JOURNAL OF APPLIED ELECTROCHEMISTRY **26** (1996) 305–309

Multiple-electrode method for estimating the polarization resistance in large structures

S. FELIU, J. A. GONZÁLEZ

Centro Nacional de Investigaciones Metalúrgicas, CSIC, Avda. Gregorio del Amo, 8, 28040 Madrid, Spain

C. ANDRADE

Instituto de Ciencias de la Construcción Eduardo Torroja, c/Serrano Galvache s/n, 28033 Madrid, Spain

Received 9 March 1995; revised 29 June 1995

A new method for estimating the polarization resistance and the corrosion current from the Stern–Geary equation in cases where the applied signal distributes unevenly over a large real structure acting as working electrode is proposed. In addition to measurements of the current response to an applied potential pulse, the new method takes into account the distribution of polarization values over the working electrode (WE) surface. To this end, relevant information is provided by multiple reference electrodes placed at different points on the WE surface. The method allows estimation of the corrosion current for steel rebars embedded in large concrete structures.

1. Introduction

Though the approach has a general applicability, in this paper we shall be mainly concerned with the measurement of corrosion rate of metal reinforcements in concrete structures. On-site nondestructive diagnosis of the corrosion rate is of great practical interest since a large number of reinforced concrete works are affected by corrosion problems in their reinforcements. However, when attempting to perform electrochemical measurements, the large dimensions of most concrete structures in civil engineering may cause a marked nonuniform distribution of the applied signal, which complicates the analysis since the response cannot be related to any specific electrode area.

The well-known polarization resistance method for corrosion rate determination allows the calculation of the corrosion current density, i_{corr} [1]. Provided the applied current (ΔI) distributes uniformly over the surface of the working electrode (WE), the polarization resistance (R_p) is given by

$$R_p = \frac{\Delta E}{\Delta I} A \quad (1)$$

where ΔE denotes the electrode polarization, which is constant over the entire electrode surface, and A is the surface area. Under these conditions, the current density is also constant at every point on the electrode surface and equal to $\Delta I/A$.

On the other hand, if the current distributes nonuniformly, then the polarization varies throughout the WE surface, and Equation 1 leads to apparent, rather than true, R_p values. This poses an important difficulty in determining i_{corr} for large metal structures by using the Stern–Geary equation [1]:

$$i_{corr} = \frac{B}{R_p} \quad (2)$$

where B is a constant dependent on the Tafel slopes for the anodic and cathodic reactions. For large structures, *in situ* measurements entail using a comparatively much smaller counterelectrode, which favours uneven distribution of the current lines. In this context, serious difficulties have been encountered in determining i_{corr} for reinforcing steel bars embedded in large concrete structures [2–9]. This problem has been addressed by using various approaches, namely:

(a) Confining the applied electric signal so that it only affects a given area of the metal structure concerned, that is, by applying the guard electrode method [2, 7–12].
(b) Using counterelectrodes of increasing size, but negligible in relation to the structure size, to obtain the actual R_p value by extrapolation [13, 14].
(c) Correcting the apparent R_p value by means of coefficients determined on the assumption that the system can be modelled by a transmission line [4, 5].

This paper proposes a new method for estimating the true R_p value. The method takes account of the uneven distribution of polarization over the WE surface and obtains R_p from the sum of partial polarization values. Among other advantages, the method is sufficiently flexible for adaptation to a variety of situations, it has a sound foundation and provides reliable measurements.

2. Theoretical foundation

Consider an electrical signal imposed via a small counter electrode (CE) to give rise to a current flux that distributes unevenly over the WE surface (Fig. 1). Each point of the WE will have a different applied current density value, i (i_j, i_{j+1}, $i_{j+2}, \ldots$). Also, each point will feature a different polarization increment denoted by ΔE_j, ΔE_{j+1}, $\Delta E_{j+2}, \ldots$

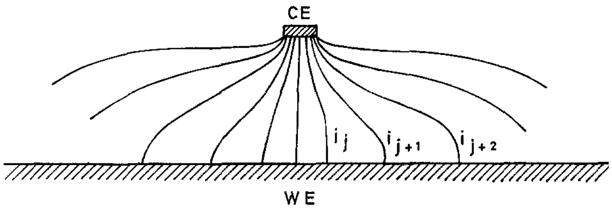

Fig. 1. Representation of the uneven distribution of current lines between a small CE and a large WE.

