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Estimation of steel corrosion rate in reinforced concrete by means of equivalent circuit fittings of impedance spectra

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National Research Council

Three equivalent circuit models were utilized to fit the alternating current (AC) impedance spectra obtained from the 5-year-old, 'lollipop-like' reinforced concrete samples. The RC parameters obtained from two of the equivalent circuit fittings were compared. Specifically, the differences in polarization resistance, R_p , and double layer capacitance, C_{dl} , were evaluated and the variation in the values of these elements found to be up to 70%. These two parameters were also determined from the fitting of the low-frequency portion of the corresponding impedance spectrum for the third equivalent circuit, and the differences were within 40%. The other RC parameters and their relationship with R_p , were also discussed. Finally, the corrosion rates of the 'lollipop-like' samples, determined from both the AC impedance and linear polarization methods, were compared and the differences in this study found to be about 100%.

Introduction

The alternating current (AC) impedance spectroscopy technique is a powerful method used in determining many of the electrical properties of materials and their interfaces in solid physics. It is also often used to investigate the kinetics of electrochemical reactions, liquid-solid interface properties, metal corrosion and the behaviour of batteries etc. The early literature, for example Cole and Cole¹ and Randles² in the 1940s and Macdonald³ in the 1950s, provides the fundamental basis of the impedance theory and its application. The application of the impedance technique in the study of reinforced concrete was not significant until the early 1980s. Papers by Dawson *et al.*⁴ and John *et al.*⁵ are probably among the earliest, and these were followed by many others.⁶⁻²⁰ These investigations focused on revealing information on the steel-concrete interface behaviour and corrosion rate. Various models based on the use of electrical equivalent circuits were used in the

data interpretation. Qualitative assessment of the rebar corrosion rate was quite successful.¹²⁻¹⁶ A quantitative approach to calculate the rebar corrosion rate was also attempted^{5,6,8} using the Stern-Geary equation.^{21,22} However, the accuracy of such an approach depends significantly on the fitting process from which the corrosion polarization resistance, R_p , is determined, and the value assigned to the term ' B ' (i.e. the Stern-Geary constant).

Determining R_p using AC impedance technique, two main factors should be considered: the validation of the electrical equivalent circuit, which should represent the steel-concrete interface properly and the requirement that each circuit parameter has a corresponding physical meaning. This paper highlights the differences between the RC parameters determined by various equivalent circuit fittings, the differences in corrosion rate determined from AC impedance and linear polarization methods and the relationships between R_p and other RC parameters.

Equivalent circuit models

The equivalent circuit data fitting is common practice in AC impedance spectra interpretation.²³ The

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usefulness of such an approach depends on whether the assigned parameters have the appropriate physical meaning for the actual system studied. Many different equivalent circuits can be similar mathematically; however, only the one that possesses terms having reasonable physical meaning can provide reliable data for sensible interpretation. Many equivalent circuits have been suggested to represent the steel-concrete interface. John *et al.*,⁵ in the early 1980s, proposed an equivalent circuit (Fig. 1(a)) consisting of the elements R_c , C_f , R_f , C_{dl} , R_θ and Z_D . R_c is the concrete resistance, and C_f and R_f are film capacitance and resistance, terms that John *et al.* used to explain the 'spur' observed in the frequency range from 10 KHz to 10 Hz. It was suggested that this was due either to the dielectric properties of a surface film or to the steel-concrete interface. R_θ , C_{dl} and Z_D are transfer resistance, double-layer capacitance and diffusion impedance (or Warburg impedance) of the steel surface. R_θ ($= R_p$) was used in the corrosion rate calculation.

