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Feasibility of determining corrosion rates by means of stray current-induced polarisation

C. Andrade · I. Martínez · M. Castellote

Abstract To measure metal corrosion it is necessary to make direct physical contact with the specimen or component acting as the working electrode. The most widely used method for determining the corrosion current is electrochemical, the so-called polarisation resistance method. The feasibility of a new method to polarise the metal without the need for direct physical contact was investigated in the present study. The required potential shift is obtained by induction of a current using an external electrical field. The model used for calculation of the corrosion rate assumes that the applied current runs in parallel through the electrolyte and the metal, and electrostatically polarises the metal. The overall electrical resistance of the system can then be expressed as $\frac{1}{R_{e+M}} = \frac{1}{R_e} + \frac{1}{R_M}$, where R_{e+M} is the total resistance measured, R_e is electrolyte resistance and R_M is resistance due to the metal. This latter resistance to electrostatic polarisation is related to the faradaic reaction, which was verified by comparison with the gravimetric losses. This resistance has been called inductive polarisation resistance R_{pi} to distinguish it from the traditional polarisation resistance R_p.

Keywords Corrosion · Equivalent circuit · Induction · Non-contact method · Polarisation resistance

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1 Introduction

Corrosion is a process that involves dissolution of a metal by transformation into oxides or other salts. Traditionally, metal loss has been measured by gravimetric methods after the removal of oxides or corrosion products. Gravimetric methods yield average corrosion rates because they consider behaviour over a certain period of time. However, corrosion of a metal immersed in an aqueous electrolyte is an electrochemical phenomenon [1] and the major techniques used to study corrosion are electrochemical in nature [2–6]. These techniques are based on applying an external voltage or current to the metal and measuring the resulting response. Commonly, the change in potential is monitored by means of a reference electrode.

Various techniques for measuring corrosion rates have been developed based on either extrapolation of the linear (Tafel) sections of polarisation curves to the free corrosion potential, or the so-called polarisation resistance or linear polarisation (R_p). The latter method was introduced by Stern and Geary [2] as an extension of the mixed potential theory of Wagner and Traud [3]. In this method the corrosion current is determined by measuring the slope of the polarisation curve over the free potential range in such a way that the polarisation applied to the metal is small enough not to alter the characteristic of the corrosion process.

The polarisation resistance, R_p, is defined as:

$$R_p = (\Delta E / \Delta I)_{\Delta E \to 0} \tag{1}$$

The corrosion rate or current density, i_{corr} is related to R_p according to:

$$i_{corr} = B / R_p, \tag{2}$$

where B is a constant with a value between 13 and 52 mV, depending on the type of metal and its electrochemical

condition, i.e. active or passive. By monitoring the R_p values and integrating the instantaneous corrosion rates calculated from them, it is possible to quantify the faradaic process involved in corrosion, as can be verified by comparison with gravimetrically determined weight losses measured for the same specimens.

The R_p technique is essentially non-destructive in character, which is the main reason for its widespread use in spite of initial criticisms [4]. At present, R_p determination is accepted as a fast and reliable method for calculating corrosion rates in numerous metal/electrolyte systems [5]. The authors have used it successfully to determine the corrosion rate of steel reinforcements embedded in cement-based concrete [7, 8].

