

Monitoring of Corrosion Rates of Carbon Steel in Mortar under a Wet-Dry Cyclic Condition

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Abstract : The corrosion behavior of metal covered with mortar under a wet-dry cyclic condition were investigated to apply for the measurement of corrosion rates of reinforcing steel in concrete structure. The carbon steel in mortar having $t = 3$ mm cover thickness was exposed to the alternate condition of 6 h immersion in chloride containing solution and 18 h drying at 25°C and 50%RH. The electrochemical phenomena of a carbon steel and mortar interface was explained by an equivalent circuit consisting of a solution resistance, a charge transfer resistance and a CPE (Constant Phase Element). The corrosion rates were monitored continuously during exposure using an AC impedance technique. Simultaneously, the current distribution over the working electrode during impedance measurement was analyzed from the phase shift, θ , in an intermediate frequency. The result showed that corrosion rate monitoring using an AC impedance method is suitable under the given exposure conditions even during the drying period when the metal is covered with the wetted mortar.

Keywords : Mortar, Wet-dry cyclic, Corrosion rates, AC impedance

1. Introduction

Generally, corrosion rates are accelerated with velocity of oxygen diffusion. Stratmann¹⁾ obtained the monitoring results for carbon steel through corrosion potential monitoring by Kelvin method and the corrosion rates were evaluated on the basis of oxygen consumption monitoring. Nishikata et al.^{2,7)} used the electrochemical impedance spectroscopy(EIS) technique to study the corrosion of metals covered with an extremely thin electrolyte layer. They found the EIS data obtained that the equivalent circuit of metal-thin electrolyte layer interface can be described by a transmission line model(TML). It was found from the theoretical analysis based on the TML model that the current distribution profile becomes uniform at least in the low frequency limit when the phase shift θ goes further than -45° on a plot of θ vs. $\log(f = \text{frequency})$. In such a condition, an accurate corrosion rate can be determined from the obtained polarization resistance R_p .³⁾

On the other hand, the application of the electrochemical techniques to the corrosion monitoring of reinforcing steel in concrete is quite difficult. The largest problem in its application is that the solution resistance becomes extremely high. In such a condition, an extremely high ohmic drop and a non-uniform current distribution over the working electrode

produce serious errors in the measurement of corrosion rate.⁵⁾

By the measurements of AC impedance the solution resistance is estimated from impedance measured in high frequency range, and the sum of the solution resistance R_s and the polarization resistance R_p is determined by subtracting $Z_{H\omega}$ impedance at high frequency, from Z_L impedance at low frequency. The corrosion rate is widely accepted to be inversely proportional to the R_p value. In this study, AC impedance technique was used to measure the atmospheric corrosion rates of carbon steel in mortar under cyclic wet-dry conditions. The main objective was to investigate the feasibility of using an AC impedance monitoring technique to detect the corrosion rates of carbon steel and develop an accurate monitoring method under the wet-dry cyclic environment.

2. Experimental Methods

2.1 Electrode system

A schematic diagram of the electrochemical cell used in impedance measurement is shown in Fig. 1. The whole cell in Fig. 1 was immersed and dried in given experimental wet and drying condition. 3-electrodes cell arrangement were used in this study. The employed mortar consisted of normal Portland cement and standard sand, and they were mixed with tap water with 0.6 water-cement ratio by weight.¹¹⁾ The cover thickness of mortar is 3mm and the only top surface of steels in mortar was exposed to the wet-drying condition.

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The corrosion potential E_{corr} was monitored when the specimen was immersed for 6 h and dried for 18 h in several cycles using Silver-Silver chloride Electrode.⁹⁾

2.2 Impedance measurements

The electrochemical measurements of specimen were monitored by the AC impedance method under a cyclic wet-dry condition, which were exposed to the alternate conditions of 6h-immersion in 0.5M NaCl solution, 18 h drying at 25°C and 50%RH for 40days. The impedance measurements using