Wenger and Galland,⁶ in the late 1980s, proposed a mortar-lime-layer-metal-pore solution interface model to describe the steel-mortar interface. A corresponding equivalent circuit (Fig. 1(b)) was presented which consisted of mortar resistance, R_0 ; resistive and capacitive properties of the lime precipitation layer, R_1 and C_1 ; the transfer resistance, R_2 , and a double-layer capacitance, C_2 . Instead of a Warburg impedance, Wenger and

Galland⁶ introduced a relaxation process involving an adsorbed intermediate which was represented by R_3 - C_3 . A capacitive component, C_0 , was introduced into the same equivalent circuit later to represent the concrete dielectric properties.⁷ The model attributes a lime-layer precipitation formed on the surface of the steel to the 'spur' indicated in John's work.⁵

Sagoe-Crentsil *et al.*¹² suggested the electrical circuit shown in Fig. 1(c), which consists of three parallel circuits in series, $R_c//C_c$, $R_i//C_i$ and $R_p - Z_D//C_{dl}$, to represent the concrete matrix, the interfacial film, the steel-liquid interface Faradaic process and a diffusion process. It is generally accepted that the physical model of the steel-concrete interface consists of a compact layer of iron oxide (in the passive stage) and an interfacial film adjoined to the concrete matrix.^{6,7,12} The interfacial film consists of $\text{Ca}(\text{OH})_2$ deposits and other cement hydration products formed on the surface of the steel. The change of dielectric constant due to the diffusion of iron oxides into the steel-concrete interface may also be a factor in interfacial behaviour.⁵

Several equivalent circuits have been proposed to describe the different stages of the steel-concrete corrosion process including active or passive corrosion processes involving diffusion control, iron oxide film passivation, localized corrosion, etc.^{9,19} A more complicated model based on the one dimension transmission line analysis was also used to describe corrosion in a large reinforced concrete slab.¹⁷

In this study, three equivalent circuit models (see Fig. 2) were used for the estimation of the polarization resistance, double layer capacitance and other parameters associated with the rebar-concrete interface. The three equivalent circuit models are given below:

Fig. 1. Various equivalent circuits representing the steel-concrete (or cement paste) interface after: (a) John *et al.*; (b) Wenger and Galland; (c) Sagoe-Crentsil *et al.*

Model 1. This equivalent circuit is basically that of Sagoe-Crentsil's,¹² excluding the diffusion process parameter. It consists of three parallel combinations of a pure resistor and a frequency-dependent capacitor to represent the concrete matrix, interface film and the steel surface kinetic process arcs (Fig. 2(a)). This circuit appears to be more logical in describing the proposed physical model by assuming the three combinations are in series. The RC parameters are defined as follows: R_c and C_c are the concrete resistance and matrix capacitance; R_i and C_i the steel-concrete interface film resistance and capacitance; and R_p and C_{dl} the rebar polarization resistance and double layer capacitance.

The total impedance of the equivalent circuit is

$$Z_1 = Z_c + Z_i + Z_k$$

$$= \frac{R_c}{(1 + \tau_c(j\omega)^{1-\alpha_1})} + \frac{R_i}{(1 + \tau_i(j\omega)^{1-\alpha_2})}$$

$$+ \frac{R_p}{(1 + \tau_k(j\omega)^{1-\alpha_3})} \quad (1)$$

Fig. 2. The three electrical equivalent circuits used in the AC impedance spectra fitting. (a) Model 1. (b) Model 2. (c) Model 3

The relaxation times are represented by τ ; α is a constant that reflects the amount of arc depression.

Model 2. This equivalent circuit consists of the concrete matrix R_c/C_c in series with the interface film-steel surface kinetic process circuit in which R_p/C_{dl} is in series with R_i , then in parallel with C_i (Fig. 2(b)). This equivalent circuit (without the solution dielectric element C_c) is often used in an electrochemical system involving adsorbed intermediates; however, it may not represent the steel-concrete interface as well as model 1. The RC parameters are again defined as follows: R_c and C_c are the concrete resistance and matrix liquid-solid interface capacitance; R_i is the steel-concrete interface film resistance and C_i is a corresponding capacitance; R_p and C_{dl} are the rebar polarization resistance and double-layer capacitance. The total impedance of the equivalent circuit is

$$Z_t = Z_c + Z_{i-k} \\ = \frac{R_c}{(1 + \tau_c(j\omega)^{1-\alpha_1})} + \left[\left(R_i + \frac{R_p}{(1 + \tau_k(j\omega)^{1-\alpha_3})} \right)^{-1} + C_i(j\omega)^{1-\alpha_2} \right]^{-1} \quad (2)$$

