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Study on the corrosion behavior of reinforcing steel in cement mortar by electrochemical noise measurements

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Abstract

The corrosion behavior of reinforcing steel in cement mortar has been studied by electrochemical noise (EN) compared with the electrochemical impedance spectroscopy (EIS). The wavelet transform, as well as the statistical methods including the standard deviation of current noise (σ_I) and noise resistance (R_n), has been employed to analyze the EN data of reinforcing steel in mortar. It is revealed that there exist three different corrosion stages of reinforcing steel in cement mortar, including a competition process between breakdown and repassivation of passive film, a pitting development and an active corrosion during the 20 cyclic immersion and drying tests. The energy distribution plot (EDP) is able to provide useful information about the dominant process for the different corrosion stages.

Keywords: Reinforcing steel; Corrosion; EIS; Electrochemical noise; Wavelet transform

1. Introduction

Corrosion of reinforcing steel is a major cause of failure of reinforced concrete structures. Normally, the reinforcing steel is protected from corrosion due to the formation of the passive film on the steel surface in high alkaline concrete. However, the passive film may be destroyed because of carbonatation and/or chloride ingress (from deicing salts or seawater, etc.) during the industrial services. Once the corrosion initiates, it progresses almost steadily and finally causes detrimental effects on the durability of reinforced concrete structures due to the rust formation and/or loss in cross-section of the reinforcing steel.

Reinforced concrete structures exposed to aggressive environments are subjected to the simultaneous action of a number of physical, chemical and electrochemical deterioration processes. However, the corrosion of reinforcing steel in concrete is essentially an electrochemical process. Various electrochemical techniques, such as measurements of half-cell potential, polarization resistance, electrochemical impedance spectroscopy (EIS) [1,2], galvanostatic pulse technique [3,4], etc. have been developed for the detection of corrosion of reinforcing steel embedded in concrete.

The half-cell potential technique described in the ASTM C876 [5] is a simple and rapid electrochemical method, widely used for the inspection of reinforced concrete structures. However, the misleading results may encountered because the measured potential is influenced by a number of factors [6,7]. The half-cell potential mapping [8] is a better way to correlate the measured half-cell potential to corrosion activity of the reinforcing steel. It is able to locate corroding zones precisely and have been applied both in condition assessment and in concrete repair.

The polarization resistance measurements [9–11] are the mostly frequently used methods for quantitative assessment of corrosion rates in concrete. This technique has been applied since 1970s. The fundamentals of this technique are based on the Stern–Geary equation [12]:

$$I_{\text{corr}} = \frac{B}{R_P}, \quad \text{where } B = \frac{\beta_a \beta_c}{2.3(\beta_a + \beta_c)} \tag{1}$$

where R_P is the polarization resistance and β_a and β_c the anodic and cathodic Tafel constants, respectively. The detailed aspects of this technique were described in an international RILEM recommendation ([13] and literatures cited therein). A modified

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method for R_P measurements so-called guard ring technique [14,15] was investigated and established to overcome some limitations of polarization resistance technique.

Electrochemical noise (EN) technique has been widely used to study the corrosion process of various metallic materials, such as metals [16,17] and organic coated metals [18–20], and it can provide useful information about the corrosion mechanism [21–27] through measuring the fluctuations of the current and potential simultaneously generated during the corrosion process. One of the most advantages for electrochemical noise technique is not conducting any disturbing signal, and it is able to avoid the artificial disturbances to the system during the measurement [28]. The sensitivity of EN measurement is much higher than that for the other traditional techniques to the localized corrosion process [29].

Many methods have been developed to analyze the EN data [30] including statistical analysis [31,32], spectral analysis [33–35], and wavelet analysis [28,36,37]. Regarding the statistical methods, the standard deviation of potential or current noise can be calculated at different times to monitor the intensity of a corrosion process. Another widely used parameter is the noise resistance, defined as the ratio of the standard deviations of the potential and current noise. It can represent roughly the resistance of the electrochemical process, and is equal to the polarization resistance under certain conditions. In spectral analysis, the signals are transformed from the time domain into the frequency domain by the faster Fourier transform (FFT) or the maximum entropy method (MEM) and the characteristics of power spectral density (PSD) plots are investigated.

