Investigation of Surface Condition on Electrochemical Behavior of Steel in Alkaline Environments

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In this study, the effects of the surface condition of rebar on its capacitance are investigated. Five rebars with different surface conditions were prepared. The results of ac-impedance experiments on these rebars in saturated calcium hydroxide solution were fitted into an equivalent circuit program. Parameters such as n and Y_0 for Constant Phase Element (CPE), dependent on surface condition, were determined. The frequency dependence of impedance was also compared for rebars with different surface conditions.

INTRODUCTION

Reinforcing steel bars (rebars) in concrete initially have passive surfaces due to their highly alkaline environment. Passivity might be lost locally because of chloride ion ingress or carbonation of the concrete [1]. Corrosion macrocells can then develop with a considerable portion of the cathodic reaction (usually oxygen reduction) taking place on passive steel surfaces [2,3]. The condition that a metal surface possesses (metal finish, presence of mill scale or prior corrosion products) is expected to have an effect on the rate of the cathodic reaction. This effect is important in the long-term deterioration of a structure. In addition, surface condition may strongly influence the apparent interfacial capacity of the rebar surface. Since the apparent interfacial capacitance in concrete tends to be considerably high [4-7], variations in its magnitude can introduce significant changes in the results of electrochemical corrosion rate measurements [6,7]. This, in turn, affects the reliability of diagnostic structural determination tests.

Frequency dispersion will cause the display of an ideally polarizable electrode in the complex plane not to be a vertical straight line. Instead, it will appear as a straight line intersecting the real axis at an angle of less than ninety degrees [8,9].

For a non-polarizable electrode, the impedance representation demonstrates a semicircular arc with its center displaced below the real axis [10,11]. Therefore, a simple resistance-capacitance circuit does not repre-

sent a true ac-response for a rough surface electrode. Consequently, it is necessary to introduce a Constant Phase Element (CPE) whose impedance is in the following form:

$$Z(\omega) = Y_0^{-1}(j\omega)^{-n}, \qquad (1)$$

where u' is angular frequency, $j = -1$, and $0.5 < n < 1$ [12]. Y_0 is a proportionality constant that contains all frequency independent factors including the electrolyte resistance and double layer capacitance. Since a rough surface electrode-electrolyte interface can be considered to have a fractal dimension, D_F, the parameter n, which is an exponent and typically less than one, is related to fractal dimension D_F [13,14] by the following relationship:

$$n = \frac{1}{D_F - 1}. \qquad (2)$$

This investigation sought to obtain additional information on the effect of surface condition on transient electrochemical response of rebar surfaces in concrete.

EXPERIMENTAL PROCEDURES

Sample Preparation

Two types of rebar no. 4 were selected; one was new steel rebar (NS) and the other was a rebar that had been in a highway bridge deck for thirty years (HS). Samples with a length of five inches were cut from straight sections of the rebars. One end of each rebar was drilled and tapped with a 6/32-inch hole without using oil or water. Both ends of the rebars were coated with gray epoxy coating for $1/2''$ (1.27 cm) from the

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bottom and 1.25″ (3.175 cm) from the top leaving a 3.25″ (8.25 cm) length of rebar bare. Different surface roughnesses were produced on the rebars:

1. One rebar of type NS was used as received and rusted (NS-R). The rusting procedure was performed by immersing the rebar in 3.5 percent salt solution for few seconds and placing it in a dry laboratory for a day. This alternating wetting and drying cycle lasted for a week.

2. One rebar of type NS was used as received (NS-AR).

3. One rebar of type HS was used as received (HS-AR).

4. One rebar of type HS was sand blasted (HS-B).

5. One rebar of type HS was sand blasted and rusted (HS-BR) as in rebar 1.

After cleaning with distilled water, these samples were placed in a tank containing saturated calcium hydroxide solution. The potential of the rebars was measured daily with respect to a saturated calomel reference electrode. When the rebars showed a steady potential and passive behavior, Electrochemical Impedance Spectroscopy (EIS) experiments were performed. In the above electrochemical tests, a titanium wire mesh was placed in one side of the tank wall as a counter electrode. A titanium wire was also used as a quasi-reference electrode. To check the reproducibility of the test results, five more rebar samples with the same surface treatments were prepared and the same electrochemical experiments were conducted.