In all cases, to polarise the metal acting as the working electrode and measure its response, it is necessary to establish physical contact between all the electrodes involved and the potentiostat through appropriate wires. This paper presents a measurement method in which direct physical contact between the potentiostat and the metal is not necessary to measure equivalence to the R_p value. The method is based on the observation that an electrode can be polarised by placing it under the influence of an external electrical field generated by applying a current between two external electrodes. The feasibility of measuring the corrosion rate without physical contact to the working electrode opens up new application possibilities, for example, for steel reinforcements in concrete structures, for which easy access to the working electrode is not available because the metal is surrounded by hardened concrete.
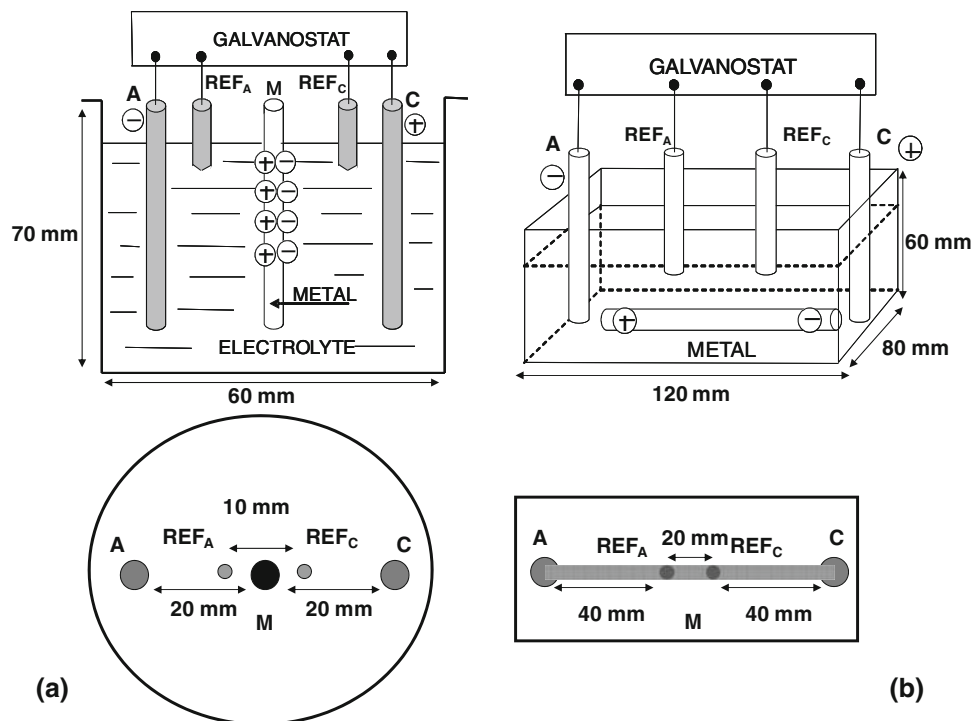
2 Experimental

Two sets of experiments were conducted using electrolytic cells to explore the effect of applied current on polarisation of the metallic piece and to define a relation between R_M and R_p through gravimetric calibration.

2.1 Materials, cells and specimens

The corrosion cell containing a four-electrode system used for this set of experiments is presented in Fig. 1. The system comprises a carbon steel bar as the working electrode and distilled water as the electrolyte. The steel bar was placed either horizontally on the bottom of a flask of appropriate size in parallel to the current direction (orthogonal to the counter-electrodes; Fig. 1b), or vertically, i.e. perpendicular to the direction of the applied current (parallel to the counter-electrodes; Fig. 1a). The steel bars were made of standard carbon steel generally used in reinforcement, containing approximately 0.1% C and with dimensions of 6 mm in diameter and 100 mm in length (Fig. 1b) or 6 mm in diameter and 50 mm in length (Fig. 1a). The area exposed to corrosion attack thus amounted to 1508 or 565 mm^2, corresponding to the central 80- or 30-mm portion of the bar, respectively, which was delimited by wrapping both ends of the bar with electrical insulating tape.

Two graphite electrodes (A and C), located on either side of the bar were used to apply a current with a galvanostat/potentiostat (AMEL 530 and AUTOLAB PGSTAT30). The voltage variation at both sides of the working electrode before and after current application was measured using two

Fig. 1 Electrode arrangement for solution experiments in solution with the metallic piece placed (**a**) parallel or (**b**) orthogonal to the current direction. REF$_A$ and REF$_C$ are the reference electrodes

saturated calomel reference electrodes (REF$_A$ and REF$_C$) placed conveniently near the bar. The electrolyte was distilled water of high initial electrical resistance, which decreased during experiments due to the production of soluble corrosion products during the corrosion process.

2.2 Measurements

Measurements were first used to demonstrate polarisation of the immersed bar following induction of an external electrical field in the surrounding electrolyte by passing a current, I_{ap}, without touching the metal. Measurements were then performed to determine the R_M values obtained over a certain time period without touching the metal. In parallel, traditional R_p measurements were made by making contact with the metal. Finally, the residual weight of the bar was measured at the end of the experiment to calculate the gravimetric loss.

