Pergamon

Cement and Concrete Research, Vol. 26, No. 8, pp. 1151-1156, 1996

0008-8846/96 $15.00 + .00

PII S0008-8846(96)00110-X

COMMUNICATED PAPERS

CORROSION RESISTANCE OF STAINLESS STEEL IN CHLORIDE CONTAMINATED CONCRETE*

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(Communicated by M. Moranville-Regourd)
(Received May 1, 1996; in final form June 11, 1996)

ABSTRACT:

The results of an investigation of the performance of 2-year-old stainless steel reinforced concrete specimens which were previously placed in an aggressive aqueous solution containing chlorides are presented. This study consisted of corrosion rate testing of reinforced concrete samples with normal reinforcing steel and stainless steel rebars by means of the a.c. impedance spectroscopy. The equivalent circuit simulation analysis method was applied in the data interpretation. The performance and effectiveness of stainless steel in preventing corrosion in chloride contaminated concrete was evaluated.

RÉSUMÉ:

Cette étude présente les résultats d'une analyse de la performance de spécimens de bétons armés d'acier inoxydable, aprés deux ans dans une solution aqueuse contenant desions chlore. L'étude s'intéresse particulièrement le taux de corrosion d'échantillons de béton armé avec des barres en acier au carbone conventionnel et des barres en acier inoxydable. Le taux de corrosion est évalué par spectroscopie d'impédance a.c.. L'interprétation des données utilise la méthode de simulation d'un circuit équivalent. La performance et l'efficacité de l'acier inoxydable, dans la prévention de la corrosion des amatures de bétons contaminés par le chlore, sont évaluées.

Introduction

The Strategic Highway Research Program (SHRP)'s estimate for the unfunded liability to correct corrosion-induced distress in bridges in the United States is about 20 billion dollars.

*This paper was presented at the 1996 Spring Convention, American Concrete Institute, Denver, Colorado, U.S.A., March 14-19, 1996.
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It may increase at the rate of 0.5 billion annually[1]. Life-cycle cost has become a very important factor to construction engineers and repair practitioners and owners of buildings and bridges due to the increase of repair and maintenance expenditures. Much research has been performed to investigate possible solutions to the problem. Some of the remedial measures that have been studied include use of; corrosion-inhibiting admixtures, epoxy coated reinforcing steel, waterproofing membranes, penetrants and sealers, galvanized reinforcing steel, electrochemical removal of chlorides and cathodic protection. However, these methods are secondary measures and some of them have failed to provide satisfactory protection for the steel reinforcement. Recently, a review article by McDonald et al.[2] summarized the investigations of the use of stainless steel reinforcement in concrete as corrosion protection. The corrosion rate of stainless steel is orders of magnitude less than that of black steel in the aggressive environments and chloride tolerance is at least several times higher than the amount necessary to initiate corrosion in black rebar in concrete[3-4]. These characteristics make stainless steel an attractive alternative material to replace the black steel bars for national highway and bridge infrastructure because of the longer service-life and reduced repair and protection expenditures. However, there is a lack of information on the corrosion behavior of stainless steel in concrete. Many questions associated with stainless steel corrosion such as the length of the corrosion initiation period, the corrosion mechanism and volume increment of the corrosion products etc. are still unknown. This investigation was intended to provide additional information on the long-term corrosion resistance of stainless steel as a concrete reinforcement in aggressive environments. This paper presents an evaluation of the first two-years results.

Evaluation of the Corrosion Rate for Reinforced Concrete

Corrosion resistance of the rebar can be estimated through an equivalent circuit simulation analysis of the a.c. impedance spectra (Figure 1a). This equivalent circuit consists of three parallel combinations of a pure resistor and a frequency dependent capacitor. The latter is called a constant phase element, $C = C_o(j\omega)^{-\alpha}$ (C_o is a constant and equal to the capacitance of a pure capacitor), introduced to account for the shape of the depressed complex plot. The three R//C circuits represent the concrete matrix, interface film and steel surface corrosion processes respectively. The impedance of the equivalent circuit is[5] :

$$Z_t = \frac{R_c}{(1+tc(jw)^{1-a1})} + \frac{R_i}{(1+ti(jw)^{1-a2})} + \frac{R_p}{(1+tk(jw)^{1-a3})} \qquad (1)$$

where and $\omega = 2\pi f$, and $j = \sqrt{-1}$. and the $\tau_c = R_cC_c$, $\tau_i = R_iC_i$, $\tau_k = R_pC_{dl}$ are relaxation times, and the term $\alpha(s)$ ($0< \alpha(s) <1$) are constants used to represent the degree of perfection of the capacitor and measures of how far the arc is depressed below the real impedance axis. The RC parameters in equations (1) are described elsewhere[6-11] and they are defined as: R_c and C_c -- the concrete resistance and matrix solid/liquid interface capacitance; R_i and C_i -- steel/concrete interface film resistance and capacitance; and R_p and C_{dl} -- rebar polarization resistance and steel surface double layer capacitance.

