Electrochemical Impedance Analysis of Reinforcement of Corrosion of Reinforcing Bars in Concrete

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ABSTRACT
Owing to the presence of loops related to the time constants originating from the structure and interfacial reactions, it is difficult to select a suitable equivalent circuit for curve fitting of the impedance spectrum of reinforced concrete. To investigate the time constants observed in the impedance spectrum of reinforced concrete and propose an appropriate equivalent circuit, electrochemical impedance measurements of reinforced concrete with different cover thicknesses were performed using a two-electrode system. In this case, two parallel reinforcing bars were embedded in the concrete, and a cyclic wet–dry test was conducted to accelerate the corrosion of the reinforcing bars. It was confirmed that part of the large loop in the low-frequency range was related to the reinforcing bar/concrete interface, a distorted loop in the middle-frequency range was associated with rust formation on the reinforcing bars, and the small loop in the high-frequency range was attributed to the water distribution and pore structure in concrete.

Keywords: Electrochemical Impedance Spectroscopy, Reinforced Concrete, Corrosion, Equivalent Circuit

1. Introduction

Reinforced concrete (RC) structures have been widely used for structural infrastructure because they have high durability and good mechanical performance. However, the corrosion of the reinforcing bars in concrete has a serious problem worldwide. Thus, it is important to clarify the corrosion mechanisms of reinforcing bars in concrete in order to ensure the proper maintenance and management of infrastructure.

Electrochemical impedance spectroscopy (EIS) has been applied to investigation of the corrosion of reinforcing bars in concrete because the impedance spectrum over a wide frequency range can provide detailed information about the electrochemical properties of the reinforcing bar/concrete interface. In 1978, Dawson et al.1 reported electrochemical impedance measurements of RC, demonstrating that the corrosion rate of reinforcing bars in concrete can be determined by curve fitting of the impedance spectrum using an equivalent circuit. Subsequently, EIS has been widely used to study RC, and many equivalent circuits have been proposed in the literature.1–9 Figure 1 shows the schematics of typical equivalent circuits used for curve fitting of the impedance spectrum of RC and mortar specimens. Dawson et al.1 applied the equivalent circuit in Fig. 1(a) for interpretation of the impedance spectrum. In this equivalent circuit, a film and electrolyte resistance, $R_w$, is connected to a parallel circuit involving a charge-transfer resistance, $R_b$, a double-layer capacitance, $C_d$, and a Warburg impedance, $Z_w$. John et al.3 reported the equivalent circuit in Fig. 1(b), which is composed of a solution resistance of the concrete, $R_s$, and two parallel circuits in series. These parallel circuits in Fig. 1(b) comprise a film capacitance, $C_f$, a film resistance, $R_f$, a charge-transfer resistance, $R_{ct}$, a charge-transfer capacitance, CPE$_{ct}$, and a Warburg impedance, $Z_w$. For impedance analysis, Koleva et al.4 used an equivalent circuit comprised of two parallel circuits in series with an electrolyte resistance involving a contribution from the mortar bulk resistance, $R_{db}$, as shown in Fig. 1(c). In this equivalent circuit, the first parallel circuit ($R_{db}$ and CPE$_{db}$) is related to the properties of the cementitious matrix in terms of the pore network, and the second parallel circuit ($R_s$ and CPE$_{el}$) is associated with the electrochemical reaction on the surface of the reinforcing bar. These equivalent circuits indicate that the impedance spectra of RC and mortar specimens will exhibit some loops related to the time constants originating from the structure and interfacial reactions.

![Figure 1](image-url)
Therefore, it is difficult to select a suitable equivalent circuit for curve fitting of the impedance spectrum of reinforced concrete.

In the present study, we proposed an equivalent circuit for the analysis of the impedance spectrum of RC. To simplify the impedance measurements of RC, two reinforcing bars were embedded in parallel in concrete, and the impedance measurements were performed using a two-electrode system. In addition, the impedance measurements of mortar specimens at arbitrary curing times were conducted to examine the effect of the water distribution and pore structure in concrete on the impedance spectrum of RC. The pore structures in concrete are complicated owing to the fabrication of a transition zone around aggregates and the low homogeneity of concrete. Herein, the interpretation of the impedance spectrum of RC is discussed based on the impedance measurements of the RC and mortar specimens.