Let us assume that the WE surface is divided into n portions of area $A_1, A_2, \ldots, A_n$, having a mean polarization $\Delta E_1, \Delta E_2, \ldots, \Delta E_n$, and a mean current density $i_1, i_2, \ldots, i_n$, respectively. If ΔI is the overall current between CE and WE, then

$$\sum_{k=1}^{n} i_k A_k = \Delta I \tag{3}$$

Based on the polarization resistance concept, the following expression holds for each portion of area

$$i_k = \frac{\Delta E_k}{R_\mathrm{p}} \tag{4}$$

which, in combination with Equation 3, and assuming a constant true R_p value over the entire WE surface, gives

$$\frac{1}{R_\mathrm{p}} \sum_{k=1}^{n} \Delta E_k A_k = \Delta I \tag{5}$$

hence,

$$R_\mathrm{p} = \frac{1}{\Delta I} \sum_{k=1}^{n} \Delta E_k A_k \tag{6}$$

Therefore, R_p can be estimated from ΔI provided one knows the value of the expression

$$S_n = \sum_{k=1}^{n} \Delta E_k A_k \tag{7}$$

In practice, determining the ΔE_k values entails simultaneously using many reference electrodes placed at different points on the WE surface.

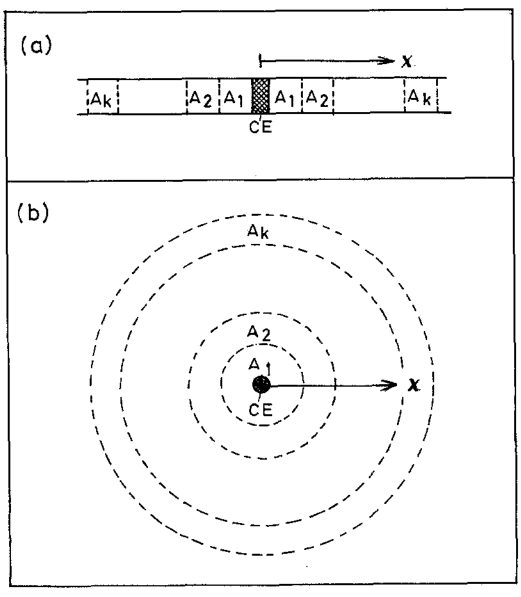

Fig. 2. One-dimensional (a) and two-dimensional (b) models of WE.

A comparison of Equations 1 and 6 reveals that the $\Delta E \times A$ product for a uniform distribution is replaced by the above summation for a nonuniform distribution. There is a remarkable analogy between the two equations, taking into account that R_p for a nonuniform distribution is obtained by summing over the individual contributions from the different portions of area.

The portions of area A_k in Equation 7 can represent both consecutive segments in a one-dimensional structure or annuli of increasing radius concentric with the CE in a two-dimensional structure (Fig. 2). On the assumption that the width of these segments or annuli is sufficiently small, the S_n value in Equation 7 for a distance x between the orthogonal projection of the CE on the WE plane and the points of this plane, is given by

$$S_n = 2W \int_0^x \Delta E(x) \mathrm{d}x \tag{8}$$

for the one-dimensional structure, W being the WE width and $\Delta E(x)$ the function relating the polarization to the distance x. Similarly, for a two-dimensional structure:

$$S_n = 2\pi \int_0^x \Delta E(x) x \mathrm{d}x \tag{9}$$

2.1. *Estimation of S_n*

Even if the function $\Delta E(x)$ is unknown, Equation 8 or 9 can be used to determine S_n provided a discrete series of values $(\Delta E_1, x_1), (\Delta E_2, x_2), \ldots, (\Delta E_n, x_n)$ can be obtained. In this case, S_n is estimated by approximate integration, for example, using the trapezoidal rule method.