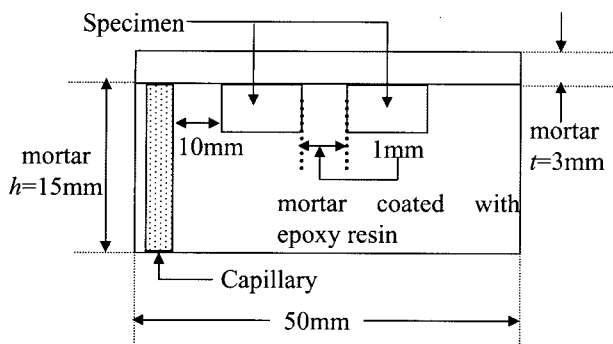


Fig.1. Two electrode electrochemical cell employed for the ac impedance measurement of carbon steel in mortar.

Frequency Response Analysis (S-5720S of NF Circuit Block) with a multiplexer controlled by a computer through the GPIB interface were made by applying a small amplitude perturbation, 10 mV, and at the several frequency ranges.⁹⁾

3. Results and Discussion

3.1 AC impedance characteristics dependent on monitoring time

Impedance measurements in Fig. 2 were performed when the mortar was immersed in 0.5M NaCl solution. The range of frequency for the measurements was 10 kHz to 1 mHz. The measurement was started 1hour later after 1hour exposure in the immersion condition. In the initial stage (2nd and 15th day), only one semi-spherical trace emerged and the semi-sphere diameter tended to decrease with increasing time and, from 25th day, additional Warburg impedance emerged in the low frequency range. To appreciate this experiment result,⁵⁾ curve fitting was tried on the basis of the equivalent circuit as indicated in Fig. 3. It appears that the curve fitting points coincide well with the experimental data points. In the equivalent circuit, R_c represents the charge transfer resistance, R_s the solution resistance, CPE the constant phase element, and W the warburg impedance of diffusion.⁴⁾ Table 1 summarizes values of the parameters used for the curve fit-

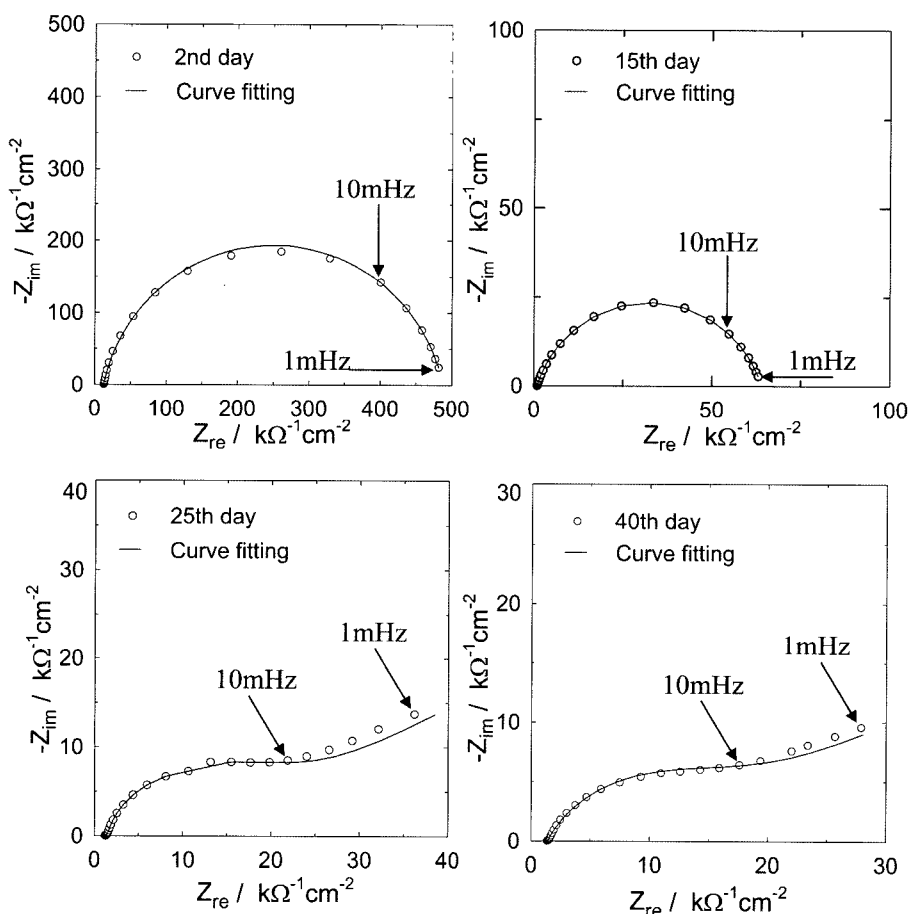


Fig. 2. Nyquist plots and curve fitting for carbon steel in mortar for 40 days.