2. Experimental

2.1 Preparation of reinforced concrete

Table 1 presents the concrete mixture proportions, including the water to cement ratio (W/C), the volume ratio of sand to total aggregates (s/a), and the contents of water (W), cement (C), fine aggregate (S), and coarse aggregates (G). The slump test and air concrete test, which provide information about the flowability and strength, respectively, were performed to investigate the properties of fresh concrete. Ordinary Portland cement and crushed aggregates were used for the concrete mixtures. Chloride ions were premixed in the concrete as a 10% NaCl solution to accelerate the corrosion of the reinforcing bars in concrete. After the curing period of 28 days, the RC was dried in air for 7 days. To fabricate RC, reinforcing bars (φ 0.9 × 15 cm) were embedded in concrete according to the following procedure. An insulated copper wire was connected to the edge of the reinforcing bar, and both ends of the reinforcing bar were covered with insulating tape. The effective surface area of the reinforcing bar was approximately 28.27 cm². The reinforcing bars were then embedded in concrete. Figure 2(a) shows a cross-sectional schematic of the side view of the RC specimen (10 × 10 × 20 cm). Two reinforcing bars were placed parallel to each other in the concrete with a separation of 2.0 cm. A cross-sectional schematic of the front view of the RC specimen is shown in Fig. 2(b). To investigate the effect of the cover thickness on the corrosion of the reinforcing bars in concrete, the cover thickness between the reinforcing bars and the concrete surface of RC, as defined in Fig. 2(b), was varied (1.0 or 3.0 cm), and the other concrete surfaces were insulated using an epoxy resin.

Table 2. Mixture proportions for mortar specimens.

<table>
<thead>
<tr>
<th>W/C (%)</th>
<th>Unit content (kg)</th>
<th>Air content (%)</th>
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<tbody>
<tr>
<td>W/C (%)</td>
<td>s/a (%)</td>
<td>Weight per unit volume (kg/m³)</td>
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<tr>
<td>60</td>
<td>45.5</td>
<td>165</td>
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Figure 2. Cross-sectional schematics of (a) the side view and (b) the front view of RC.

Figure 3. Schematic of the setup for impedance measurements of mortar specimens.

2.2 Electrochemical measurement

2.2.1 Electrochemical impedance and rest potential measurements of reinforced concrete

The electrochemical impedance measurements of RC were performed using a two-electrode system. A cyclic wet-dry test was conducted to accelerate the corrosion of the reinforcing bars in concrete. The RC was first immersed in 10% NaCl solution for 2 days and then exposed to air for 5 days to dry. This process was repeated 19 times. The electrolyte solution was prepared from doubly distilled water and analytical-grade sodium chloride. The electrochemical impedance of the RC specimen was measured during the 2 days immersion period. In addition, the rest potential of each reinforcing bar embedded in the concrete was measured using a KCl-saturated Ag/AgCl electrode (SSE).

2.2.2 Electrochemical impedance measurements of mortar specimens

Electrochemical impedance measurements of mortar specimens were performed at arbitrary curing times using a two-electrode system. Table 2 shows the mixture proportions for the mortar specimens. Ordinary Portland cement was used to fabricate the mortar specimens, which had W/C values of 40%, 50%, or 60%. The size of each mortar specimen was 10 × 10 × 10 cm. Figure 3 represents a schematic of the measurement setup for the mortar specimens. For the impedance measurements, two stainless steel plates were used as the electrodes. The mortar specimen was sandwiched between the electrodes, which were symmetrical face to face. The size of each electrode was 10 × 12 × 1 cm, and the surface area of the mortar was 10 × 10 cm. An electrode gel (Signagel, Parker Laboratories, Inc.) was used between the mortar surface and the stainless steel electrode to improve the conductive properties during the measurements.

Rest potential measurements were performed using a potentiogalvanostat (SI1287, Solartron). For electrochemical impedance measurements, the potentiogalvanostat (SI1287, Solartron) and a frequency response analyzer (SI1255B, Solartron) were used. The electrochemical impedance was measured in the frequency range of

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<tr>
<td>W/C (%)</td>
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</tr>
<tr>
<td>40</td>
<td>2.26</td>
<td>6.02</td>
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<tr>
<td>50</td>
<td>2.70</td>
<td>5.68</td>
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<tr>
<td>60</td>
<td>3.09</td>
<td>5.37</td>
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1.0 MHz to 0.1 Hz at five frequencies per decade with an AC amplitude of 10 mV. The applied DC voltage was 0 V.