In practice, determining S_n entails using a limited number of WE surface portions and, hence, a relatively small number of reference electrodes. Also, the electrodes should not be too distant from one another. For these reasons, four or five consecutive surface portions, spreading over a relatively short distance, should provide an S_n value sufficiently close to the limiting value for $n \to \infty$. This requisite is met when the electrical signal, applied by means of a small CE, concentrates on a WE area near CE.

Although the current lines between the CE and WE can spread in many ways, one can consider two extreme situations, namely: (a) the current lines conform to a primary current distribution model, or (b) they conform to a transmission line model. A primary distribution occurs when the effect of the ohmic resistance prevails over that of polarization [15]; fulfillment of this model is favoured by a high electrolyte resistivity (ρ), a large separation between opposite electrodes and a low polarization resistance. The contrary conditions favour the transmission line model.

With a primary current distribution for a small CE placed opposite to a large metal surface (WE), the current tends to concentrate on a small area of the WE below the CE, in such a way that most of the current lines are roughly normal to the WE throughout great part of their trajectory. On the other hand, with the transmission line model, the current lines tend to be parallel to the WE surface. The risk of current dispersion over the WE is obviously higher in this latter case, although, large ρ values and small R_p values also favour concentration of the current lines in an area relatively near the CE, particularly if the thickness of the electrolyte layer is relatively small, as in reinforced concrete structures [4, 5].

3. Experimental details

The proposed multiple-electrode method was used to determine the corrosion current per unit surface area for reinforcing bars (rebars) embedded in large concrete slabs (Fig. 3). The slabs were 150 cm × 150 cm and included 13 steel rebars of 0.8 cm diameter arranged parallel to and at a distance of 10 cm from one another. The rebars could be externally short circuited or left insulated from the rest. The rebar length exposed to the attack was ca. 130 cm. One concrete slab contained 3% $CaCl_2$ by cement weight, whereas a second slab contained no chloride. The steel rebars developed active corrosion in the former slab but remained passive in the latter.

Electrochemical measurements were made using an assembly similar to the three-electrode configuration but including three additional, auxiliary reference electrodes (Fig. 3). The counter electrode was a stainless steel ring of 3 and 0.6 cm outer and inner diameter, respectively, holding the main reference electrode (RE_1) in the centre. Both CE and RE_1 were placed on the surface of the concrete slab. The other three reference electrodes (RE_2, RE_3 and RE_4), similar to the first, were also placed on the slab surface, but 4, 7 and 15 cm away, respectively, from the CE centre. All four reference electrodes were $Cu/CuSO_4$ electrodes. A pad soaked in tap water was inserted between

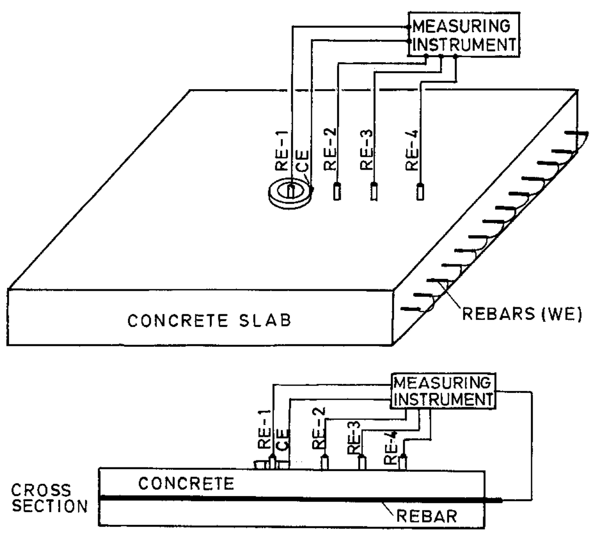

Fig. 3. Representation of the reinforced concrete slabs, electrodes arrangement and electrical connections.

the slab surface and the electrodes in order to ensure ionic conductivity across the interfaces.