Table 1. The parameters used for curve fitting in Fig. 2.

Elements	2 nd day	15 th day	25 th day	40 th day
$R_s(\text{k}\Omega\text{cm}^2)$	12.6	0.94	1.37	1.36
$T(\mu\text{Fcm}^{-2})$	16	46	65	85
$R_c(\text{k}\Omega\text{cm}^2)$	418.65	63.07	26.00	17.90
α_1	0.86	0.81	0.60	0.61
$W_R(\Omega\text{cm}^2)$	-	-	50	67
W_T	-	-	69	87
α_2	-	-	0.20	0.19

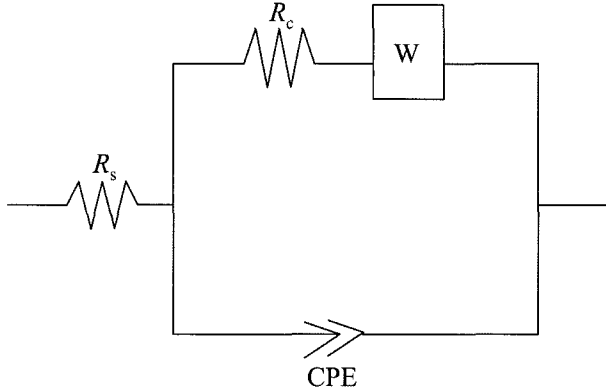


Fig.3. Proposed equivalent circuit for carbon steel in mortar.

ting. Here, T is capacitance, α_1 and α_2 is calibration factor, W_R and W_T is resistance and capacitance component. CPE parameters are explained by T and a_1 . When $a_1=1$, CPE would become capacitive, being equal to the electric double layer capacitance C_{dl} (μFcm^{-2}). Impedance Z_{CPE} of CPE is represented by

$$Z_{CPE} = 1/[T(j\omega)^{\alpha_1}] \quad (1)$$

Where j refers to the complex number and ω angular frequency ($\omega = 2\pi f$). That is, impedance, consisting of a parallel connection of R_c and CPE, would yield a semi-circular trace when $\alpha_1 = 1$ and, as the a_1 value becomes smaller, the semi-circle would become increasingly distorted. Warburg impedance W is composed of a resistance component W_R , a capacitance component W_T , and a calibration factor α_2 . Impedance Z_w of W is represented by

$$Z_w = [W_R \tanh(jWT\omega)^{\alpha_2}]/(jWT\omega)^{\alpha_2} \quad (2)$$

When $\alpha_2 = 0.5$, impedance of diffusion yields a straight line with a slope of 45° over the Nyquist plot and, with further decrease of α_2 , the slope of straight line becomes smaller. For now, the exact physical significances of the parameters, α_1 and α_2 , are not clear but these parameters certainly refer to some aspects of electrode reaction heterogeneity.⁵⁾

3.2 Validity of the parameters used for the curve fitting

The validity of the parameters listed in Table 1 is reviewed.⁵⁾ First, R_s values is difficult to estimate but we can see the trend of the decreased R_s with monitoring time, to 15th cycle : $R_s = 12.61 \text{ k}\Omega\text{cm}^2$ for 2nd cycle, $R_s = 0.94 \text{ k}\Omega\text{cm}^2$