Model 3. This model is a R_p/C_{dl} circuit (Fig. 2(c)) used to fit only a portion of the impedance spectrum that is associated with the steel corrosion process. The values of R_p , C_{dl} and α_3 are estimated through the

fitting of the low-frequency portion of the spectrum. This approach has the advantage of being simple. The entire impedance is equal to

$$Z_t = R' + \frac{R_p}{(1 + \tau_k(j\omega)^{1-\alpha_3})} \quad (3)$$

where $\tau_c = R_c C_c$, $\tau_i = R_i C_i$ and $\tau_k = R_p C_{dl}$ are relaxation times, and α_i ($0 < \alpha_i < 1$) are constants as defined above. The term R' is a constant (ideally, it is equal to the sum of R_c and R_i). The capacitive terms expressed in equations (1)–(3) are frequency-dependent elements.^{1,24}

It should be noted that there are a few simplifications associated with the above equivalent circuit fitting process. The diffusion process (involving use of the Warburg impedance, Z_D), that usually is the controlling step in the low-frequency measurement is not considered. Points, showing a 45° straight line at very low frequencies, were omitted to reduce the error introduced by such a process. The term 'interfacial film' is used to describe an interfacial zone or layer formed on the steel surface (similar to the aggregate-cement paste transition zone). The microstructure of such a layer is quite different from that of concrete matrix, and its impedance properties are affected by cement hydration products deposited in the layer and/or corrosion products of steel diffused into the layer. The fitted values of R_p and C_{dl} represent 'overall conditions' of the surface steel corrosion and the R_p value does not identify the passive or active corrosion areas even though the latter has the major contribution to the measured R_p . The value of C_{dl} is not a true double layer capacitance and may include pseudo-capacitance due to the presence of various ions.¹⁰ Regardless of the deficiencies, the fitting process of the equivalent circuit still provides a reasonable approximation for this study.

Estimation of corrosion current density

The corrosion current density is estimated through the polarization resistance, R_p , obtained in the equivalent circuit fitting of the experimental impedance spectra. This approach is useful, especially at very low frequencies when data are difficult to obtain experimentally due to time or equipment limitations. Corrosion current density is estimated using the Stern-Geary equation as expressed below and the value of R_p obtained from the impedance spectra fitting process:²¹

$$I_{\text{corr}} = \frac{B}{R_p} \quad (4)$$

where B is a function of the anodic and cathodic Tafel slopes, b_a and b_c ($B = b_a b_c / 2.303(b_a + b_c)$). It can be determined by a mass loss experiment.^{5,6,8} Values between 13 and 52 mV were used. For example, 50 mV was used by John *et al.*⁵ and 35 mV by Wenger and Galland.⁶ Andrade⁸ suggested a value of 26 or 52 mV

to be utilized in the calculation for the bare steel in the active and passive stages, respectively. The calculated R_p may have an inherent error of about two times since the B constant varies between 13 and 52 mV.^{8,25}

Experimental

Sample preparation and experimental set-up

Nine concrete specimens containing 0–4% chloride ions and 5% (percentages are based on mass of cement) of the various corrosion inhibitors were made (Table 1). Type 10 Portland cement was used for all the specimens. The cement:sand:aggregate ratio (by mass) was 1:2:3, and a water/cement ratio of 0.5 was used. The concrete mix composition including additives is given elsewhere.²⁶ The 'lollipop-like' specimen fabrication configuration is shown in Fig. 3. Black steel reinforcing bars (1.27 cm $\phi \times$ 14 cm long) were sand blasted prior to use. Both ends of the rebar were sealed with silicone. Only the middle section (7 cm) of the bar was left exposed to the concrete. The exposed rebar area was approximately 28 cm². Specimens were moist cured for 7 days or more before they were placed in a 3.4% (by mass of cement) sodium chloride solution. The solution was aerated for at least 15 min prior to testing and throughout the tests. A copper/copper sulfate reference electrode of diameter about 2.54 cm was used for each test. The counter electrode consisted of a stainless steel cylindrical shell (20 cm in height and 10 cm in diameter) to ensure a symmetric current distribution during the measurement.