3. Results and Discussion

3.1 Rest potential and impedance measurements of reinforced concrete

Figure 4 shows the rest potentials of the reinforcing bars in concrete. The white and black circles denote the rest potentials of each reinforcing bar embedded in the concrete with 1.0 cm cover thickness, \( E_{\text{rest},1.0}\), and \( E_{\text{rest},1.0}\) respectively, and the white and black squares indicate \( E_{\text{rest},3.0}\) and \( E_{\text{rest},3.0}\) respectively. The \( E_{\text{rest},1.0}\), \( E_{\text{rest},1.0}\), \( E_{\text{rest},3.0}\), and \( E_{\text{rest},3.0}\) values were measured under wet conditions during each wet–dry cycle, and the values for the 0th cycle were obtained at the rest potential before the cyclic wet–dry test. In Fig. 4, the \( E_{\text{rest},1.0}\), \( E_{\text{rest},1.0}\), \( E_{\text{rest},3.0}\), and \( E_{\text{rest},3.0}\) values were between −0.65 and −0.80 V vs. SSE for the 0th cycle. The \( E_{\text{rest},1.0}\) and \( E_{\text{rest},1.0}\) values showed positive shifts for the 1st cycle, and then exhibited negative shifts with increasing cycle numbers. After the 6th wet–dry test cycle, both values became stable. By contrast, the \( E_{\text{rest},3.0}\) and \( E_{\text{rest},3.0}\) values only shifted positively and became stable after the 4th wet–dry test cycle.

During rest potential measurements of reinforcing bars in concrete, the anodic and cathodic reactions are considered to be the dissolution of the reinforcing bar or passive film formation on the surface of the reinforcing bar and oxygen reduction. Because chloride ions were premixed into the concrete, the low values of \( E_{\text{rest},1.0}\), \( E_{\text{rest},1.0}\), \( E_{\text{rest},3.0}\), and \( E_{\text{rest},3.0}\) for the 0th cycle imply the dissolution of the embedded reinforcing bar. The values of \( E_{\text{rest},1.0}\) and \( E_{\text{rest},1.0}\) were higher than those of \( E_{\text{rest},1.0}\) and \( E_{\text{rest},1.0}\) under stable conditions, and this difference is related to the cover thickness of the RC specimens. In the present study, the corrosion of reinforcing bars in concrete accelerates by the cyclic wet–dry test. In this test, the electrolyte solution penetrates into the concrete, then the electrolyte solution in the concrete is dried, and this process is repeated. When the cover thickness of the RC is thin like 1.0 cm, the electrolyte solution reaching to the reinforcing bars in concrete is dried during drying process. In the case of thick cover thickness like 3.0 cm, the concrete near the reinforcing bars is still moist even after drying. Thus, the corrosion of reinforcing bars in concrete with 1.0 cm cover thickness progresses by the cyclic wet–dry test compared to that with 3.0 cm cover thickness, leading to the difference of the rest potential of the reinforcing bars in concrete with 1.0 cm (\( E_{\text{rest},1.0}\), \( E_{\text{rest},1.0}\)) and 3.0 cm (\( E_{\text{rest},3.0}\), \( E_{\text{rest},3.0}\)) under stable conditions.

Figure 5 presents the impedance spectra of the RC specimens during the 2nd wet–dry test cycle. The circles and squares denote the RC specimens with cover thicknesses of 1.0 and 3.0 cm, respectively. Impedance spectra in Fig. 5 can be described as containing a locus in the high-frequency range and part of a loop in the low-frequency range. Each impedance at real axis to which the high-frequency locus converged shows different values in Fig. 5 because the locus in the high-frequency range is related to the moisture conditions of concrete. Figure 6 represents the impedance spectra of the RC specimens during the 19th wet–dry test cycle. The circles and squares indicate the RC specimens with cover thicknesses of 1.0 and 3.0 cm, respectively. The full impedance spectra in Fig. 6(a) can be described as containing a small loop in the high-frequency range and part of a loop in the low-frequency range. These small loops, which is attributed to the moisture conditions of concrete, were almost similar in the high-frequency range. On the other hand, the impedance plots for RC with 1.0 cm cover thickness are lower than those for RC with 3.0 cm cover thickness in the low-frequency range. It implies that the difference of impedance values in the low frequency range is affected by the cover thickness of RC specimens. Expanded views of the high-frequency range of the impedance spectra in Fig. 6(a) are shown in Figs. 6(b) and (c). Although these impedance spectra can be described as containing a small loop and part of a loop, distorted impedance appears in the middle-frequency range for the RC specimen with 1.0 cm cover thickness (Fig. 6(b)).