for 15th cycle. It is also noticed that R_s for 3 mm cover thickness tended to diminish with increasing the monitoring time reflecting the increasing chloride level in the mortar. Probably, R_s seemed to reach a certain steady-state level after any period. From R_s monitoring in such a wet-dry cycle test, the time for chloride penetration rates into a mortar to reach the steady state can be determined. In table 1, the T parameter on 2nd day must have represented the capacitance component, noting that the a_1 value was 0.86 (close to 1). The values of T were in the range of several decades of μFcm^{-2} and thus it must have been the electric double layer capacitance C_{dl} . It is listed in Table 1 that T tended to rise and α_1 to decrease with the increasing monitoring time. This evidence appears to represent the situations of increasing heterogeneity of the specimen surface and of the increasing contribution from pseudo-capacitance arising from deposition of corrosion product with the increasing wet-dry cycles. On the other hand, R_c showed a trend of decrease with wet-dry cycles, implying that R_c represented the charge transfer resistance for corrosion reaction. This evidence seemed to suggest that the corrosion rate estimation is feasible with the R_c monitoring. In the present experiment with $t = 3 \text{ mm}$, the Warburg impedance was not detected in the range of 15th day, $R_c = 63.07 \text{ k}\Omega\text{cm}^2$, while it became detectable at 25th day when R_c decreased to $26.00 \text{ k}\Omega\text{cm}^2$. This evidence indicated that the impedance that is indicative of diffusion control of the corrosion reaction in the mortar would emerge when R_c came down to the $26.00 \text{ k}\Omega\text{cm}^2$ level from $481.65 \text{ k}\Omega\text{cm}^2$. The values of α_2 in Table 1 was no higher than 0.2. Noting that α_2 becomes 0.5 in the case of linear diffusion in a homogeneous medium, the observed small value of α_2 must have represented the fact that the diffusion path in the mortar was not at all simple and straight. From the Fitted results in Fig. 2, impedance values showed that impedances at 10 mHz of 25th and 40th day are corresponded with R_c , charge transfer resistance.

The corrosion rate estimation from the data acquired by the ac impedance method must be through curve fitting as demonstrated in Fig. 2 and table 1 to evaluate R_c and, accepting the R_c value as the polarization resistance R_p , to calculate the corrosion current density.^{5,9)}

The corrosion current density i_{corr} has been calculated by using the Stern-Geary equation.⁶⁾

$$i_{corr} = k/R_p \quad (3)$$

$$k = -b_a b_c / 2.303(b_a + b_c) \quad (4)$$

Where b_a and b_c are Tafel slopes of anodic and cathodic polarization curves.

The rate of corrosion was determined by taking impedance of specimen at the low frequency, Z_L and at the high frequency, Z_H . The polarization resistance, R_p was then calculated by subtracting Z_L from Z_H and i_{corr} was obtained from the R_p value using Eq.(3).

Fig. 4 was plotted. 0.050 V/dec^5 as the value for k was used to calculate i_{corr} . In this figure, R_c determined from curve fitting and $Z_{1\text{mHz}}$ (impedance at 1mHz) are plotted as a function of monitoring time. To 15th day, the Nyquist plot

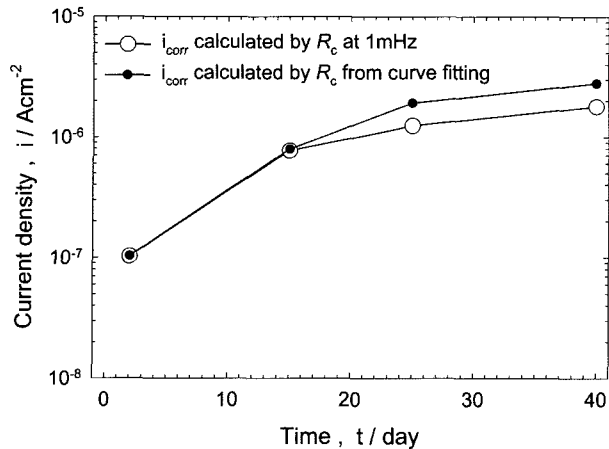


Fig. 4. i_{corr} comparison calculated by the charge transfer resistance R_c obtained from curve fitting and impedance at 1 mHz.