The apparatus used to obtain the EIS measurements has been described elsewhere [15].

RESULTS AND DISCUSSION

Figure 1 shows a plot of potential with respect to time for samples of different surface roughness in saturated calcium hydroxide solution. During the initial days of immersion, the potentials of samples HS-BR and NS-R were more negative than those of the other samples.
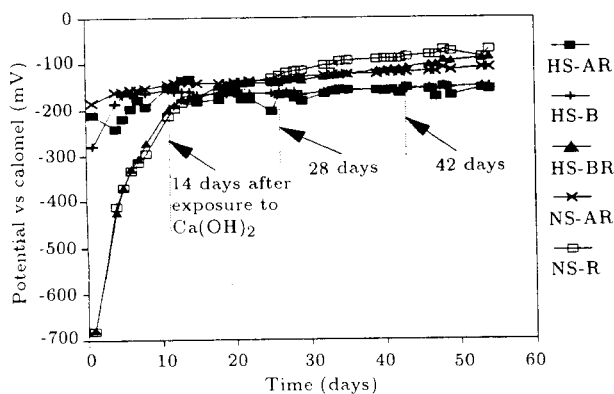
The potential of all samples shifted towards a more positive direction with time and after approximately two weeks, the potentials stabilized, indicating passivity in saturated calcium hydroxide solution. Similar results were observed with the duplicate samples.

Figure 2 illustrates the Nyquist plot obtained from EIS experiments. The depression angle has been defined as $\{(\pi/2) - (\pi/2)n\} = \Theta$ [16] and the data here demonstrates that samples with more surface irregularity, like samples (NS-R) and (HS-BR), have higher depression angles than those with smoother surfaces (see Figure 2). This agrees with the result of Rammelt [17] for iron in H_2SO_4 solution with a pH of 1. The higher the depression angles, the more displacement of the center of the semi-circular complex plane plot below the abscissa is observed [16]. In other words, the diameter of the semicircles not only decreases but the semicircles are more depressed.

When the surface of the rebar is rough, a simple resistance capacitance circuit does not represent an ac response and a non-ideal capacitance with a constant phase element must be taken into consideration. The ac response for the samples in saturated calcium hydroxide solution was modeled as a resistance (R_p) parallel to a Constant Phase Element (CPE) with this sub-circuit in series with the solution resistance (R_s) as shown in Figure 3. The results of EIS experiments were analyzed with equivalent circuit program [18] using the model described above. The values of n and Y_0 in Equation 1 for each sample were determined from this model. A typical Nyquist plot obtained from the above model for sample (HS-B) is shown in Figure 4. This figure indicates that the Nyquist plot for actual data and the simulation obtained from the above model fit quite well. The values of Y_0 were plotted with respect to n values as shown in Figure 5. The results demonstrate that for samples with more surface irregularities and corrosion products, such as samples (NS-R) and (HS-BR), the value of n is lower than that
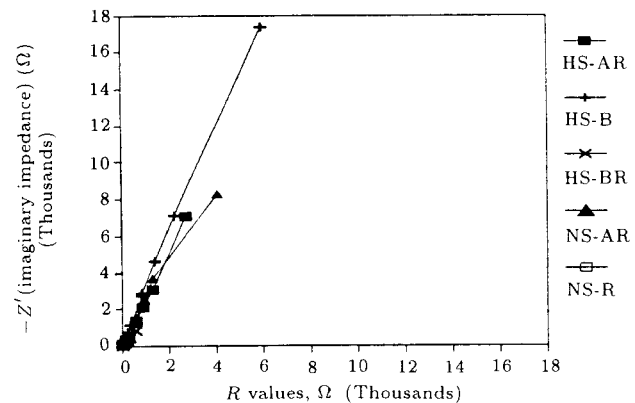

Figure 1. Potential of rebars with different surface conditions with respect to time.