Electrical measurements were carried out by means of a GECOR-5 corrosion rate meter [16]. This device applied a potential step to the surface of the WE and automatically determined the experimental values needed, namely, ΔI (the current between CE and WE) and the polarizations ΔE_1, ΔE_2, ΔE_3 and ΔE_4, measured by the electrodes RE_1, RE_2, RE_3 and RE_4, respectively. To exclude any effect of the ohmic drop, ΔE values were read immediately after the applied electrical signal was interrupted.

Specifically, the equipment performed the following operations: (i) reading the potential between the rebar or interconnected rebars (WE) and each of the four reference electrodes (RE_1–RE_4) prior to application of the electrical signal; (ii) applying a potential of 100 mV between CE and WE; (iii) measuring the current ΔI between CE and WE; and (iv) interrupting the current and immediately determining the potential at each electrode (RE_1–RE_4). The difference between these four measurements and those made in (i) determined ΔE_1, ΔE_2, ΔE_3 and ΔE_4.

Calculations were made on the simplifying assumption that the electrical signal spread over a finite distance L over WE. This distance was determined by extrapolation to zero of decreasing polarization values as a function of the distance to the CE. The multiple-electrode method was used to perform two types of measurement, namely: (i) with the 13 rebars connected to one another (i.e., simulating a rebar mesh) and (ii) with a single rebar isolated from the rest. Both types of measurement should provide similar, though not necessarily identical, i_{corr} values. For the former type of calculation, the effect of the interconnected rebars was assumed to distribute uniformly over the geometric plane containing the rebars, so properties distributed in a continuous fashion throughout it. A coverage ratio was introduced to the calculations [5, 9], by assigning to unit area of the ideal WE surface a current density equal to 0.25 of the value for the actual rebar surface (ratio between surface areas of rebars and concrete slab). In case (i), S_n was computed from Equation 9, and in case (ii) from Equation 8. In this latter equation, W is equal to the circumference of the rebar (i.e., 2.51 cm).

Equations 8 and 9 were integrated after the ΔE_1, ΔE_2, ΔE_3 and ΔE_4 values were determined at a distance of 0, 4, 7 and 15 cm from the CE centre,

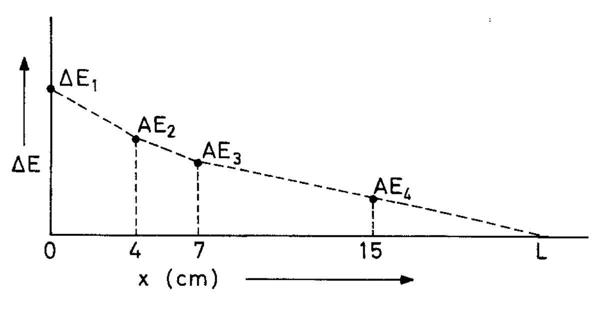

Fig. 4. The variation of polarization with distance.

Table 1. Values obtained from the experimental slabs with all the reinforcing bars short circuited

Conditions	$\Delta I/\mu A$	ΔE_1/mV	ΔE_2/mV	ΔE_3/mV	ΔE_4/mV	L/cm	R_p^*/kΩ cm^2	i^*_{corr}/μA cm^{-2}
Concrete with Cl^-, very dry	13.95	7.0	5.7	4.6	1.9	20.6	53.1	0.49
Concrete with Cl^-, very wet	78.33	12.5	6.5	4.3	1.6	19.7	8.8	2.96
Concrete without admixtures, very dry	6.01	14.9	11.5	9.4	6.9	37.1	566	0.046
Concrete without admixtures, very wet	46.7	34.6	34.0	33.0	28.0	59.8	449	0.058

* Calculated values.