To aid in the interpretation of the impedance spectra in Figs. 6(b) and (c), we investigated the conditions of the reinforcing bars in concrete. Images of the reinforcing bars before the wet–dry test and after the 19th wet–dry test cycle are shown in Fig. 7. As shown in Fig. 7(a), no corrosion sites were present on the reinforcing bars before the wet–dry test. After the 19th cycle, rust was formed on the entire surface of the reinforcing bars embedded in concrete with 1.0 cm cover thickness (Fig. 7(b)). However, in the case of the reinforcing bars embedded in concrete with 3.0 cm cover thickness (Fig. 7(c)), only a small amount of rust was formed on part of the surface. It implies that the impedance in the middle-frequency range of RC specimen is affected by the rust formation on the reinforcing bars in concrete. In addition, the rust formation on the reinforcing bars is associated with the difference of the cover thicknesses of the RC specimens.

Based on the impedance measurement results and the condition of the reinforcing bars, the time constants in the impedance spectra can be interpreted as follows. During the 2nd wet–dry test cycle, the RC specimens with 1.0 and 3.0 cm cover thickness exhibited similar impedance values (Fig. 5). In contrast, during the 19th wet–dry test cycle, the impedance of RC with 1.0 cm cover thickness in the low-
frequency range was drastically lower than that of RC with 3.0 cm cover thickness (Fig. 6(a)). These results indicate that the part of the loop in the low-frequency range is related to the charge-transfer resistance, $R_{ct}$, namely, the reinforcing bar/concrete interface. In the middle-frequency range, a distorted locus appeared for the RC specimen with 1.0 cm cover thickness (Fig. 6(b)). John et al.\textsuperscript{2} implied that a distortion of the impedance in this frequency range is associated with a nonuniformity of the interface owing to rust formation. As Fig. 7(b) shows that the surface of the reinforcing bar is not uniform because of rust formation, it is considered that the distortion of the impedance is related to the current distribution on the nonuniform surface. In the high-frequency range, the locus observed during the 2nd wet–dry test cycle for each RC (Fig. 5) became a small loop by the 19th wet–dry test cycle (Figs. 6(b) and (c)). McCarter and Garvin,\textsuperscript{11} who measured the impedance of mortar in the frequency range of 20Hz to 110MHz, indicated that a locus in the high-frequency range is strongly related to the moisture conditions of mortar. Thus, the locus and the loop observed in the high-frequency range of the impedance spectra in Fig. 5 and in Figs. 6(b) and (c) are attributed to the moisture conditions of concrete.

Though it is important to investigate the changes of impedance of RC specimens with different cover thicknesses based on the results of the corrosion conditions of the reinforcing bars, we focus on the feature of the impedance related to the moisture conditions of concrete in the present study. To simplify the appearance of the locus or small loop in the high-frequency range, we conducted impedance measurements on mortar specimens. The curing time and the changes in the impedance of mortar specimen were correlated, as discussed in the next section.

3.2 Impedance measurements of mortar specimens with different curing times

As discussed in the previous section, the impedance spectra of the RC specimens with 1.0 and 3.0 cm cover thickness exhibited part of a loop in the low-frequency range related to the reinforcing bar/concrete interface and a distorted locus in the middle-frequency range associated with the rust layer formed on the reinforcing bar. Next, the appearance of the loop in the high-frequency range was further investigated using impedance measurements for mortar specimens with different curing times.

Figure 8(a) represents the typical impedance spectrum of mortar with $W/C = 40$ after a curing time of 3 days. The impedance spectrum can be described as containing part of a large loop in the low-frequency range. This feature is related to the electrode/solution interface of stainless steel because the impedance measurement was conducted using both the electrodes in a two-electrode system. An expanded view of the high-frequency range of the impedance spectrum in Fig. 8(a) is shown in Fig. 8(b), in which a small loop is clearly observed on the Nyquist plane. In addition, inductive behavior resulting from the wiring was observed in the high-frequency range. Electrochemical impedance measurements of the
mortar specimens were performed 15 times at arbitrary curing times, and all the obtained impedance spectra can be described as containing a small loop in the high-frequency range. To analyze this small loop, the equivalent circuit in Fig. 9 was used for curve fitting of the impedance spectra of the mortar specimens. In Fig. 9, \( R_{\text{sol,pore}} \) is the solution resistance in the pores, \( R_{\text{M,pore}} \) is the mortar resistance between the pores in mortar, and \( Z_{\text{CPE,M}} \) is the impedance of the mortar involving a constant phase element (CPE), \( Z_{\text{CPE,M}} \), which is expressed as:

\[
Z_{\text{CPE,M}} = \frac{1}{(j\omega)^{1/p} T_{\text{CPE}}} (1)
\]

where \( j \) is an imaginary unit, \( \omega \) is the angular frequency, \( p \) is the CPE index number, and \( T_{\text{CPE}} \) is the CPE constant. The capacitance between the pores in mortar, \( C_{\text{pore}} \), is obtained using the following equation:

\[
C_{\text{pore}} = T_{\text{CPE}} R_{\text{M,pore}}^{1/p} (2)
\]

The details of the theoretical equations associated with the CPE have been described in the literature. Figure 10 displays plots of \( R_{\text{sol,pore}} \), \( R_{\text{M,pore}} \), and \( C_{\text{pore}} \) with curing time. The circles, squares, and triangles denote mortar specimens with \( W/C = 40, 50, \) and 60, respectively. The parameters in Fig. 10 were determined by curve fitting of the impedance spectra using the equivalent circuit in Fig. 9.

