Corrosion Monitoring of Reinforcing Bars by Electrochemical Noise Measurement

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ABSTRACT: The electrochemical noise of reinforcing bars embedded in mortar containing NaCl was continuously measured with the aim of developing a technique of monitoring reinforcement corrosion by electrochemical noise measurement. After the measurement, the noise resistance and pitting index were calculated in an attempt to grasp the changes in the corrosion rate and estimate the state of corrosion using these parameters. As a result, it was found that changes in the corrosion rate can be monitored by the noise resistance and that local or uniform corrosion can be judged by the pitting index. These parameters are therefore found applicable as indices for corrosion diagnosis.

1 INTRODUCTION

Simple techniques for inspecting reinforcement corrosion are demanded to carry out adequate maintenance of reinforced concrete structures. Despite the large number of experimental and analytical studies conducted to grasp the state of reinforcement in reinforced concrete structures, techniques for corrosion monitoring without concrete chipping or by embedding sensors are still in the development stage. Though polarization resistance and AC impedance have been employed in conventional electrochemical techniques, it is difficult to non-destructively measure the state of corrosion or obtain constant information about corrosion by these techniques, as the electrical resistance varies depending on the conditions of concrete.

The goal of this study is to establish a method of diagnosing the state of corrosion of steel bars in reinforced concrete in a non-destructive manner. To this end, this study aims to apply the electrochemical noise (EN) method, which has primarily been practiced in the metal industry, to the corrosion analysis of steel bars in reinforced concrete, thereby developing methods of monitoring and detecting reinforcement corrosion at an early stage.

This paper reports on the measurement and analysis of the EN of reinforcement embedded in chloride-laden mortar and comparison between the analysis results and the actual state of corrosion to examine the applicability of the EN method. Experimental and analytical investigation into the effects of various factors on the EN is reported as well.

2 ELECTROCHEMICAL NOISE METHOD

2.1 Electrochemical noise

The EN method is a technique whereby the EN of electrodes exposed to a medium are measured and analyzed to estimate the uniform corrosion rate or sensitivity to localized corrosion of the system. EN refers to a phenomenon in which the average anodic or cathodic current of electrodes vibrates due to the fluctuation of the oxidation-reduction reaction on the surfaces of the electrodes. The phenomenon in which the corrosion potential of electrodes fluctuates due to such current vibration is also referred to as EN. EN observed in a corroded system includes sporadic noise and continuous noise. Sporadic noise results from the initiation/termination of pitting corrosion and the propagation of stress corrosion cracking and is related to non-periodic fluctuation, such as sudden acceleration/deceleration of reaction. Continuous noise represents the information related to slow changes of a corroded system resulting from continuous and small fluctuations or slow and long-lasting fluctuations (Inoue et al. (2005)).

2.2 Measurement of EN

The measurement of EN for monitoring corrosion can be classified into three techniques: measurement of short-circuit current noise, measurement of potential noise, and simultaneous measurement of both. The short-circuit current noise method and the potential noise method are primarily used for estimating the sensitivity to localized corrosion, whereas the simultaneous measurement method is primarily used for estimating the rate of uniform corrosion.

Figure 1 shows a schematic configuration of EN measurement. A counter electrode made of a material equivalent to the working electrode is used for the short-circuit current noise method, with which the vibration component of the short-circuit current between these electrodes is measured using a zero resistance ammeter. The vibration component of the corrosion potential of the working electrode is measured by the potential noise method using a reference electrode and a voltmeter. A pseudo reference electrode made of platinum or titanium may be used for measuring EN, as the reference electrode for EN measurement does not necessarily have to be thermodynamically reversible. The use of pseudo reference electrodes made of platinum, titanium, etc., facilitates the installation and maintenance of electrodes at the job site. The EN method is also advantageous in that it requires no external current during measurement. This facilitates measurement, while allowing adequate measurement even for a system sensitive to electrochemical disturbance (Inoue et al. (2005)).

