SM in mortar block at 10 mm from the surface.

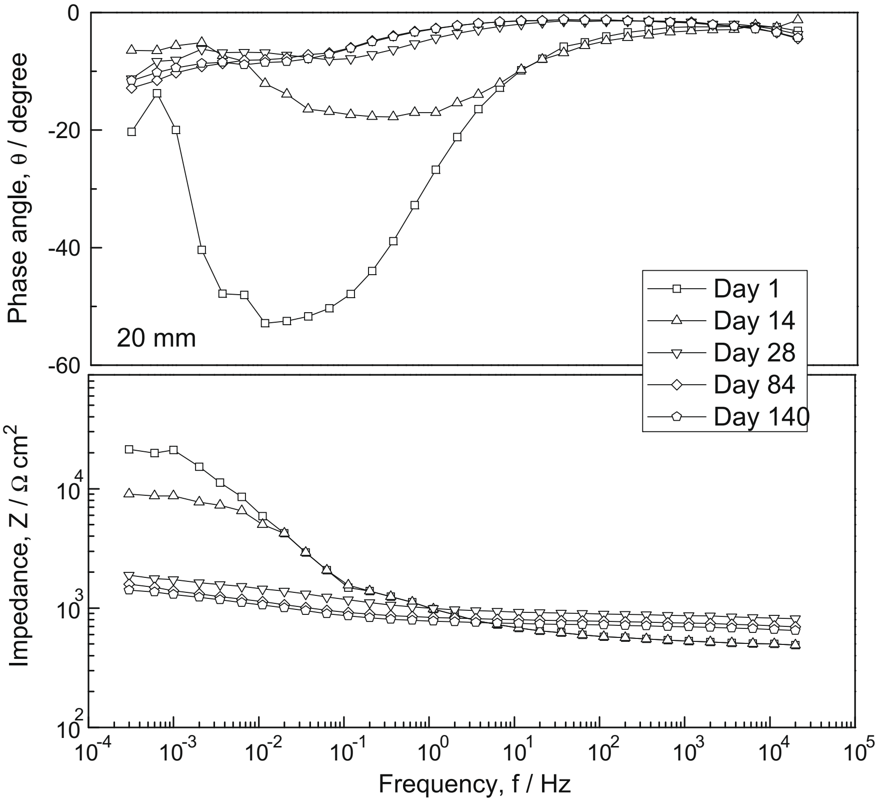

Fig. 3. EIS spectra of the SM in mortar block at 20 mm from the surface.

expressed because of showing the general cases in mortal. The EIS results of the carbon steel reinforcing steel (SM) at a mortar cover thickness of 20 mm in Fig. 2 can also be explained by a similar equivalent circuit. The impedance spectrum shows high value until

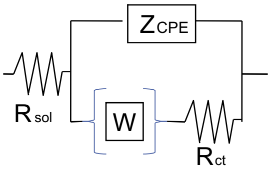

Fig. 4. Equivalent circuit for the corrosion of SM rebar in mortar block (R_{sol}: solution resistance in mortar block, Z_{CPE}: Constant Phase Element, W: Warburg impedance, R_{ct}: Charge transfer Resistance).

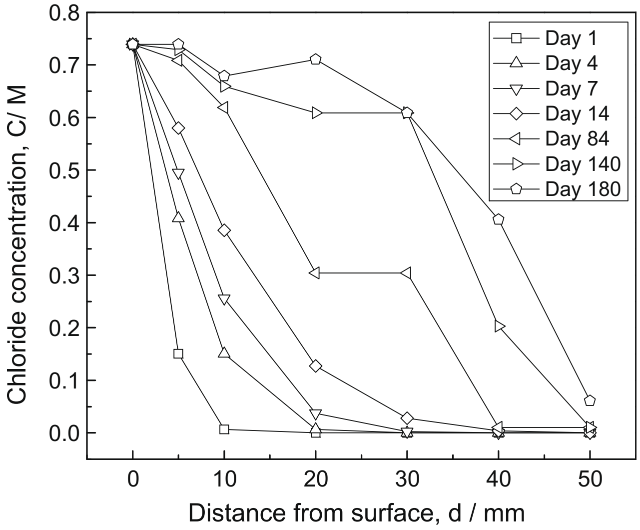

Fig. 6. Monitoring of chloride concentration using micro-electrodes in the mortar block exposed to 0.5 M NaCl solution of pH 4 for 180 days.

Day 14. However, after Day 28, the impedance spectrum on the low frequency region assumes a non-uniform electrode reaction.