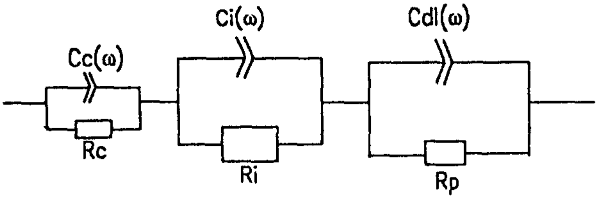

FIG. 1.
The equivalent circuit consisting of three parallel combinations of a pure resistor and a frequency dependent capacitor.

The corrosion current density can be calculated by knowing the polarization resistance, Rp, determined through a computer equivalent circuit simulation and using the Stern-Geary equation as expressed below[12]:

$$I_{corr} = \frac{B}{R_p} \text{and} \qquad B = \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)} \tag{2}$$

where B is a function of the anodic and cathodic Tafel slopes β_a and β_c. A "B" value of 50 mV has been utilized in the calculation for the rebar corrosion[11]. The corrosion rate, C.R. (μm consumption of steel per year) can be computed using Faraday's Law as follows[12]:

$$\text{C.R.}(\ \mu\text{m/year}) = 3.3 I_{corr} M/zd \tag{3}$$

where z = ionic charge (2 for iron), M = atomic weight of metal (56 for iron), d = density of iron, 7.9g/cm^3, and I_{corr}, is in μA/cm^2.

Experimental

The test specimens are concrete cylinders (4"ϕ x 8"long) and the rebar diameters are 0.79" and 0.43" for the stainless steel and black rebars respectively. The specimens were all made from the same basic mix which consisted of 6 kg cement, 3 kg water, 9 kg fine aggregate, and 18 kg coarse aggregate. Table 1 summarizes the additives to each mix where C refers to the control group and SS refers to the stainless steel (Ntronic 33) samples. The samples were

TABLE 1
Composition of Test Samples

Mix	$CaCl_2$ (g)
C1 & SS1	0
C2 & SS2	30 (0.5%)
C3 & SS3	90 (1.5%)
C4 & SS4	270 (4.5%)

kept in an aqueous 3.5 % sodium chloride aerated bath. The SS samples were 25 months old at the time of testing. The C samples were 27 months old.

Test specimens were placed in a tap water bath containing 3.5% sodium chloride. The solution was aerated for at least fifteen minutes prior to testing and throughout the tests. A copper/copper sulphate reference electrode of 1" diameter was used for each test. The counter electrode consisted of a stainless steel cylindrical shell 8"ϕ x 6"long. This type of counter electrode was used to obtain a better current distribution. The a.c. impedance measurements were conducted using a Schulumberger SI 1255 HF Frequency Response Analyzer and a Schulumberger SI 1286 Electrical Interface 273 and associated software (Zplot from Scribner Associates Inc.) to control the test procedures and analyze the data. Three tests were performed on each specimen with at least 15 minutes between consecutive tests on the same sample to allow the reinforcement to depolarize.

Results and Discussion

A typical example of the experimental data simulation using the electrical equivalent circuit is shown in Figure 2. Data are presented in the plots of Real vs. Imaginary (Figures 2a&b), and Phase angle vs. Log(frequency) (Figures 2c) and Log(modulus) vs. Log(frequency) (Figures 2d). The circles represent the experimental data and the solid line is the computer simulation. Only a portion of the concrete matrix arc (Figure 2b) and a tail of an arc associated with steel corrosion (Figure 2a) were observed in the Real vs. Imaginary plot. The appearance of Ri/Ci arc, e.g. the interface film arc, is a result of diffusion of rebar corrosion products into the interface zone which changes the dielectric properties of the steel/concrete interface[6-11]. In the present study, this interface arc was not observed in all the tested specimens (except C4). There is an excellent agreement between the cycles and solid line not only in the Real versus Imaginary plot, but also in phase angle and log (modulus) versus log

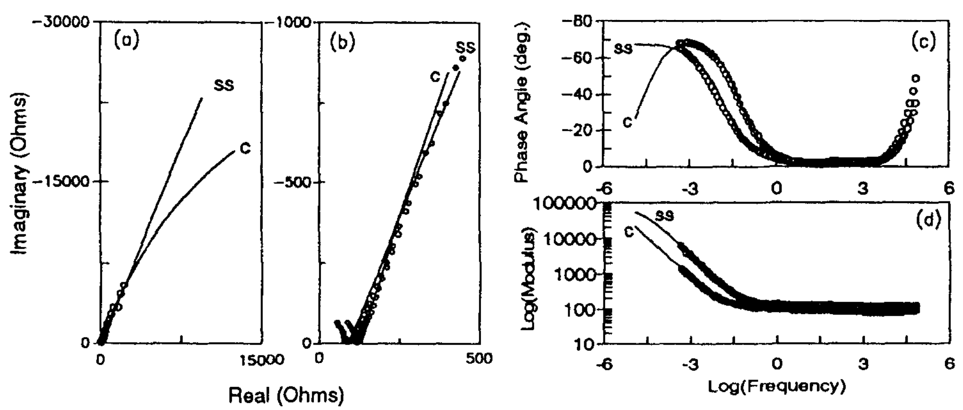

FIG. 2.