2.3 Method of analyzing EN data in past studies

The analysis methods for time series EN data obtained from a corroded system are roughly classified into two types: those that statistically analyze EN regardless of the sequence and those that take the sequence into account. Parameters for the sequence-independent methods include the average, scatter, standard deviation, skewness, and kurtosis. The tendencies of the EN are grasped using these parameters to estimate the state of corrosion. When using a statistical technique, noise resistance and pitting index (PI) are generally determined. When taking the sequence into consideration, power spectrum analysis is most commonly practiced. Analysis by autocorrelation functions is also employed. In an analysis using power spectra, EN is converted to power spectrum density for the calculation of noise impedance and analysis using $1/f$ noise (Cottis (2001)).

2.4 Analysis method adopted in this study

2.4.1 Estimation of polarization resistance by noise resistance calculation

In the uniform corrosion rate monitoring using EN, the potential noise and current noise at a working electrode embedded in mortar are simultaneously measured, and the polarization resistance of the working electrode is estimated from the measurements. The corrosion rate, $i_{\text{corr.}}$, which can be estimated by polarization resistance, is defined as:

$$i_{\text{corr.}} = \frac{K}{R_p} \tag{1}$$

where K : Constant determined by metal type and environmental conditions (V),

R_p : Polarization resistance ($\Omega\,\text{cm}^2$).

In EN measurement using three electrodes, it is assumed that the potential noise is exited by the current noise through the impedance at the interface between the working electrode and the medium. It follows that the noise resistance, R_n, is equivalent to the polarization resistance. Noise resistance is defined as:

$$R_n = \frac{\sigma_V}{\sigma_I} \tag{2}$$

where σ_V : Standard deviation of potential noise (V),

σ_I : Standard deviation of current noise (A).

The noise resistance was calculated in this study to grasp the changes in the corrosion rate.

2.4.2 Estimation of corrosion form by pitting index calculation

Pitting index, an index for estimating the form of corrosion, is defined as:

$$\text{PI} = \frac{\sigma_I}{I_{\text{rms}}} \tag{3}$$

where σ_I : Standard deviation of current noise (A),

I_{rms} : Root mean square of coupling current (A).

The initiation of localized corrosion such as pitting corrosion entails relatively large transient current, which increases the standard deviation. The root mean square of coupling current is regarded as mean current, which is the sum of all currents flowing between two electrodes regardless of directions. Current noise is the superposition of localized fluctuations of electrodes.

Table 1 shows a classification of the state of corrosion estimated from PI (Kearns et al. (1996)), which ranges from 0 to 1. The range of $1 > \text{PI} > 0.1$ is regarded as being indicative of localized corrosion of the metal. The range of $0.1 > \text{PI} > 0.01$ indicates coexistence of localized and uniform corrosion. In the range of $0.01 > \text{PI} > 0.001$, the entire metal surface can be regarded as being corroded in a relatively uniform manner. Localized corrosion in this context refers to non-stationary pitting corrosion and minute fissures occurring on metal surfaces. It is microscopic corrosion, whose initiation and termination are triggered by chloride ions breaking the passive film on the surfaces of electrodes.

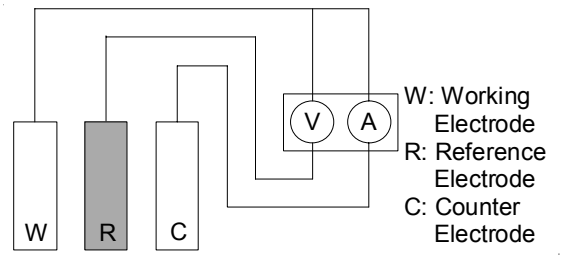

Figure 1. A schematic configuration of EN measurement.