showed a single semi-circular trace and consequently $Z_{1\text{mHz}}$ became comparable to R_c . After then, $Z_{1\text{mHz}}$ became greater than R_c from curve fitted. However, R_c values to 25th and 40th day were well corresponded with impedance at 10mHz. The reason for this deviation of $Z_{1\text{mHz}}$ from R_c is the emergence of impedance by the diffusion in low frequency range. Therefore, if it is considered that the corrosion rate on the initial stage is very low, 10 mHz is thought to be a reasonable frequency for corrosion monitoring to predict R_c value.⁵⁾

3.3 Current distribution over the working electrode under wet-drying condition

Fig. 5(a) and (b) show the typical Bode plots obtained for the carbon steel specimen exposed to alternate wet-drying cyclic conditions of 6 h immersion in 0.5 M NaCl solution and 18h drying at 25°C and 50%RH. R. P. Vera Cruz et al.⁷⁾ showed that the interface of a metal-thin electrolyte layer can be interpreted by a one-dimensional transmission line circuit model and the current distribution over the working electrode at comparatively lower frequencies becomes uniform if the phase shift θ goes further than -45° on the plot of θ vs. frequency f . Therefore, the impedance value measured at a low frequency might be taken as the polarization resistance without error derived from the presence of uneven current distribution during monitoring. All plots in Fig. 5(a) and (b) except the measurement at 18h drying condition indicated that went further than -45° even during the drying condition. This indicates that the corrosion rate was correctly for the other measurements. In the following experiments, 1Hz was the frequency value chosen to monitor the phase shift in the mid-frequency range.

Fig. 6(a) and (b) show the measurements of corrosion rates, corrosion potentials and phase shifts at 1Hz for a carbon steel in $t=3$ mm mortar which was exposed to same wet-drying condition of Fig. 2.^{5,7,12)} Additionally, the rates of carbon steel, the straight line, under a immersion condition, not a wet-drying condition, were monitored at the same time in Fig. 6(a). The corrosion rates of the steel, measured with 10 mHz, were increased with time, while the carbon steel in mortar under the immersion condition showed the very low

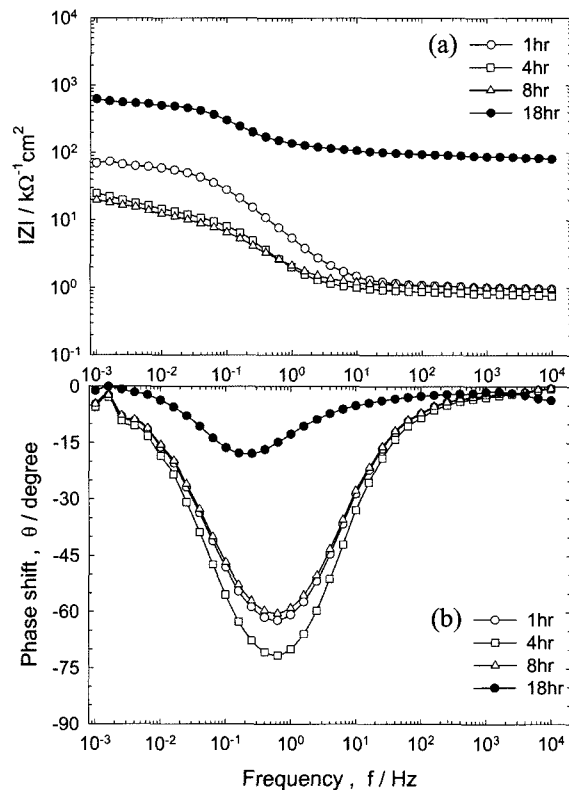


Fig. 5. (a), (b) Typical Bode plots for one cycle for carbon steel in a mortar thickness, $t=3$ mm, under 6 h wetting-18h drying cyclic condition.

rates for whole cycles. The corrosion rates were accelerated during the drying condition. The rates under wet-drying condition were much higher than the immersion condition. The monitoring of phase shifts at 1Hz were done in Fig. 6(b) to observe the onset of inhomogeneous current distribution over the working electrode; i.e. θ goes no further than -45° degrees. If the values under 45° are shown in drying process, it indicates no sufficient water, not existed with C_{dl} , electric double layer, between steel and mortar. The R_p vs. t , E_{cor} vs. t and phase shifts vs. t plots for one cycle can be divided into three regions as shown in Fig. 6(a),(b). The phase shifts at 1Hz in the region of drying up were gone to over -45° . This evidence showed the correct measurements in the region of wetting and drying condition.^{5,7)}