AC impedance

A small sinusoidal voltage signal of 20 mV was applied over the range of frequencies 75 kHz to 0.5 mHz. The current resulting from this voltage perturbation was measured as well as the phase shift of the current and voltage characteristics. A three-electrode configuration was used with the reference electrode shorted to the working electrode. These tests were done using an SI 1255 HF Frequency Response Analyzer and an SI 1286 Electrical Interface and the associated

software (Zplot) to control the test procedures and analyse the data.

Linear polarization

Tests were conducted using a Potentiostat/Galvanostat and an associated software package to control the test procedures and analyse the data. Polarization experiments were performed at a scan rate of 0.1 mV/s (ASTM G59 recommends a scan rate of <0.167 mV/s). They were initiated at 20 mV below the corrosion potential and terminated at a maximum of 20 mV above the corrosion potential. The duration of each test was between 6 and 7 min. Three tests were performed on each specimen with at least 15 min between consecutive tests on the same sample to allow the reinforcement to depolarize. The polarization resistance was corrected for the IR drop ($R_p = \Delta V / (I_{\text{measured}} - R_c)$), using the concrete resistance obtained in impedance measurement (Table 1).

Results and discussion

The following discussion includes: (a) a comparison of the differences of the RC parameters obtained from the fitting of three electrical equivalent circuits; (b) comment on the relationship between R_p and other RC parameters; and (c) a comparison of the differences of the corrosion rate values determined from AC impedance and linear polarization techniques.

Impedance spectra fitting

Typical examples of the experimental data fitting using the electrical equivalent circuit models 1, 2 and 3 are shown in Figs 4–6, respectively. Data are presented in the plots of real versus imaginary (Figs 4(a)–6(a)), and Bode plots, such as phase angle versus log(frequency) (Figs 4(b)–6(b)) and log(modulus) versus log(frequency) (Figs 4(c)–6(c)). The circles represent the experimental data, and the solid lines the computer fitting results. Three arcs or partial arcs were observed in the real versus imaginary plot. These arcs represent the concrete matrix, the steel–concrete interface film and steel surface corrosion process effects starting from high frequencies to low. Very good agreement was obtained between the circles and the solid line as can be seen in Figs 4–5. This is not only for the real versus imaginary plot but also for phase angle and modulus $|Z|$ versus log(frequency) plots using models 1 and 2. Very good agreement was also obtained in the low-frequency region using model 3 (Fig. 6). The values of R_p and other RC parameters were determined using this 'best-fit' condition, and their values are listed in Table 2.

Comparison of RC parameters determined using different equivalent circuits

Concrete matrix resistance, R_c and capacitance, C_c . These two parameters are related to the physical

Table 1. Specimen mix conditions

Specimen	% NaCl (mass of cement)	% inhibitor (mass of cement)
A1	0	0
A2	2	0
A3	4	0
B1	0	5 (sodium nitrite)
B2	2	5 (sodium nitrite)
B3	4	5 (sodium nitrite)
C1	0	5 (dinitrobenzoic acid)
C2	2	5 (dinitrobenzoic acid)
C3	4	5 (dinitrobenzoic acid)

Fig. 3. A schematic diagram of a typical concrete test specimen

properties of the concrete matrix. The concrete resistance, R_c , depends on the microstructure or porosity and ionic conductivity of the pore solution of the concrete.^{27,28} The concrete capacitance, C_c , is associated with dielectric properties of the concrete. The $R_c//C_c$ circuit is involved in both the equivalent circuit models 1 and 2. The values of these two parameters from the fittings should be very close. It appears true for the values of R_c as indicated in Fig. 7, the plot of R_c , model 1 versus model 2. A good correlation was obtained. The values of C_c obtained from both the fittings are in the nanofarad range. However, the correlation is not as good as that for R_c .