McCarter and Garvin\textsuperscript{11} reported the application of EIS to characterize the moisture conditions of cement. They discussed the appearance of the loop in the impedance spectrum of cement based on the water distribution and pore structure in the cement.\textsuperscript{11} They suggested that charges in the water-filled capillaries lead to an ionic conduction effect, whereas charges in closed or dead-end pores give rise to interfacial polarization in cement under an alternating voltage.\textsuperscript{11} In the present study, \( R_{\text{sol,pore}} \), \( R_{\text{M,pore}} \), and \( C_{\text{pore}} \) first increased and then became stable at \( t_c = 17 \) days (Fig. 10). It is considered that these changes in the values of \( R_{\text{sol,pore}} \), \( R_{\text{M,pore}} \), and \( C_{\text{pore}} \) are related to the densification behavior of mortar caused by curing. Typically, it takes 28 days to cure concrete.\textsuperscript{11} In this period, the fabrication of void structures in concrete is accompanied by a hydration reaction of Portland cement, and the amount of quite small void spaces increases with an increase of the hydration rate of cement.
cement. In the present study, the values of $R_{\text{sol,pore}}$, $R_{\text{M,pore}}$, and $C_{\text{pore}}$ drastically increased until $t_c = 17$ days, and then stabilized. These behaviors indicate that the fabrication rate for void structures and the hydration rate of Portland cement in mortar are high until $t_c = 17$ days. After $t_c = 17$ days, the fabrication of the void structure progresses at a low rate. In addition, it is interesting to note that a relative permittivity on the order of $10^6$ was estimated from the $R_{\text{sol,pore}}$ values at $t_c = 17$ days (Fig. 10(c)), which implies that a huge number of micrometer-sized pores were fabricated in the mortar specimens.

Based on the impedance analysis of the RC and mortar specimens, an equivalent circuit for interpreting the impedance spectra of RC under the present conditions was proposed, as shown in Fig. 11. This equivalent circuit is composed of $R_{\text{sol,pore}}$ and three parallel circuits in series. The first parallel circuit ($R_{\text{C,pore}}$ and $C_{\text{pore}}$) is attributed to the properties of the water distribution and the pore structure in concrete, the second parallel circuit ($R_{\text{rust}}$ and $C_{\text{PCE}}$) is associated with rust formation on the reinforcing bars in concrete, and the third parallel circuit ($R_{\text{M,pore}}$ and $C_{\text{PCE}}$) is related to the reinforcing bar/concrete interface. We hope that application of this equivalent circuit can aid in the elucidation of the corrosion mechanisms of reinforcing bars in concrete.

4. Conclusions

Electrochemical impedance measurements of RC were performed using a two-electrode system. The findings of the present study are as follows:

1. Cyclic wet–dry tests were performed to investigate the impedance spectrum of RC. During the 2nd wet–dry cycle, the impedance spectra of RC with 1.0 and 3.0 cm cover thicknesses were described by a small locus in the high-frequency range and a part of a large loop in the low-frequency range. During the 19th wet–dry cycle, the RC with 1.0 cm cover thickness exhibited a distorted locus in the middle-frequency range and the part of the large loop in the low-frequency range became small. As rust was formed on the entire surface of the reinforcing bars, these features were related to the current distribution caused by surface roughness and the reinforcing bar/concrete interface, respectively.

2. Impedance measurements of mortar specimens at arbitrary curing times were conducted to investigate the appearance of the small loop in the high-frequency range of the impedance spectra of RC. Estimation of the values of the solution resistance in the pores, $R_{\text{sol,pore}}$, the mortar resistance between the pores in mortar, $R_{\text{M,pore}}$, and the capacitance between the pores in mortar, $C_{\text{pore}}$, using an equivalent circuit indicated that these parameters were correlated to the curing time of RC.

3. Equivalent circuit to investigate the impedance spectrum of RC was proposed based on the impedance analysis of the RC and mortar specimens.

References