Table 2. Values obtained from the experimental slabs with one of the reinforcing bars insulated from the rest

Conditions	$\Delta I/\mu A$	ΔE_1/mV	ΔE_2/mV	ΔE_3/mV	ΔE_4/mV	L/cm	R_p^*/kΩ cm^2	i^*_{corr}/μA cm^{-2}
Concrete with Cl^-, very dry	13.93	7.1	5.4	4.4	2.0	21.7	36.8	0.71
Concrete with Cl^-, very wet	78.33	12.5	6.8	4.3	1.5	19.3	6.7	3.90
Concrete without admixtures, very dry	5.79	19.9	16.6	15.1	12.4	51.7	559	0.047
Concrete without admixtures, very wet	29.2	59.2	58.0	57.7	54.0	65.0	829	0.031

* Calculated values.

respectively, using the trapezoidal rule method for approximate integration (Fig. 4). After R_p was determined, i_{corr} could be calculated from Equation 2 taking the constant B in this equation as 26 mV [17].

The R_p and i_{corr} values from measurements made with interconnected and isolated rebars were compared with those obtained when a uniform current distribution over the entire surface of the WE was assured. These last measurements were taken as reference. In the particular case of our experiments, the uniform current distribution was obtained by using an isolated rebar as WE and the adjoining two rebars in the slab as CE. It should be noted that this procedure of achieving a uniform current distribution is inapplicable to real concrete structures, where a single rebar can rarely be isolated from the other elements of the rebar mesh.

4. Results and discussion

In the theoretical analysis it has been assumed that the metallic structure corrodes at a uniform rate. This is to a first approximation nearly true when i_{corr} represents the average corrosion rate resulting from the action of a great number of microcells in close proximity and the oxygen availability is quite uniform. A more important deviation from theory may arise from the presence of macrocells. In this respect, experimental information on macrocell activity can be obtained by measuring the current flowing between parallel bars in the test slab when they are interconnected. This has been made joining, via a zero resistance ammeter (ZRA), an isolated bar with the rest of the bars electrically interconnected between themselves, and repeated the operation with every rebar. The values measured in this manner by the ZRA, and referred to the unit of rebar surface, were compared with the i_{corr} values in Table 1. In general, it was found that macrocell activity was only about 10% the value of i_{corr}, or less, in agreement with the conclusions of some other studies [18]. It seems therefore plausible, as a first approximation, the above simplified picture of a uniform corrosion rate on the rebar surface.

Tables 1 and 2 show typical results obtained by using the multiple-electrode system. They give the i_{corr} values obtained with all the rebars in short circuit and those for a single isolated rebar. Some measurements were made on highly dry slabs (after a few months of no wetting) while others were carried out on highly wet slabs (after repeated irrigation over a few days). The i_{corr} values clearly reflect the effect of the experimental conditions, namely, the presence or absence of chloride in the concrete and its degree of wetting. In fact, i_{corr} values varied by about 100 times from conditions favouring corrosion to those hindering it. The maximum i_{corr} value was obtained for wet, chloride-containing concrete.

Quantitatively, it was interesting to determine the consistency between the values provided by the multiple-electrode method and the actual i_{corr} values as given in Table 3; the latter were obtained by polarizing an isolated rebar uniformly.

A comparison of the values given in Tables 1 and 2 with those listed in Table 3 for identical concrete conditions reveals the multiple-electrode method can provide accurate i_{corr} values in those cases where it is impossible to ensure a uniform distribution of the electrical signal applied to the WE. The fairly small differences between the two sets of values are reasonable considering that the methods (the reference one included) rely on approximations.