Interface film resistance, R_i , and capacitance, C_i . R_i and C_i are parameters associated with the steel-concrete interface film properties.¹² This film is a layer characterized by solid precipitation of cement hydration products that deposit on the surface of the steel bars. It has been reported that the arc in the real versus imaginary plot was not observed in the freshly made and non-corroded reinforced concrete or steel in calcium hydroxide solution.^{5,7} This layer is distinguished from the concrete matrix because of its dielectric changes when significant steel corrosion has taken place. The different arrangement of R_i and C_i in the models 1 and 2 accounts for the discrepancy between their corresponding fitted values. The values of C_i (in nF) obtained from the model 2 fitting are 2–3 orders of magnitude smaller than those of the values obtained from model 1 (in μ F) (see column 6 in Table 1). It appears the values from model 1 may represent

the steel-concrete interface better. The R_i values, however, seem to be in closer agreement than those of the C_i , as shown in Fig. 8.

Polarization resistance, R_p and double-layer capacitance, C_{dl} . The steel surface corrosion process in reinforced concrete is normally represented by a double-layer capacitance, C_{dl} and the polarization resistance, R_p , in parallel. The impedance response of the steel corrosion process arises at very low frequencies. This makes data difficult to obtain due to the time and equipment limitations. However, C_{dl} and R_p can be easily obtained from the equivalent circuit fitting. Figs 9(a) and 10(a) show the comparison of the values R_p and C_{dl} obtained from the fittings using models 1 and 2, respectively. The fitted values of R_p and C_{dl} are reasonably close (except for one point, specimen B1) regardless of the difference of the equivalent circuit models. The largest difference is about 70% for R_p and 37% for C_{dl} using values from model 1 as the basis for comparison (Table 3). A simple equivalent circuit model, such as the Randles circuit, was applied to fitting only a portion of the impedance spectrum. The R_p and C_{dl} values were plotted against the corresponding values obtained using model 1 (Figs 9(b) and 10(b)). Similar values were obtained and the largest differences are about 36% for R_p and 32% for C_{dl} (Table 3). The partial fitting of the impedance spectrum provided acceptable results of R_p and C_{dl} evaluation for the samples studied.

Dispersion angle, α . The term α is introduced in

Fig. 4. An impedance spectrum for a mild steel reinforced concrete specimen (A1, Table 1) and the corresponding fitting using model 1. (a) Real impedance versus imaginary impedance plot; (b) phase angle versus log(frequency) plot and (c) log(modulus) versus log(frequency) plot. The circles represent the experimental data and the solid line is a computer-fitting curve

Fig. 5. An impedance spectrum for a mild steel reinforced concrete specimen (A1, Table 1) and the corresponding fitting using model 2. (a) Real impedance versus imaginary impedance plot; (b) phase angle versus log(frequency) plot and (c) log(modulus) versus log(frequency) plot. The circles represent the experimental data and the solid line is a computer-fitting curve

Fig. 6. An impedance spectrum for a mild steel reinforced concrete specimen (A1, Table 1) and the corresponding fitting using model 3. (a) Real impedance versus imaginary impedance plot; (b) phase angle versus log(frequency) plot and (c) log(modulus) versus log(frequency) plot. The circles represent the experimental data and the solid line is a computer-fitting curve

the equivalent circuit to account for the dispersion of the impedance arc. The α_3 value is of particular interest since it provides information related to reinforced concrete corrosion. The fitted α_3 values (listed in the last column of Table 1) show little variation using the three equivalent circuit fittings (model 1 versus 2 and 3) as indicated in Fig. 11(a) and 11(b).