Fig. 5 shows the change in the values of Z ($Z_{1mHz} - Z_{sol}$) in the impedance spectra in Figs. 3 and 4. As the solution resistance Z_{sol} is high in the mortal, the charge transfer resistance (R_{ct}) is presented by Z ($Z_{1mHz} - Z_{sol}$). As there is no Warburg impedance at 10 and 20 mm, Z shows almost charge transfer resistance (R_{ct}). With the cover thickness both of 10 and 20 mm, the spectra show high values in the initial period. However, from Day 28, the values are decreasing and showing the constant value at around 600–1000 Ω cm^2. Furthermore, as compared with R_{ct} at 10 mm, R_{ct} at 20 mm shows higher value after Day 84. As R_{ct} is caused by the corrosion reaction after a longer time, these results also suggest that corrosion is suppressed if the cover thickness is increased.

3.2. Measurement of changes in environmental factors in mortar

Simultaneously with the EIS measurements, the mortar specimens were immersed in a 0.5 M chloride solution (pH 4.0, 25 °C), and the changes in the environmental factors in the mortar during a period up to a maximum of 180 days were measured periodically using the micro-electrodes. Fig. 6 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 mol/l from the voltage obtained with the Ag/AgCl micro-electrodes, 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 0.2 mol/l 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 0.5 mol/l NaCl of the mixing water used when the mortar was prepared are thought to have been fixed in the form of salt. Or the pre-mixed NaCl was thought to be diluted during the curing process because the curing was done in Cl^- free water. On Day 7, the concentration of Cl ion at 10 and 20 mm increased to 0.5 and 0.25 mol/l, respectively. Moreover, also on Day 14, the concentration at 5 mm showed higher value of 0.6 mol/l, and at 10 mm and 20 mm were 0.38 and 0.13 mol/l, respectively, confirming the penetration of Cl ions into the mortar. 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.

Fig. 7 shows the change over time in the pH in the mortar at distances (cover thicknesses) of 10 mm and 20 mm from the surface. Here, pH was converted from the voltage obtained with the W/WO$_x$ micro-electrodes, and shows the pH in the measurement holes in the mortar. Initially, at the position 20 mm from the surface, pH decreased from pH 10.5, and was constant at pH 8.4 after Day 100. At the 10 mm position, pH also decreased over time from pH 10, but showed at constant value of less than 8.0 after Day 100. Because the 10 mm position is relative close to the surface, this is considered to show the effect of strong neutralization by penetration of the immersion solution (0.5 M-Cl ion, pH 4) from the surface. At the position more distant from the surface, i.e., the

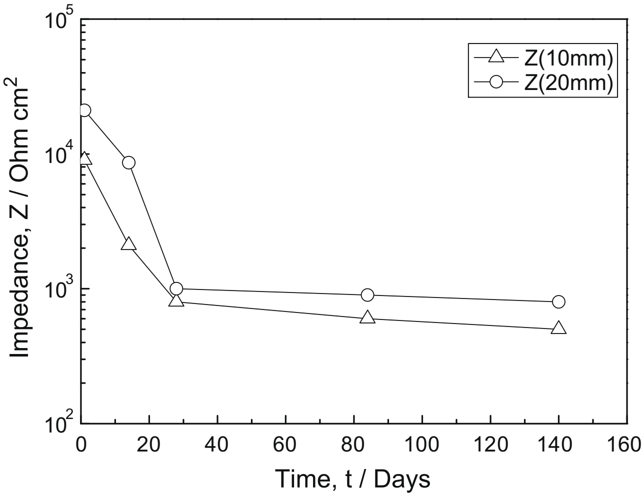

Fig. 5. Changes in impedance values of Z ($Z_{1mHz} - Z_{sol}$) of SM rebar in mortar block.

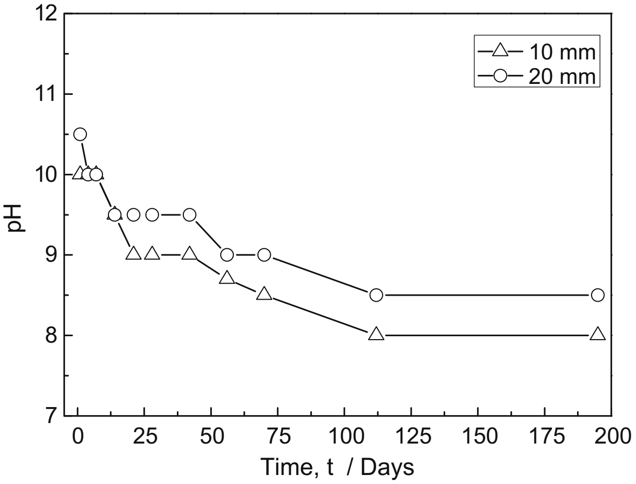

Fig. 7. Monitoring of pH using micro-electrodes in the mortar block at 10 mm and 20 mm from the surface in 0.5 M NaCl solution of pH 4.