2.2.1 Contact-less method: effect of applied current

As mentioned earlier, an initial set of experiments was carried out to detect changes in potential along the metallic bar due to the application of several currents, I_{ap}. In this first set, the procedure was based on measuring the difference between REF$_A$ and REF$_C$ before and after current application through the graphite electrodes.

Thus, the voltage drop between REF$_A$ and REF$_C$ before testing, V_0, was measured with the bar M introduced into the solution. Current I_{ap} was applied for a certain length of time (in general < 30 s) to obtain a stable reading. Then the voltage drop between REF$_A$ and REF$_C$ was re-measured and referred to as V_2. V_{e+M} was calculated as $V_{e+M} = V_2 - V_0$. The potential V_{e+M} contains two contributions: V_1, just after application of the current, and V_2 after passage of the time interval. The following statements can then be made:

– $V_2 - V_0$ is termed V_{e+M};
– $V_1 - V_0$ is termed V_e; and
– $V_2 - V_1$ is termed V_M.

Other measurements were made during application of a new identical current using an external voltmeter, which allowed measurement of the polarisation of the submerged bar by making an electrical connection to it and using one of the calomel reference electrodes (REF$_A$). In discussing these measurements, the following notation is used for changes in the steel potential:

(a) E_0, initial rest potential (E_{corr});
(b) E_{pol}, potential reached after current application;
(c) E_{e+M}, difference $E_{pol} - E_0$;
(d) E_e, ohmic drop component of E_{e+M}; and
(e) E_M, polarisation after subtracting the ohmic drop ($E_{e+M} - E_e$).

Likewise, the nomenclature used for values of the different resistances is:

(a) R_e, resistance of the electrolyte;
(b) R_M, resistance due to the presence of the metal (this is finally denoted R_{pi}); and
(c) R_{e+M}, total resistance when the bar is immersed in the electrolyte.

2.2.2 Contact-less method vs. traditional methods: evolution with time

After this first set of experiments to explore the effect of the external electrical field, a second set was conducted to determine the feasibility of using this phenomenon to measure the corrosion rate. To do this, before immersing the metal piece in the cell, it was necessary to measure the electrolyte resistance using the four-electrode arrangement. Then the metal piece was introduced into the cell and the new resistance value, R_{e+M}, was calculated using the same electrode arrangement. In this manner, a so-called R_M value was determined, which was compared to the R_p value determined by the traditional method involving physical contact with the metal. Finally, the R_p and R_M values were compared and translated to i_{corr} values, and both were compared to the gravimetric losses.

The sequence of operations was as follows:

(1) The first step was to calculate the electrolyte resistance from $R_e = V_{Re}/I_{ap}$. V_{Re} was measured with the four-electrode arrangement without the metallic bar in the electrolyte. Then the electrolyte resistivity, ρ_e, was measured using a conductivity meter to calculate the geometric cell constant, k, $\rho_e = kR_e$. The cell constant $k = R_e/\rho_e$ allows further calculation of R_e without having to remove the bar from the electrolyte.

(2) The steel bar was then introduced into the electrolyte and V_{e+M} was measured using the same arrangement for R_{e+M} calculation.

(3) V_{e+M} was subsequently measured periodically after several hours and days to obtain values for R_M and investigate whether it is equivalent to R_p.

(4) In addition to these measurements without electrical contact to the immersed bar, for comparison, the value of the polarisation E_{e+M} was also measured in contact with the bar using the REF$_A$ electrode and a voltmeter.

(5) To verify the reliability of the method, simultaneous traditional measurements of R_p were made [7] by applying a potential shift of ∼10 mV to the corrosion potential E_0 of the steel bar and measuring the applied current. In both cases (with and without bar contact), a value of $B = 26$ mV was used to calculate i_{corr} according to Eq. 2.

(6) Finally, the bar was removed from the solution, oxides were cleaned off, and the gravimetric loss was calculated by subtracting the final weight of the cleaned bar from the initial weight.