The relationship between R_p and other fitted parameters

The above comparisons have demonstrated that a 'best fit' can almost always be achieved using more than one model. Therefore, the equivalent circuit that represents the physical model well is important in order to provide a more reliable and realistic interpretation of the data. Using the series arrangement (model 1) as an example, the following sections demonstrate the relationship between R_p (since it represents the corrosion resistance both quantitatively and qualitatively) and other parameters, that is, R_i , C_i , C_{dl} , α_3 and phase angle shift, in characterizing the steel corrosion.

Interface film resistance, R_i , and capacitance; and C_i . R_i and C_i are associated with the steel-concrete interface film, which is distinguished from the concrete matrix because of its dielectric changes when significant steel corrosion takes place. This change is due to many factors including the diffusion of corrosion products into the steel-concrete interfacial zone and the filling up of the pores as well as some chemical reactions between the steel corrosion products and cement hydrates. In these situations the change of the electrical properties in this zone is indicated by the appearance of the second arc in the kilohertz frequency range of the impedance spectrum. The detectable values of R_i and C_i therefore may reveal a certain amount of accumulation of steel corrosion products at the steel-concrete interface. Plots of R_i and C_i versus R_p are given in Figs 12 and 13, respectively, to examine their relationship with R_p . There is no simple correlation between R_i and R_p since R_i is dependent on the thickness and conductivity of the interface layer, both of which are highly variable and hard to define. However, C_i appears to have a logarithmic relation with R_p , and it may reflect the severity of steel corrosion in concrete, especially in a semi-quantitative way.

Double-layer capacitance, C_{dl} . The formation of double-layer capacitance, C_{dl} , is due to the existence of a boundary between the electrode and concrete matrix. This is the structural basis of the potential difference across the interphase and results in the charge alignment at both the concrete (with its electrolyte) and electrode surfaces. A 'pure' double-layer capacitance is normally $\sim 40\text{--}60 \mu\text{F}/\text{cm}^2$ for a non-corroded surface. However, it tends to increase as the steel corrosion propagates. This may be explained by the increase of surface area and roughness as

Table 2. RC Parameters determined in the impedance spectra fitting using various models

Sample	$R_c: \Omega$	$C_c: \text{nF}$	$1 - \alpha_1$	$R_l: \Omega$	$C_l: \mu\text{F}$	$1 - \alpha_2$	$R_p: \Omega$	$C_{dl}: \text{mF}$	$1 - \alpha_3$
Model 1									
A1	315	2.03	0.95	243	146	0.47	6894	21.9	0.6
A2	190	4.55	0.99	139	135	0.57	3313	5.96	0.43
A3	110	1.24	1.0	156	649	0.37	1406	55.5	0.57
B1	500	7.41	0.80	320	148	0.43	11459	4.56	0.74
B2	275	1.62	0.99	368	150	0.49	3680	7.76	0.51
B3	150	4.14	1.0	224	165	0.52	6181	4.45	0.51
C1	247	36.2	0.80	242	116	0.54	8339	9.76	0.57
C3	80	0.96	1.0	264	349	0.36	1224	23.0	0.47
Model 2									
A1	287	0.078	1.0	390	0.326	0.39	6607	23.4	0.62
A2	193	5.91	0.97	133	267	0.62	5241	5.72	0.40
A3	107	0.809	1.0	186	1.70	0.38	883.5	76.0	0.66
B1	471	0.635	0.98	418	0.025	0.34	19303	4.52	0.79
B2	285	22.3	0.81	315	37.9	0.53	5591	5.50	0.45
B3	149	3.65	1.0	240	48.2	0.52	6196	4.29	0.51
C1	237	10.29	0.89	201	24.4	0.51	8273	9.69	0.57
C3	95	17.6	1.0	231	2.55	0.41	1620	16.7	0.40
Model 3									
A1	—	—	—	—	—	—	6415	23.7	0.61
A2	—	—	—	—	—	—	4139	5.65	0.41
A3	—	—	—	—	—	—	904	73.5	0.65
B1	—	—	—	—	—	—	14006	4.84	0.76
B2	—	—	—	—	—	—	4379	6.77	0.50
B3	—	—	—	—	—	—	7108	4.16	0.49
C1	—	—	—	—	—	—	8652	9.44	0.56
C3	—	—	—	—	—	—	1472	16.9	0.41