20 mm position, it is thought that the decrease of pH was suppressed at around 8.4 by the pH buffering property of the mortar.

Fig. 8 shows the changes over time in the solution in the holes in the mortar at distances (cover thicknesses) of 10 mm and 20 mm from the surface. At 10 mm position, until Day 7 the Cl ion concentration increases to 0.2 mol/l, then, increases with the decrease of pH. On Day 140, Cl ion concentration reaches to 0.6 mol/l, and pH shows below 8.0. At the 20 mm position, Cl ion concentration shows below 0.2 M on Day 28, and below 0.3 M on Day 84, which shows that the increase of Cl concentration is very slow. In this way, chloride ion concentration and pH are changing by the diffusion and penetration of Cl and H^+ ions into the mortar. Moreover, these results also show the possibility of continuously monitoring the changes of solutions in holes in mortar using micro-electrodes.

3.3. Calculation of diffusion velocity of Cl ions in mortar

As described above, because penetration of the immersion solution also occurs simultaneously in mortar, the penetration behavior of Cl ions into the mortar is not simple. However, in the following, the authors will attempt to obtain a diffusion coefficient, assuming that mainly diffusion is controlling. From Fick's diffusion equation, the Cl ion concentration in mortar can be expressed as follows:

$$C = C_0[1 - \mathrm{erf}\ (x/2(D_c \cdot t)^{0.5})]$$

where x: distance from surface (mm), t: time (s), C: Cl ion concentration at x (mol/l), C_0: Cl ion concentration at surface (mol/l), D_c: diffusion coefficient (mm^2/s), and erf: error function.

Fig. 9 shows a comparison with the experimental results when the value of D_c (diffusion coefficient: mm^2/s) was changed to various values. Here, if D_c is assumed to be 9.5×10^{-5} mm^2/s, the results are in agreement with the experimental results at depths of 20 mm and more. Based on the above, in this experiment, the diffusion coefficient was determined to be $D_c = 9.5 \times 10^{-5}$ mm^2/s.

Fig. 10 shows the calculated results of the diffusion of Cl ions in the mortar assuming a diffusion coefficient of 9.5×10^{-5} mm^2/s. In comparison with Fig. 6, which shows the actual results, the condition of penetration of Cl ions in mortar due to diffusion shows good agreement in the relatively early period. The diffusion equation for semi-infinite medium was used conventionally in this study. However, as a result of mortal block of 80 mm, the concentration of chloride ion was very low and the diffusion rate was slow at the early period. This fact implies that the size of mortal block does not affect the diffusion equation during the early period of the diffusion. Although more detail calculations by using finite equation [30] are needed, the semi-infinite equation is thought able to be applied at least during early period of the diffusion.

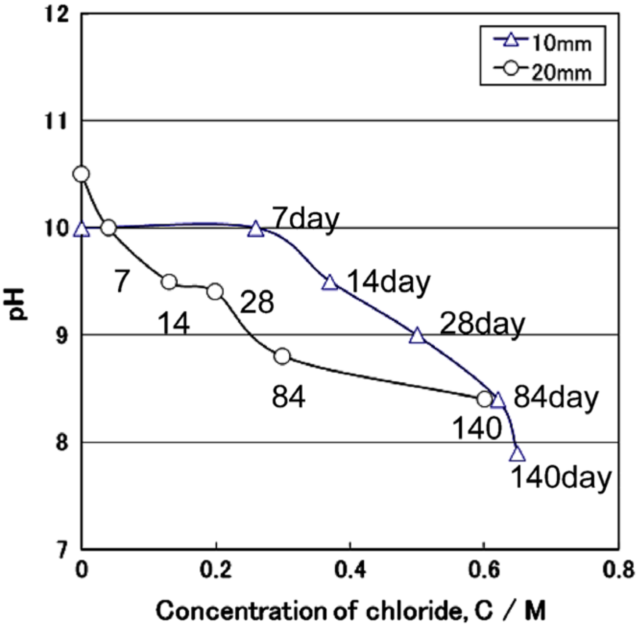

Fig. 8. Changes in the pH and Chloride concentration in mortar block measured by micro-electrodes.