3 Results

3.1 Contact-less method: effect of applied current

3.1.1 Parallel electrode arrangement (Fig. 1a)

Figure 2 presents values of the stray current-induced polarisation measured through REF_A and REF_C by applying a current of 50 or 100 µA for 5 s without contacting the bar, while Fig. 3 shows polarisation values obtained by making electrical contact with the bar. In both cases the polarisation values are relatively high. It is possible to distinguish very clearly an initial voltage step $(V_1 - V_0)$ recorded instantaneously after application of the current and attributed to the ohmic drop, as well as a polarisation $(V_2 - V_1)$ that varies with time according to the charge or discharge curve.
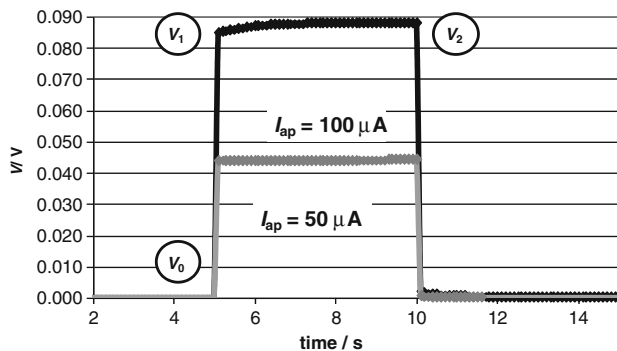
3.1.2 Orthogonal electrode arrangement (Fig. 1b)

Figure 4 shows inductive polarisation measured through REF_A and REF_C when the electrode arrangement (Fig. 1b) was changed to study the effect of the distance between the current inlet and outlet. It is evident that the polarisation increases with distance along the bar between the points of current injection and ejection $((V_2 - V_1)$ in Fig. 3 vs. Fig. 4).

It is worth mentioning that the signs of V and E change when the polarity of the electrodes applying the current is reversed. In other words, the polarisation is observed with respect to cathodic rather than anodic values. This phenomenon is illustrated in Fig. 5, which shows the case of contact measurement, but after applying current in the two polarities. The total polarisation is similar, with a clear noticing of the ohmic drop.

Finally, Fig. 6 shows V_2 and $V_{e+M} = (V_2 - V_0)$ as a function of the current applied, I_{ap}. It is notable that the polarisation is relatively high and increases almost linearly with I_{ap}. This is also observed when the polarisation is measured directly in the steel (using an independent reference electrode and a voltmeter), where E_2 is the potential shift relative to E_0, $E_{e+M} = E_2 - E_0$, and E_0 is the rest potential before applying the current. It can also be verified that E_{e+M} and V_{e+M} follow

Fig. 2 $REF_A - REF_C$ potential variation before and after application of a current of 50 and 100 µA for 5 s to the configuration shown in Fig. 1a (without contact) using distilled water as the electrolyte
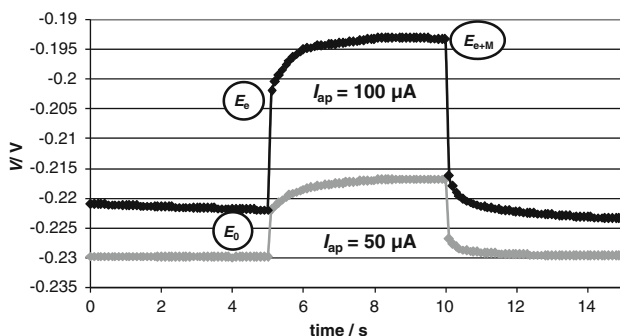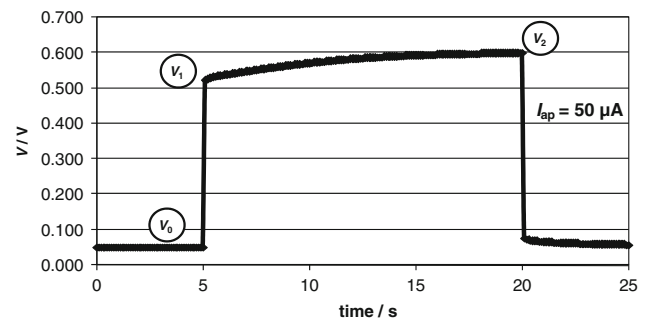