Fig. 7. Plot of R_c , model 1 versus model 2 Δ , control concrete; $\diamond$, concrete containing 5% sodium nitrite; $\circ$, concrete containing 5% dinitrobenzoic acid by mass of cement

Fig. 8. Plot of R_l , model 1 versus model 2 Δ , control concrete; $\diamond$, concrete containing 5% sodium nitrite; $\circ$, concrete containing 5% dinitrobenzoic acid by mass of cement

Fig. 9. (a) Plot of R_p , model 1 versus model 2 and (b) model 1 versus model 3 Δ , control concrete; $\diamond$, concrete containing 5% sodium nitrite; $\circ$, concrete containing 5% dinitrobenzoic acid by mass of cement

Fig. 10. (a) Plot of C_{dl} , model 1 versus model 2 and (b) model 1 versus model 3 Δ , control concrete; $\diamond$, concrete containing 5% sodium nitrite; $\circ$, concrete containing 5% dinitrobenzoic acid by mass of cement

corrosion reactions take place. Fig. 14 illustrates the relation between C_{dl} and R_p . There is a trend indicating that a larger C_{dl} may correspond to more corrosion activities. This is, however, a rather weak indication. Adsorption of corrosion products, increase of surface area and roughness may also lead to an increase of apparent C_{dl} if the geometrical area normalization is applied. Also, adsorption of other chemicals may result in a high value of C_{dl} . There-

fore, C_{dl} is not an ideal indicator for steel surface corrosion in reinforced concrete.

Dispersion angle, α_3 . Normally, the impedance spectrum plotted in a complex plane is an inclined semi-circle with its centre depressed below the real axis by an angle $\alpha\pi/2$. This behaviour is associated with a spread of relaxation times and can be described by a disperse, frequency-dependent capacitor defined as: $C = C_0(j\omega)^{-\alpha}$, where C_0 is a constant representing the

Table 3. Differences between R_p and C_{dl} values determined from each of the three equivalent circuits

Sample	Percentage (%) = $100 \times (M_1 - M_2)/M_1$		Percentage (%) = $100 \times (M_1 - M_3)/M_1$	
	R_p	C_{dl}	R_p	C_{dl}
A1	4.16	-7.09	6.95	-8.22
A2	-58.19	4.03	-24.93	5.20
A3	37.16	-36.94	35.70	-32.43
B1	-68.45	0.74	-22.22	-6.14
B2	-51.93	29.12	-18.99	12.76
B3	-0.25	3.59	-14.99	6.52
C1	0.79	0.72	-3.75	3.28
C3	-32.35	27.39	-20.26	26.52

(a)

(b)

Fig. 11. (a) Plot of α_3 , model 1 versus model 2 and (b) model 1 versus model 3 Δ , control concrete; $\diamond$, concrete containing 5% sodium nitrite; $\circ$, concrete containing 5% dinitrobenzoic acid by mass of cement

capacitance of a pure capacitor, and $\omega = 2\pi f$, and $j = \sqrt{-1}$. The element $-\alpha$ is introduced in the equivalent circuit to account for the dispersion of the impedance arc. In this study, the α_3 value is of the particular interest since it provides information related to reinforced concrete corrosion. It has been suggested that the depression angle, $\alpha_3\pi/2$, be used to characterize the severity of corrosion.¹⁴ A large depression angle is often associated with severe rebar corrosion activity. Fig. 15 is a plot of $1 - \alpha_3$ versus R_p . A linear relation was obtained which appears to agree with other results.¹⁴ It is suggested that the depression angle not be used alone in characterizing the severity of rebar corrosion since its value only varies in a very narrow range (0–1). Any error introduced in the fitting process may lead to an incorrect conclusion.