Figure 2. Nyquist plot of different surface conditions of rebar in saturated calcium hydroxide solution.
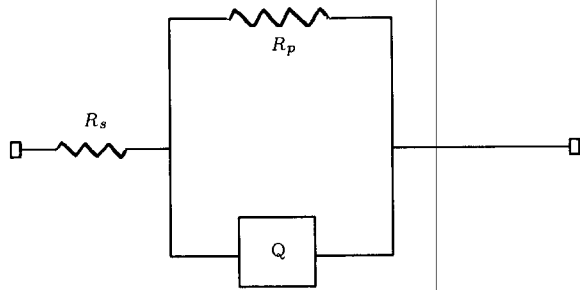
Figure 3. Schematic of equivalent circuit. R_s is the solution resistance; R_p is charge transfer resistance; Q is phase element.
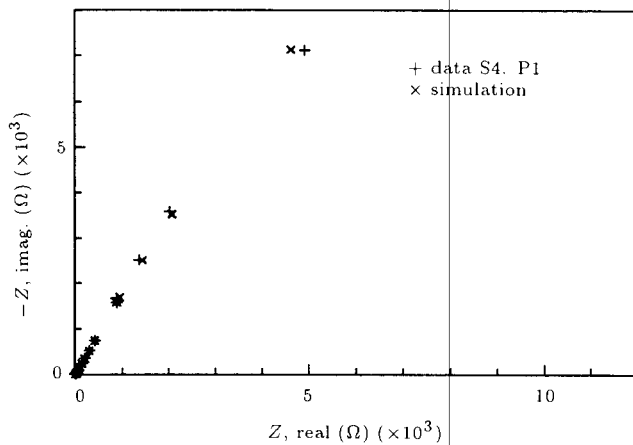

Figure 4. A typical Nyquist plot for sample HS-B from model in Figure 3.

of the other samples. However, the value of Y_0 for surfaces with corrosion product is higher than that of samples with smoother and no corrosion product surfaces. The increase in Y_0 is expected to affect the apparent capacitance of the system because the apparent capacitance is a function of parameter Y_0. Similar results were obtained from duplicate samples.

Furthermore, the dependency of apparent capacitance on parameter Y_0 is illustrated, where an increase in the value of Y_0 will also increase the value of
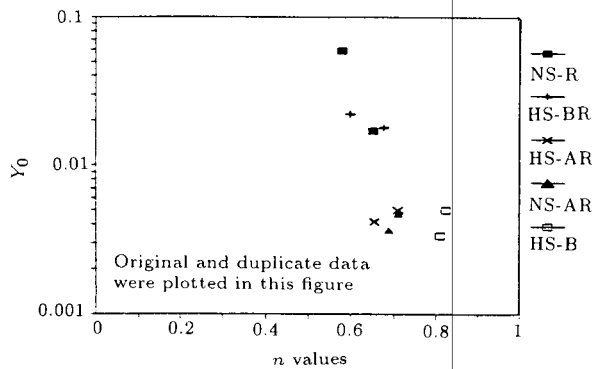

Figure 5. Y_0 with respect to n values.

capacitance. This can be clearly observed in Figure 6, which is a plot of capacitance with respect to Y_0.

Figure 7 is a plot of capacitance with respect to the parameter n. The results in this figure indicate that, as the surface becomes rougher and with corrosion products, the value of apparent capacitance becomes larger and the value of n becomes smaller.

The value of n is directly related to the degree of surface irregularity. When the surface of an electrode becomes smoother, the value of n becomes closer to one. For perfectly smooth surfaces, n becomes one and the fractal dimension, D_F, obtained from Equation 2 becomes two [19]. The experimental data in this paper show that the sample (HS-B) has a smoother surface than the other samples because the value of n for this sample is 0.81 with calculated D_F of 2.2 which is close to two (a value of two corresponds to a perfectly smooth surface). However, the values of n for the samples (HS-BR) and (NS-R) are far from one and have D_F values of 2.6 and 2.7, respectively, indicating that in these two samples, besides the surface irregularity, the reduction of oxide on the surface also plays an important role, as expected.