Fig. 4 $REF_A - REF_C$ potential variation before and after application of a current of 50 µA for 15 s to the configuration shown in Fig. 1b (without contact) using distilled water as the electrolyte
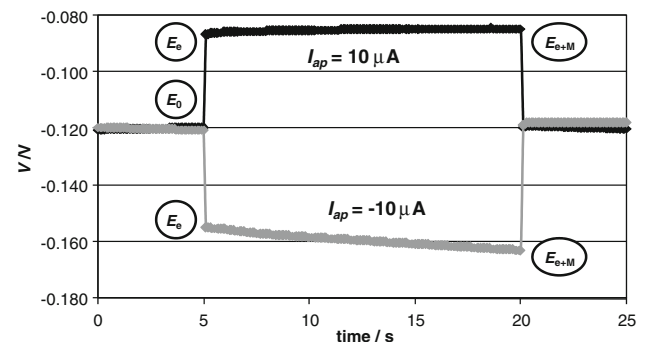

Fig. 3 Polarisation of the bar (with contact) before and after application of a current of 50 and 100 µA for 5 s, measured using REF_A shown in Fig. 1a. Distilled water was used as the electrolyte

Fig. 5 Polarisation of the bar (with contact) measured before and after application of a current of ±10 µA for 15 s to the configuration shown in Fig. 1b using distilled water as the electrolyte
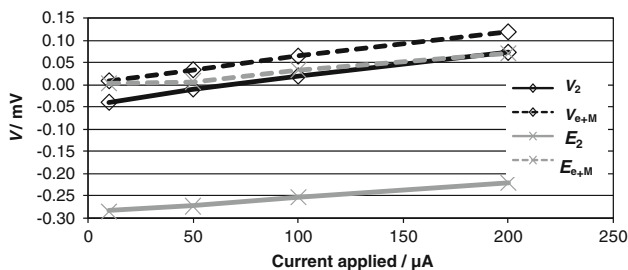
Fig. 6 Values of induced polarisation V_{e+M} and polarised potential V_2 as a function of applied current measured by means of the voltage drop at the $REF_A - REF_C$ electrodes as shown in Fig. 1a. E_2 and E_{e+M} were measured directly in the steel bar by means REF_A

the same trend but are different in magnitude. In this experiment, E_0 amounted to -0.290 mV.

3.2 Contact-less method vs. traditional methods: evolution with time

After the first set of measurements, tests were performed to establish how effectively the contact-less method can detect the evolution of corrosion over time. To this end the electrical resistance of the electrolyte was measured over time, as well as the polarisation resistance R_p, i.e. in the traditional way.

Figure 7a shows the evolution of the electrolyte resistance R_e and the traditional R_p over 15 days for a bar immersed in distilled water in the parallel electrode arrangement. Figure 7b shows the E_{corr} values measured prior to making the R_p measurements shown in Fig. 7a.

Figure 8a presents the evolution of V_{e+M} values $= (V_2 - V_0)$ in the same parallel electrode arrangement as that used in Fig. 7, but measured by the non-contact method. The applied current amounted to 10, 20, 50 and

100 μA, corresponding to a current density of 1.8, 3.5, 8.8 and 18 μA cm^{-2}, respectively, with respect to the exposed surface area of the working electrode. From these V_{e+M} values it is possible to calculate the R_{e+M} values (Fig. 8b). It should be noted that the applied current does not affect R_{e+M}. It is possible to calculate $R_M = (R_{pi})$ from R_e and R_{e+M}. Its value varies depending on the electrical circuit chosen as a model, as discussed later.

4 Discussion

The phenomenon of induced polarisation of a bar embedded in a concrete specimen has been observed in other experiments we have carried out. One was when performing experiments on so-called chloride migration tests [9], in which a solution of sodium chloride is placed externally on a concrete surface and an electrical field of several V m^{-1} is applied via two external electrodes to force the chlorides to penetrate into the concrete. Under these conditions, a piece of reinforcement steel embedded in the concrete between the two external electrodes was significantly polarised [10]. Polarisation of reinforcements has also been observed when using a so-called "pachometer" to detect their position. These pachometers usually have two coils through which an alternating current is applied. Reinforcement presence is detected when an electrical circuit is established between the coils and the ferromagnetic steel. When the pachometer is working, the corrosion potential of the reinforcement changes until the electromagnetic field is switched off.