Phase angle shift. Phase angle shift in the low-frequency range (less than 0.1 Hz) is often used to characterize the steel surface corrosion situation. For example, a decrease of the maximum phase angle of the steel surface kinetic arc has been used to describe the degree of surface corrosion of steel by Mansfeld.^{29,30} In this study the maximum phase angle shift data was obtained experimentally or determined by fitting in the case where there was insufficient data. Reduction of surface corrosion resistance results in the reduction of the maximum phase angle shift. Fig. 16 is a plot of the maximum phase angle shift versus R_p . It is not surprising that a linear relation was obtained. The phase angle shift is sensitive to steel rebar surface corrosion.

Estimation of corrosion current density

The corrosion current density was calculated by using the Stern–Geary relation (equation (4)). A 'B' value of 26 mV for active corrosion²⁵ and R_p values obtained from the impedance spectra fitting using the three equivalent circuits were applied in the calculation. A graphical comparison of the I_{corr} values, in a log–log plot with the corrosion current density determined by linear polarization measurements is presented in Fig. 17. The dashed line represents the line of equality. Numerical numbers are given in Table 3. The first column is the I_{corr} values measured using the linear polarization method. Columns 2–4 are the I_{corr} values calculated using R_p from the curve fittings. The differences in per cent (columns 5–7, Table 4) show a large variation (up to 106% in this study). They are considered acceptable in this study since the 'B' value has an inherent error of up to 2.^{21,25}

Concluding remarks

In this study of 5-year-old 'lollipop' samples, there is only a small variation in the values of the elements associated with the corrosion process using different equivalent circuit fittings. The empirical relation

Fig. 12. A plot of film resistance, R_i , versus polarization resistance, R_p . RC parameters were obtained by fitting model 1

Fig. 13. A plot of film capacitance, C_i , versus polarization resistance, R_p . RC parameters were obtained by fitting model 1

Fig. 14. A plot of double-layer capacitance, C_{dl} , versus polarization resistance, R_p . RC parameters were obtained by fitting model 1

Fig. 15. A plot of depression angle ($1 - \alpha_3$) versus polarization resistance, R_p . RC parameters were obtained by fitting model 1

Fig. 16. A plot of maximum phase angle shift versus polarization resistance, R_p . RC parameters were obtained by fitting model 1

Fig. 17. A log-log plot of the corrosion current density of steel reinforced concrete specimens determined by the linear polarization method (LPM) and AC impedance spectroscopy (ACIS)

Table 4. I_{corr} ($\mu\text{A}/\text{cm}^2$) values determined from AC impedance spectra based on RC models (using $B = 26 \text{ mV}$) and linear polarization method (LPM) and variations ($\% = 100 \times (I_{corr}(\text{LPM}) - I_{corr}(\text{ACIS}))/I_{corr}(\text{LPM})$)

Samples	I_{corr} (LPM): $\mu\text{A}/\text{cm}^2$	I_{corr} (model 1): $\mu\text{A}/\text{cm}^2$	I_{corr} (model 2): $\mu\text{A}/\text{cm}^2$	I_{corr} (model 3): $\mu\text{A}/\text{cm}^2$	Variation (model 1): %	Variation (model 2): %	Variation (model 3): %
A1	0.221	0.134	0.140	0.145	39.07	6.42	34.52
A2	0.145	0.280	0.177	0.224	-93.77	-22.49	-55.10
A3	0.951	0.660	1.051	1.027	30.58	-10.46	-7.96
B1	0.040	0.081	0.048	0.066	-102.58	-20.26	-65.74
B2	0.122	0.252	0.166	0.212	-105.98	-35.58	-73.10
B3	0.099	0.150	0.150	0.131	-51.31	-50.93	-31.58
C1	0.200	0.111	0.112	0.107	44.32	43.88	46.34
C3	0.708	0.758	0.573	0.631	-7.17	19.02	10.88

between R_p and other parameters such as the steel-concrete interface film resistance and capacitance, double layer capacitance, depression angle and phase angle shift indicated that these parameters may only be used to characterize qualitatively the severity of rebar corrosion of the studied samples.

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