Nyikos [19] has shown that Y_0 is a function of ρ, C_{dl} and other parameters that are independent of frequency. ρ is the electrolyte resistivity and C_{dl} is double layer capacitance. Therefore, the samples (NS-R) and (HS-BR) which demonstrate the highest
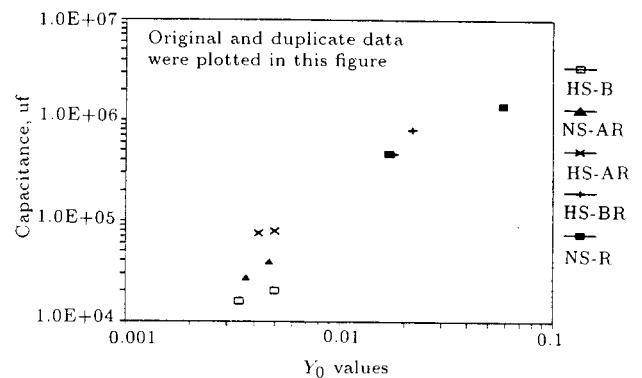

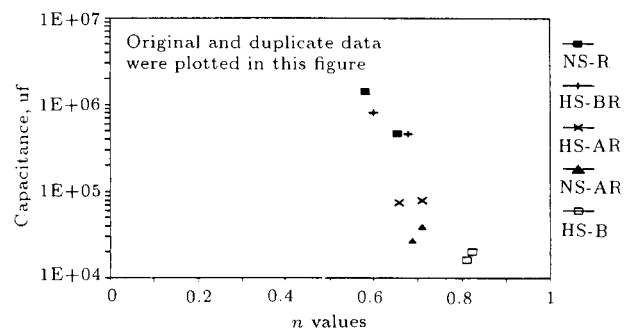**Figure 6.** Capacitance with respect to Y_0.

Figure 7. Capacitance with respect to n values.

values of Y_0 and have the highest surface roughness indicate the highest double layer capacitance compared to samples with less surface roughness and lower values of Y_0. These results are in good agreement with the results presented in Figure 6. The results in this figure demonstrate that the samples (NS-R) and (HS-BR) with the highest surface roughness and corrosion products have the highest values of double layer capacitance and the samples with smoother surfaces and no corrosion products have the lowest values of double layer capacitance.

In addition, the different behavior in frequency dispersion performance observed for the pre-rusted sample could be partly due to the reduction of oxide rather than oxygen in the cathodic reactions of macrocells.

In some other studies conducted with concrete, it is found that the values of double layer capacitance for rebar are high (in the range of 3000 $\mu F/cm^2$), which contradicts the value of 50 to 100 $\mu F/cm^2$ that is expected [20]. This can be understood in the light of the results presented in this paper. The double layer capacitance for even the smoothest sample (HS-B) was in the range of 16000 $\mu F/cm^2$, demonstrating that due to some residual surface irregularity even the sand blasted sample still has high double layer capacitance.

CONCLUSION

1. The surface condition of the rebar in an alkaline media such as concrete has a profound effect on the double layer capacitance between the rebar and its surroundings. With an increase in surface roughness and corrosion products, the capacitance increased tremendously.

2. The impedance of rebar in alkaline media decreased with an increase in the surface roughness of the rebar.

3. The impedance of samples (HS-BR) and (NS-R), with the roughest surfaces and corrosion products, in the alkaline environment, after two weeks of immersion was lower than the impedance taken after four weeks of immersion. There was no change in impedance with time thereafter. The impedance of other samples remained constant with time.

4. A reason for the different frequency dispersion performance observed for the pre-rusted samples may be the reduction of oxide rather than oxygen in the cathodic reactions of macrocells. Therefore, for studying the corrosion kinetics of a rebar in alkaline

environments such as concrete with EIS and other electrochemical techniques, the effects of surface condition on the parameters of the system must be taken into consideration to avoid misinterpretation of the results.

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