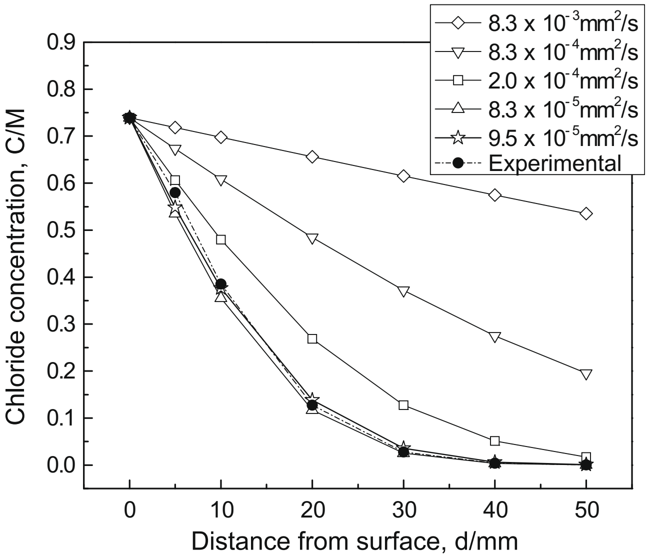

Fig. 9. Effect of diffusion coefficient on the chloride concentration profile in mortar block exposed in 0.5 M NaCl solution of pH 4. Comparison between the experimental and the calculated results on the 14th day.

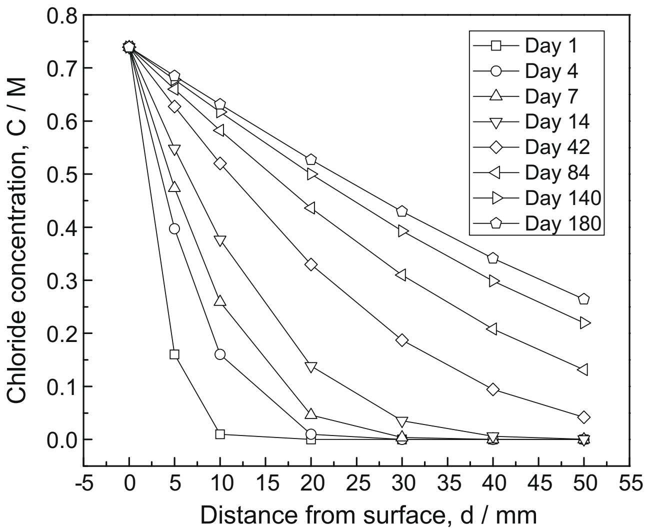

Fig. 10. Chloride concentration profile in mortar block calculated by using (D_c; 9.5×10^{-5} mm^2/s).

Moreover although in this research the diffusion coefficient took a high value, this value is comparable with reported values. A high diffusion coefficient has been reported for a sea-water cured mortar, which has a diffusion coefficient of 10^{-3} mm^2/s. [31].

After a longer period, in all cases, the results in the surface area are identical with the Cl concentration of the immersion solution, which is almost the maximum value, showing that penetration of the immersion solution into the mortar has a large effect. The surface of mortal after a long-term exposure was measured, and the micro-pits on the surface were recognized by Laser microscope. This fact indicated that chemical interaction between mortal surface and acidic solution might occur and make consequent change in physical property such as increase in porosity which allowed rapid Cl^- entry into mortal.

Thus, it was found that the progress of Cl ions into the mortar was controlled by diffusion in the initial period, but over the long term, penetration of the immersion solution from the surface area also had a substantial effect.

3.4. EIS behavior of reinforcing steel in solution simulating pores in mortar

Solutions simulating the solution in pores in mortar, as obtained using the micro-electrodes, were prepared, and the EIS behavior of reinforcing steel in those solutions was investigated. In the model solutions, only the Cl ion concentration and pH were simulated, and other ions were ignored. Fig. 11 shows the EIS behavior of reinforcing steel in the solutions prepared to simulate the results of the solutions in the artificial pores in the mortar at position of 20 mm from the surface, after various elapsed times (days). In comparison with reinforcing steel in mortar, the following differences were found in the impedance spectra of the steel 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 do not assume a crushed shape like that shown in Fig. 2. Because 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 holes in the mortar in Fig. 2.