Although these methods are useful for analyzing stationary phenomena, they are difficult to be used for non-stationary signals. Wavelet transform (WT) has been proposed as an alternative tool to overcome the limitations of FFT in the analysis of EN data [28,36]. It can provide the information on transients in time and the possibility of working with non-stationary signals [28,38], and has been used to differentiate corrosion type and to study corrosion mechanism of process [39–41]. Only a few works of EN for studying the corrosion of reinforcing steel in concrete have been reported [42,43]. Legat et al. [43] found that the electrochemical noise technique was able to follow the high corrosion dynamics in concrete, and the measured signals contained certain fluctuations, indicated that the process of corrosion initiation was consisted of a sequence of several events. Their results of the measurements also revealed that the distribution of anodic and cathodic sites may alternate during wetting and drying of concrete. Hu et al. [44] studied the corrosion behavior of reinforced steel in the simulated concrete pore solution by using electrochemical noise, and they analyzed the EN data by discrete wavelet and provided a criterion to determine the threshold value controlling the turning of corrosion state of steel in concrete.

However, the correlation between the specific EN fluctuations and the different stages in corrosion process is not quite clear [43]. And no wavelet transform method has been reported to analyze the EN data for reinforcing steel in concrete. The objective of this present work is to distinguish the different stages of corrosion process of reinforcing steel in cement mortar by the measurements of electrochemical noise, through the analysis of statistical method and wavelet transform in EN data, and the comparison with electrochemical impedance spectroscopy (EIS) measurements.

2. Wavelet analysis: background

The wavelet analysis is a relative new way to analyze signals that overcomes the problems of conventional Fourier analysis. The continuous wavelet transform was proposed by Grossman and Morlet [45] in 1984. Daubechies [46] constructed families of compact supported wavelets. Mallat [47] introduced the multiresolution signal decomposition (MRSD) algorithm. Since then the research in this field has progressed rapidly. The detailed description of the wavelet transform can be found in the dedicated literatures [48–50].

A wavelet is an oscillatory, real or complex function of zero average and finite length. The wavelets approach consists essentially in representing the time record x_n ($n = 1, \ldots, N$), using a linear combination of basis functions $\phi_{j,k}$ and $\psi_{j,k}$, which are generated from the father wavelets ϕ and the mother wavelets ψ through scaling and translation as follows:

$$\phi_{j,k}(t) = 2^{-j/2}\phi(2^{-j}t - k) = 2^{-j/2}\phi\left(\frac{t - 2^j k}{2^j}\right) \quad (2)$$

$$\psi_{j,k}(t) = 2^{-j/2}\psi(2^{-j}t - k) = 2^{-j/2}\psi\left(\frac{t - 2^j k}{2^j}\right) \quad (3)$$

where $k = 1, 2, \ldots, N/2^j$ and $j = 1, 2, \ldots, J$; J is often a small natural number which depends mainly on N and the basis function.

The time signal $x(t)$ can be presented as follows:

$$x(t) \approx \sum_k s_{J,k}\phi_{J,k}(t) + \sum_k d_{J,k}\psi_{J,k}(t) + \sum_k d_{J-1,k}\psi_{J-1,k}(t) + \cdots + \sum_k d_{1,k}\psi_{1,k}(t) \quad (4)$$

where $s_{J,k}, d_{J,k}, \ldots, d_{1,k}$ are the so-called wavelet coefficients.

Discrete wavelet transform (DWT) is used to analyze the EN data, performed by the fast wavelet transform (FWT) algorithm in practice. Filters of different cutoff frequencies (low-pass filter and high-pass filter) are used for the analysis of the signal at different scales. The signal is passed through a series of high-pass filters to collect the high frequency component of the signal (the detail), and through a series of low-pass filters to retain the low frequency component (the smooth). After filtering, the outputs are down-sampling, which consists of deleting one of every two consecutive coefficients of the filtered outputs. At the end, the signal is decomposed into the detail coefficients, $d_1, d_2, \ldots, d_J$ and the smooth coefficients, s_J, containing the information about the local fluctuations and the general trend of the signal, respectively. Each of the sets of coefficients $d_1, d_2, \ldots, d_J$ and s_J is called a crystal.

The scale range of each crystal can be computed roughly from the following equation:

$$(C_1^j, C_2^j) = (2^j\Delta t, 2^{j-1}\Delta t) \quad (5)$$