Table 1. A classification of the state of corrosion estimated from PI

Pitting Index Value Range	Type of Corrosion Expected
1 > PI > 0.1	Localized Corrosion
0.1 > PI > 0.01	Mixed Corrosion
0.01 > PI >0.001	Uniform Corrosion

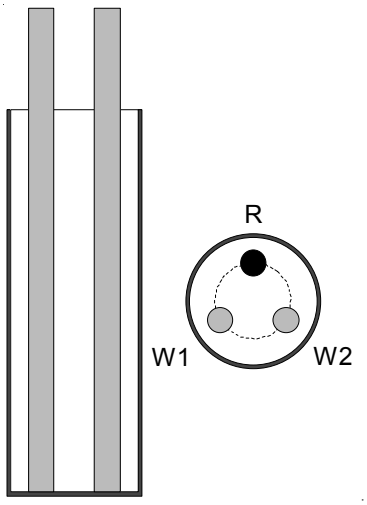

Figure 2. Mortar specimens used for the tests.

Table 2. The mixture proportions of mortar specimens

Series	W/C	W	C	S	NaCl	L1/L2
M60-3-100	60	120	200	400	3	100
M40-3-100	40	80	200	400	3	100
M60-1.5-100	60	120	200	400	1.5	100
M60-3-50	60	120	200	400	3	50

[Notes]

W/C: Water-cement ratio (%), W: Water (g),

C: Cement (g), S: Sand (g), NaCl: Sodium Chloride (g),

L1/L2: The ratio of bar exposure lengths determined by dividing the exposure length of working electrode 1 by that of working electrode 2 (%).

3 MEASUREMENT OF EN

3.1 Outline of experiment

EN was measured to grasp the state of corrosion of reinforcement in mortar.

Figure 2 shows mortar specimens used for the tests. Mortar was placed in cylindrical molds 50 mm in inner diameter and 150 mm in length, with two plain reinforcing bars 10 mm in diameter and 190 mm in length and a carbon bar of the same size being longitudinally arranged at equal intervals at a distance of 15 mm from the central axis of each mold. These bars served as working electrodes 1 and 2 and the reference electrode, respectively. The exposure length of working electrode 1 was in two levels: 60 and 120 mm, whereas that of working electrode 2 was kept constant at 120 mm.

Table 2 gives the mixture proportions of mortar specimens (M series). “L1/L2” in this table denotes the ratio of bar exposure lengths determined by dividing the exposure length of working electrode 1 by that of working electrode 2. The water-cement ratio (W/C) is in two levels: 40% and 60%. The amount of sodium chloride is in two levels: 1.5 g and 3 g. The ratio of bar exposure lengths (L1/L2) is in two levels: 50% and 100%.

The EN under each set of conditions was measured in terms of current noise and potential noise with a sampling period of 0.5 sec in an environment of a room temperature of 20 degrees C and relative humidity of 60%.

3.2 Experiment Result and discussion

After the EN measurement, mortar specimens were cleft to visually examine the state of reinforcement corrosion. No corrosion was visually recognized on working electrode 1 in all cases, while corrosion was observed on working electrode 2. It is therefore found that anodic areas developed on working electrode 2. The corrosion area was greatest in case M60-1.5-100 and smallest in case M40-3-100. In case M60-3-100, the area facing the other working electrode is entirely corroded, whereas no corrosion occurs on the other side. In case M40-3-100, corrosion develops over the upper area. The corrosion of case M60-1.5-100 covers the entire area excepting the lower portion. In case M60-3-50, corrosion develops from the side facing the mold axis around to the back side. In each case, corrosion is not limited to local areas but develops over a wide area. This is because the working electrodes are embedded in mortar. In a highly alkaline environment, even chloride-induced corrosion tends to spread over the steel surface instead of growing into deep pits. In the presence of aggressive anions such as chloride ions, low potential sites on the electrode shift over time. The observed uniform corrosion of working electrodes can be attributed to such shifts, which change the positions of localized corrosion.

The effects of W/C, NaCl amount, and exposure length ratio are discussed as follows: No appreciable difference in the corrosion area was observed between case M60-3-100 with a W/C of 60% and case M40-3-100 with a W/C of 40%. However, the corrosion area of case M60-3-100 containing 3 g of NaCl was evidently smaller than that of M60-1.5-100 containing 1.5 g of NaCl. When compared with case M60-3-50 with a L1/L2 of 50%, the corrosion area of case M60-3-100 with a L1/L2 of 100% was smaller. It is not likely that L1/L2 contributed to the increase in the corrosion area of case M60-3-50, as it was working electrode 2 that corroded, though the exposure length of working electrode 1 was 0.5 times that of working electrode 2.