Fig. 12 summarizes the impedance value (Z) of ($Z_{1mHz} - Z_{sol}$) from spectra in the simulated solutions in mortar. The value of charge transport resistance (R_{ct}) is considered to be approximately expressed by ($Z_{1mHz} - Z_{sol}$). In comparison with the results with actual mortar, the results (Z_{sim}) with the simulated solutions are in good agreement with the actual results (Z_{act}). This shows that the state (Cl concentration, pH) in the solution in pores in mortar determines the corrosion reaction of reinforcing steel. Furthermore, Z ($Z_{1mHz} - Z_{sol}$) shows large values during the initial period, but after Day 28, these become small values. Based on Fig. 8, the Cl concentration of 0.4 mol/l and pH 9.5 at Day 28 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 for depassivation of whole metal surface, i.e., active general corrosion.

Fig. 13 summarizes the impedance value Z ($Z_{1mHz} - Z_{sol}$) from spectra in 0.5 M chloride solutions of pH 4.0 and 6.0, respectively. At the position at 10 mm shown in Fig. 13a, Z shows low value from the early stage, and Z of pH 4.0 is almost the same value as that of pH 6.0. This fact implies that Z at 10 mm shows actual R_{ct}, and that the solution in the pore changes to high chloride and low pH one from early stage because of the fast diffusion and penetration from the surface of the exposed solution. On the other hand, at 20 mm position shown in Fig. 13b, Z of pH 4.0 is rather different value from that of pH 6.0. Z of pH 6.0 shows high value because of Warburg impedance by the diffusion of oxygen until Day 28. After Day 84, Z of pH 6.0 shows actual R_{ct}, and it value is still much higher than that of pH 6.0. This fact is implies that the solution in the pore at 20 mm does not change to so high chloride and low pH yet by the diffusion and penetration because the covered mortar is thick.

As described above, this research has demonstrated that it is possible to monitor the solution in pores in mortar, and further,

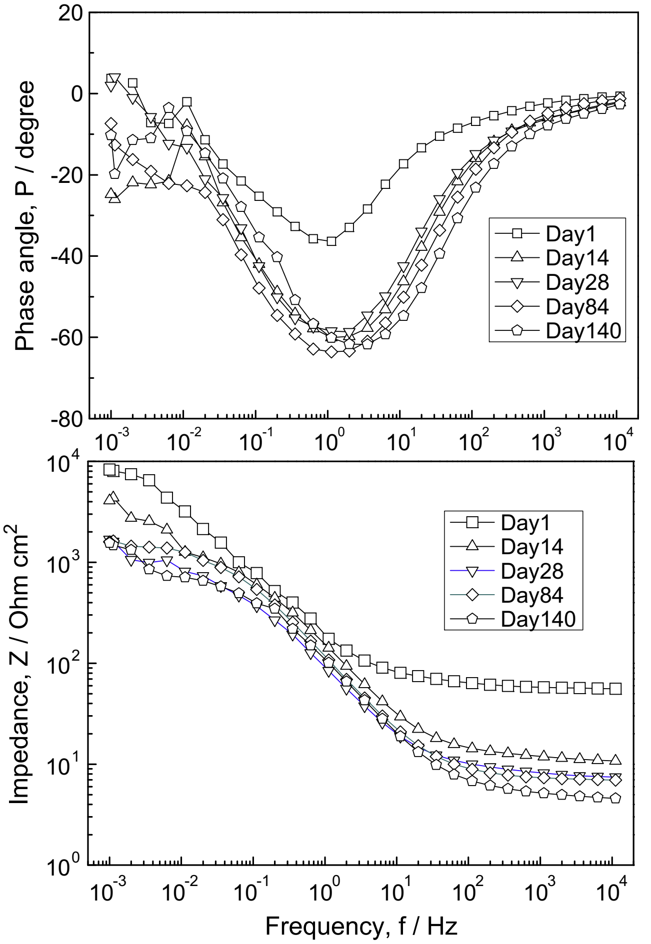

Fig. 11. Impedance spectra of SM in simulated solution of mortar block. Simulated conditions correspond to the actual result in Fig. 8 at 20 mm from the surface.