A typical impedance spectra and simulation for the stainless and black steel reinforced concrete specimens. (a) Real versus Imaginary plot; (b) enlarged Real versus Imaginary plot; (c) Phase angle vs. Log(frequency) plot and (d) Log(modulus) vs. Log(frequency) plot. The circles represent the experimental data and the solid line is a computer simulation curve. C and SS represent black and stainless steel reinforced concrete specimens respectively

TABLE 2
Parameters From the A.C. Impedance Analysis and Estimated Corrosion Rate

Sample	$R_c(\Omega)$	$C_c(F)$	$R_p(\Omega)$	$C_{dl}(F)$	$1-\alpha_3$	C.R.(μm/year)*
C1	154.8	7.71×10^{-9}	22353	0.0199	0.68	0.37
C2	117.7	1.29×10^{-8}	10764	0.0212	0.70	0.78
C3	95.7	1.69×10^{-8}	1679.4	0.0260	0.53	5.03
C4	56.0	3.81×10^{-8}	435.64	0.0401	0.57	19.4
SS1	102.8	2.09×10^{-8}	$> 10^6$	0.0446	0.69	$< 1.1\times10^{-3}$
SS2	84.0	2.29×10^{-8}	$> 10^6$	0.0567	0.74	$< 1.1\times10^{-3}$
SS3	63.6	3.63×10^{-8}	77841	0.0699	0.80	0.065
SS4	46.4	5.85×10^{-8}	23194	0.0707	0.81	0.22

*The values were calculated using equations (2) and (3).

(frequency) plots. The values of R_p and other RC parameters were determined under this "best-fit" condition and their values are listed in Table 2, columns 2-5.

The concrete resistance, R_c, and concrete matrix capacitance, C_c, are related to the concrete matrix ionic concentration of the pore solution and porosity of the hydrating concrete systems[13]. The simulated R_c and C_c are typical of values reported elsewhere[5]. The steel surface corrosion process normally is represented by a double layer capacitance, C_{dl} and the polarization resistance, R_p, in parallel. A complete arc is hard to obtain due to the time and equipment limitations especially when the measurement at very low frequencies (below 0.01mHz, see Figure 2a&b) is required. However, C_{dl} and R_p can be evaluated using equivalent circuit simulation. The value of R_p decreases significantly with an increase in the amount of pre-mixed chloride. The black steel specimens have much smaller values of R_p especially for those containing a high amount of pre-mixed chloride, indicating poor corrosion resistance. Large values of R_p were obtained from stainless steel specimens representing the high corrosion resistance. Very large values of R_p were obtained from specimens SS1 and SS2 which may be due to the passivation film of stainless steel that controls the corrosion kinetics through a very slow diffusion process.

Table 2 (last column) illustrates the comparison of the corrosion ratesof stainless steel and black steel reinforcements. The values were calculated using "*B*" = 50mV and Rp obtained from the impedance spectra simulations. The values of the corrosion rate of stainless steel specimens obtained using the impedance technique are in agreement with those reported elsewhere[3-4]. The corrosion rate of black rebar reinforced concrete increases significantly as the amount of pre-mixed chlorides exceeds 0.5% (which is about the threshold to induce rebar corrosion[14]). However, the corrosion resistance performance provided by stainless steel reinforcement is excellent, for example, the corrosion rate of SS4, 0.22μm/year, (the specimen contains 4.5% pre-mixed chlorides) is smaller than that of C1, 0.37μm/year, (the specimen contains no pre-mixed chlorides). It appears that the corrosion rate of stainless steel reinforcement is at least 50 times lower than that of black steel in chloride contaminated concrete.

Conclusions

The a.c impedance measurement in the low frequency region provides information related to surface corrosion occurring in reinforced concrete. The rebar corrosion rate can be estimated through the equivalent circuit model simulation analysis. This first two-years evaluation indicated that the corrosion resistance provided by stainless steel is far superior to that provided by black steel.

Acknowledgments

Thanks are due B. Baldock for his help with the experimental apparatus and Professor J. Gartner from Ottawa University, Department of Civil Engineering, for providing the concrete samples.

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