The current noise and potential noise were measured between working electrodes 1 and 2 and between working electrode 1 and the reference electrode, respectively. The current noise results from the superposition of currents generated by reaction on the surfaces of working electrodes 1 and 2, which excites the potential noise.

The measured current noise and potential noise were plotted on time axes with a sampling period of 10 min. The current noise and potential noise move in synchronization.

Figure 3 shows the effects of NaCl amount on the potential noise-time relationship as an example of potential noise-time relationship. In all cases, the potential becomes less negative for a short period immediately after the beginning of exposure to mortar and then becomes more negative. This is presumably because low potential/active corrosion occurred immediately after the beginning of measurement, which was followed by activation polarization. In an environment where the diffusion of oxygen is restrained and passive film is not retained, reinforcement corrosion can be activated even under highly alkaline conditions, but the rate of corrosion is very low similarly to the passive state. Activation polarization results from the low rate of reaction that proceeds on the electrode surfaces. Also, spikes in the potential noise are recognized in all cases as pointed by arrows in the figure. In regard to the effect of W/C, the potential with a W/C of 60% is less negative than that with a W/C of 40% in the beginning but then becomes more negative. As to the effect of the NaCl amount, the potential approaches zero after the sixth day, being less negative than the values at the early stage. The potential keeps a state of being less negative than the pitting corrosion potential, suggesting that the pitting corrosion proceeds. The potential patterns with L1/L2s of 50% and 100% are nearly the same.

Figure 4 shows enlarged potential noise signals of M60-3-100 including spikes of noise that result from a rapid potential drop followed by slow recovery. All graphs of potential noise-time relationship show these spikes of noise. This type of potential noise is referred to as “rapid drop followed by slow recovery (RD)” noise concomitant with the initiation of localized corrosion

(Itagaki et al. (2004)). The breakage and re-formation of the oxide film cause RD noise. In this process, the breakage of the film is instantaneous, whereas it takes relatively long to re-form the oxide film, as the re-formation reaction competes with the resolution reaction of the electrode, resulting in slow potential recovery. Such RD noise signals superimposed on the spontaneous potential permit detection of the initiation of localized corrosion.

3.3 Analysis Results and discussion

3.3.1 Estimation of polarization resistance based on noise resistance

The standard deviation of potential and current noise of each case was calculated at 60 min intervals to determine the noise resistance. A higher noise resistance represents a lower corrosion rate.

Figure 5 shows the noise resistance-time relationship of M60-3-100 as an example of noise resistance-time relationship. The noise resistance vibrates with large amplitudes at early stages of measurement in all cases. In case M60-3-100, large vibration nearly subsides by the third day, keeping a level around 70 Ω thereafter. In case M40-3-100, the noise resistance level after the seventh day is approximately 80 Ω. In case M60-1.5-100, the noise resistance continues to vibrate without subsiding, keeping the level of approximately 100 Ω. Despite the noise resistance higher than the other cases, the corrosion area of M60-1.5-100 is the largest. This can be attributed to the fact that the noise resistance was higher than the actual polarization resistance under the effect of the solution resistance between the electrodes in an environment with a high solution resistance and low electrical conductivity. In case M60-3-50, the noise resistance keeps vibrating while retaining a level of approximately 50 Ω, which is the lowest of the four cases, suggesting the possibility of the highest corrosion rate.

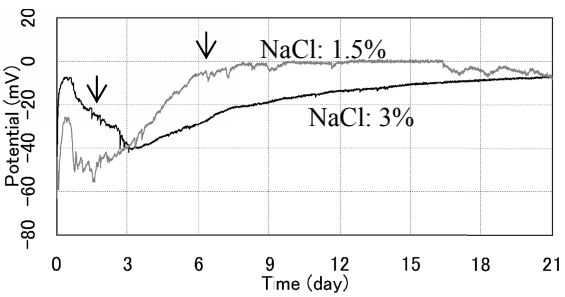

Figure 3. The effects of NaCl amount on the potential noise-time relationship.