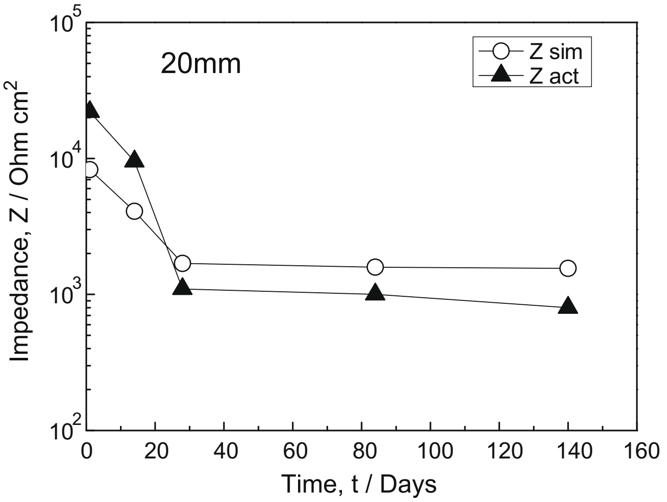

Fig. 12. Impedance values of Z ($Z_{1mHz} - Z_{sol}$) of SM rebar in mortar block (Z_{act}) and in simulated solution (Z_{sim}).

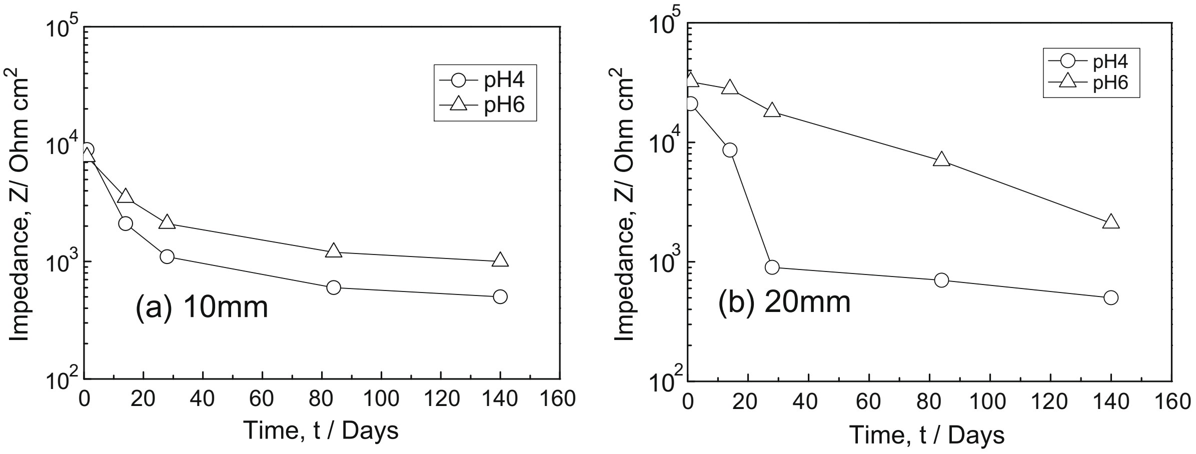

Fig. 13. Impedance values of Z ($Z_{1\mathrm{mHz}} - Z_{\mathrm{sol}}$) of SM rebar in mortar block in 0.5 M Cl ion of pH 4.0 and pH 6.0.

that the EIS behavior in a simulated solution prepared using the results of such monitoring can convincingly explain the actual corrosion behavior in mortar. 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 steel 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. Because it is possible to gain a detailed understanding of the corrosion condition of reinforcing steel by performing environmental monitoring, the corrosion mechanisms in many cases are expected to be understood more detail in the future.

4. Conclusion

To estimate the environmental factors in the mortar exposed in high chloride and low pH solution, 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 steel in these solutions and that in actual mortar.

(1) In the EIS measurements of reinforcing steel in mortar which was immersed in a 0.5 M-chloride ion solution (pH 4.0), diffusion behavior was not observed, and 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 micro-electrodes, 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 micro-electrodes, with a 20 mm cover thickness, pH was limited to approximately pH 8.4, but with a 10 mm cover thickness, pH continued to decrease to below pH 8.0. The latter phenomenon was considered to be the result of neutralization by penetration of the immersion solution of pH 4.0 from the surface.

(3) The rate of progress of Cl ions into the mortar exposed in 0.5 M chloride solution (pH 4.0) was summarized in a diffusion equation. In this work, the diffusion coefficient (D_c) showed a high value of $D_c = 9.5 \times 10^{-5}$ mm^2/s.

(4) 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 ($Z_{1\mathrm{mHz}} - Z_{\mathrm{sol}}$) 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, if these solution conditions (Cl concentration, pH) exceed threshold values in the mortal, the passivation film is destroyed, resulting in high corrosion behavior.

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