Generally, corrosion rates are accelerated with velocity of oxygen diffusion on an atmospheric condition. Water film thickness decreases very rapidly immediately before drying up. Thus, the presently observed features of corrosion behavior pattern seem to be rationally interpreted in terms of relation between atmospheric corrosion rate and water film thickness proposed by T. Tsuru.⁸⁾ Judging from observed variations for corrosion rate and corrosion potential as shown in Fig. 6(a), the influence of NaCl condensation occurring during drying on corrosion process appeared to be rather insignificant, probably because of the simultaneous occurrence of a decreasing oxygen level and an increasing anodic processing rate alongside NaCl condensation. Therefore in the region of drying condition of Fig. 6(a),(b), with the decreasing water

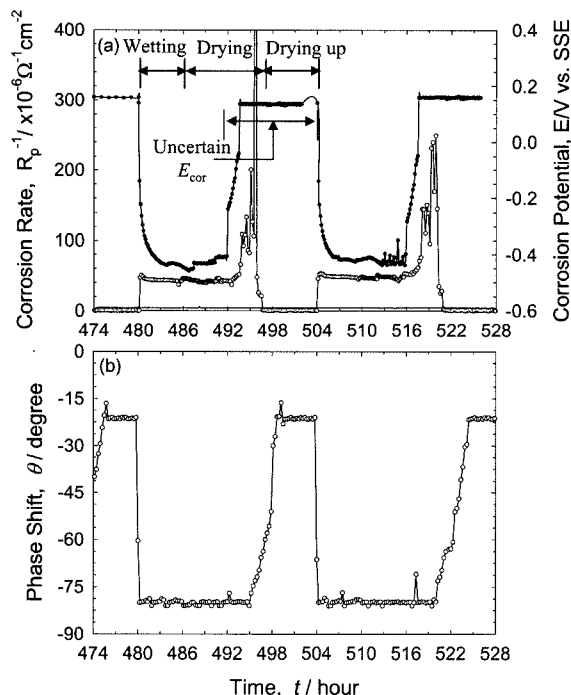


Fig. 6. (a), (b) Monitoring results in 20th and 21th cycles for carbon steel in mortar, (a) corrosion rate (○) and corrosion potential (●) under a wet-drying condition, corrosion rate (—) under immersion condition, (b) phase shift at 1Hz frequency.

film thickness in mortar, the rate of oxygen reduction tends to rise, and correspondingly, the partial cathodic current increases. Conversely, the partial anodic current of Fe dissolution tends to be suppressed with decreasing water film thickness due to diminishing amount of electrolyte solution.^{9,10} As can be seen in Fig. 6(a), corrosion rate of steel in dry process showed a increase by a acceleration of cathodic oxygen reduction, leading to maximum corrosion rate.¹³⁾

Conclusions

From the corrosion monitoring of steel in mortar under wet-drying cyclic condition, the following conclusions were drawn.

1. AC impedance corrosion monitoring is possible under the wet-drying cyclic condition without the errors of inhomogeneous current distribution on the electrode. The different processes of wetting, drying and drying up condition are distinguishable from the monitored impedance data.

2. The carbon steel/mortar interface in the initial stage was represented by an equivalent circuit that consisted of solution resistance, charge transfer resistance, and electric double layer capacitance. From the next stage, the charge transfer resistance tended to decrease and the Warburg impedance

representing an oxygen diffusion in mortar emerged in the low frequency range.

3. The corrosion rate of carbon steel in mortar was accelerated by the wet-dry cycles. Additionally, high corrosion potential was showed as the mortar was dried. From the results, the corrosion rate of steel in mortar was controlled by the velocity of oxygen reduction as the mortar was being dried.

4. Corrosion monitoring with AC impedance method was proved to be feasible under the given atmospheric condition. Additionally, solution resistance determined from the high frequency range would allow a quantitative estimation for chloride penetration level into mortar.

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