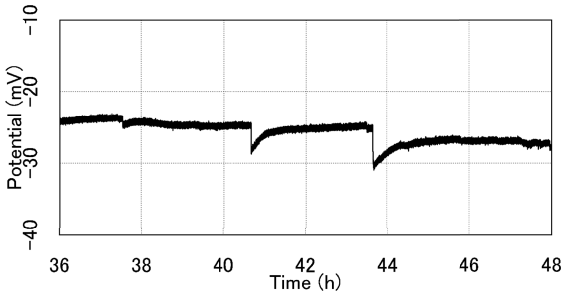

Figure 4. Enlarged potential noise signals of M60-3-100 including spikes of noise.

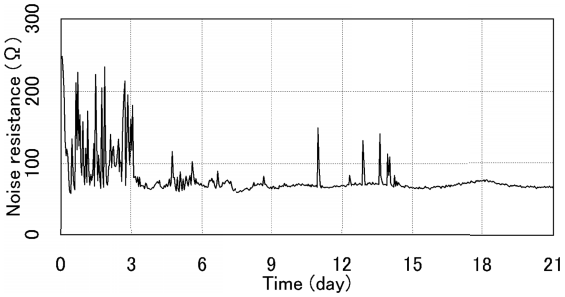

Figure 5. The noise resistance-time relationship (M60-3-100).

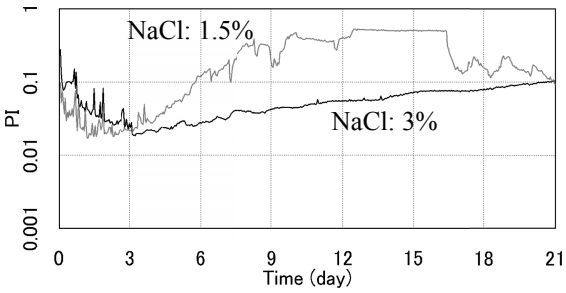

Figure 6. The effects of NaCl amount on the PI-time relationship.

3.3.2 Estimation of the form of corrosion by PI

The pitting index of each case was calculated by determining the standard deviation and root mean square of the measured current noise at 60 min intervals.

Figure 6 shows the effects of NaCl amount on the PI-time relationship as an example of PI-time relationship. The pitting index increases over time in all cases, presumably because corrosion products cover the electrode surfaces, causing localized corrosion to predominate. The PI values with W/Cs of 40% and 60% proceed in a similar manner, but the PI with 60% W/C reaches the level of pitting corrosion at around the twelfth day. In regard to the NaCl amount, the graph with a NaCl amount of 1.5 g suggests significant pitting corrosion after the sixth day. As to L1/L2, the PI values with L1/L2s of 50% and 100% are similar. The calculation of PI thus allows the detection of the initiation of a corrosion process at such an early stage as pitting corrosion and minute fissures on the electrodes that are hardly detectable by visual observation.

4 CONCLUSIONS

Reinforcement corrosion tests were conducted by the EN method to elucidate the effects of various factors on the noise. The applicability of this method was verified by comparison of the analysis results.

1 The initiation of pitting corrosion can be detected from the shape of potential noise referred to as “RD” noise.

2 Changes in the rate of corrosion can be monitored by calculating the noise resistance, as noise resistance can be regarded as being equivalent to polarization resistance.

3 The initiation of localized corrosion on the electrodes and the state of corrosion can be estimated by calculating the pitting index.

The water-cement ratio was found to scarcely affect the corrosion amount and EN. The effect of the amount of NaCl on the probability of the initiation of pitting corrosion should be further investigated. In regard to the exposure length ratio, L1/L2, it is necessary to investigate the case where corrosion occurs on both working electrodes 1 and 2.

In this study, the analysis was conducted after the completion of EN measurement for 21 days. The authors intend to develop a technique of detecting corrosion by real time analysis to discover corrosion at an earlier time.

5 ACKNOWLEDGEMENT

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