Table 3. Values obtained from the experimental slabs using an isolated bar as WE and the adjoining two bars as CE

Conditions	i_{corr}/μA cm^{-2}
Concrete with Cl^-, very dry	0.65
Concrete with Cl^-, very wet	3.6
Concrete without admixtures, very dry	0.050
Concrete without admixtures, very wet	0.068

5. Conclusions

Making *in situ* electrochemical measurements by using a small counter electrode as compared with the metal structure which acts as the working electrode poses serious problems. Because the applied electrical signal distributes unevenly on the working electrode, the ratio between the applied potential and the current response ($\Delta E/\Delta I$) provides an apparent R_p value which can greatly differ from the true R_p value (obtained in those cases where a uniform distribution of the current is achieved). A new method for determining the true R_p value (and hence the corrosion current density from the Stern–Geary equation) is proposed for a nonuniform distribution of the applied electrical signal on a large structure. The method uses information supplied by multiple reference electrodes placed at increasing distances from the counter electrode.

The experimental study carried out with large reinforced concrete slabs shows that the proposed method provides highly reliable predictions for corrosion of rebars embedded in concrete irrespective of whether the steel rebars are in an active or passive state and of the degree of concrete wetness, circumstances which markedly affect the precision of the results provided by other measurements methods [14].

Acknowledgement

The authors appreciate the financial support given by the Comisión Interministerial de Ciencia y Tecnología (CICYT) of Spain.

References

[1] M. Stern and G. Geary, *J. Electrochem Soc.* **104** (1957) 56.
[2] D. G. John, D. A. Eden, J. L. Dawson and P. E. Langford, Corrosion '87, NACE, Houston, Texas (1987), paper 136.
[3] D. D. Macdonald, M. C. H. McKubre and M. Urquidi-Macdonald, *Corrosion* **44** (1988) 2.
[4] S. Feliu, J. A. González, M. C. Andrade and V. Feliu, *ibid.* **44** (1988), 761.
[5] *Idem, Corros. Sci.* **29** (1989) 105.
[6] F. Wenger and J. Galland, *Electrochim. Acta* **35** (1990) 1573.
[7] K. Matsuoka, H. Kihira, S. Ito and T. Murata, 'Corrosion Monitoring for Reinforcing Bars in Concrete', *in* 'Corrosion Rates of Steel in Concrete' (edited by N. S. Berke, V. Chaker and D. Whiting), ASTM STP 1064, Philadelphia (1990) p. 103.
[8] A. Sehgal, D. Li, Y. T. Kho, K. Osseo-Asare and H. W. Pickering, *Corrosion* **48** (1992) 706.
[9] S. C. Kranc and A. A. Sagüés, *Electrochim. Acta* **38** (1993), 2055.
[10] E. Escalante, S. Ito and M. Cohen, 'Measuring the Corrosion Rate of Reinforcing Steel in Concrete', Report NBS IR 80-2012, National Bureau of Standards, Gaithersburg, MD (1980).
[11] F. Wenger, *Metaux* **62** (746) (1987) 307.
[12] S. Feliu, J. A. González, S. Feliu Jr. and C. Andrade, *ACI Materials J.* **87** (1990) 457.
[13] S. Feliu, J. A. González, M. L. Escudero and C. Andrade, Corrosion '90, NACE, Houston, Texas (1990), paper 142.
[14] S. Feliu, J. A. González, C. Alonso and C. Andrade, Fall ACI Convention, P. D. Cady Symposium, Minneapolis Minnesota (1993).
[15] J. S. Newman, 'Electrochemical Systems', 2nd edn, Prentice Hall, Englewood Cliffs, NJ (1991), chapter 18.
[16] Corrosion rate meter prototype, GEOCISA, Los Llanos de Jerez, 10, 28820-Coslada, Madrid, Spain. Prototype developed jointly by the firm GEOCISA and the Spanish research centres CENIM and E. Torroja ICC.
[17] J. A. González, S. Algaba and C. Andrade, *Br. Corros. J.* **15** (1980) 138.
[18] C. Andrade, I. R. Maribona, S. Feliu, J. A. González and S. Feliu Jr., *Corros. Sci.* **33** (1992) 237.