The detection of such phenomena prompted us to try to account for the current generated by these polarisations and to determine the slope of the relation between polarised

Fig. 7 (**a**) Electrolyte resistance and traditional polarisation resistance measured during the test in distilled water. (**b**) Corrosion potential measured during the test in distilled water
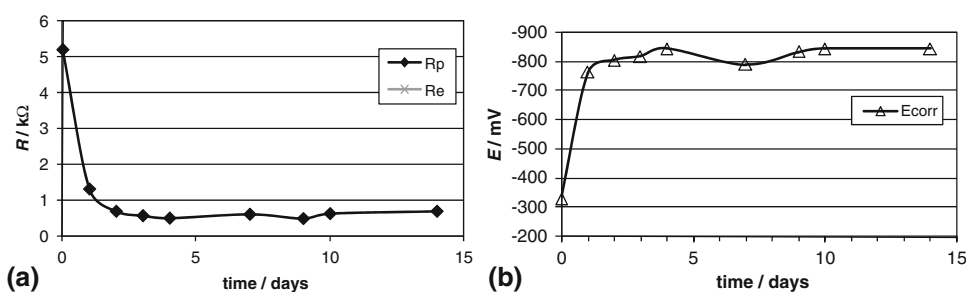

Fig. 8 (**a**) V_{e+M} potential measured during tests in distilled water for inductive current of 1.8, 3.5, 8.8 and 18 μA/cm^2. (**b**) R_{e+M} values calculated from V_{e+M} values
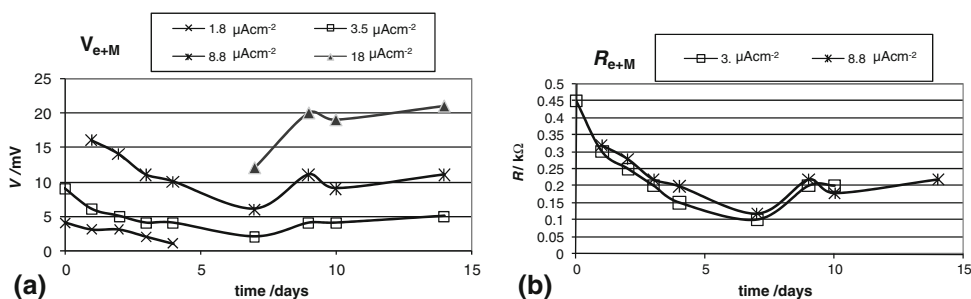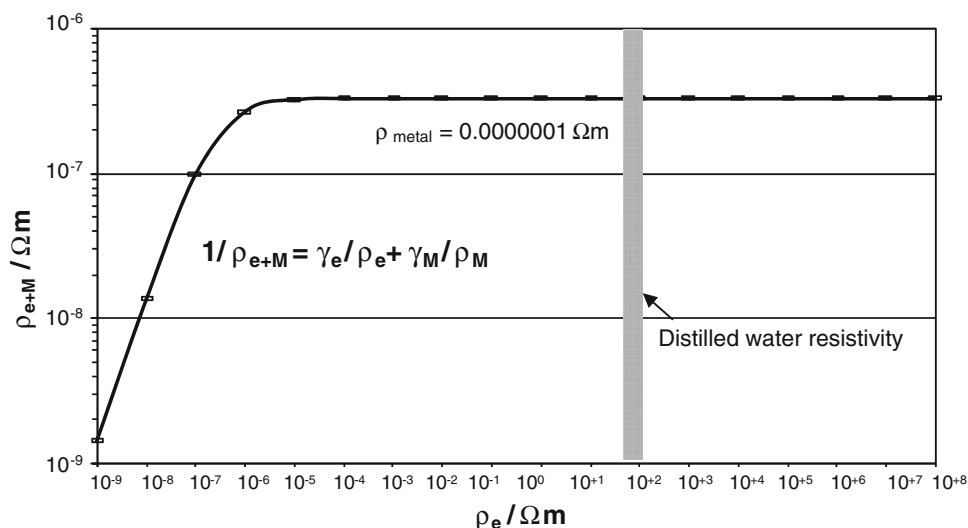
Fig. 9 Values obtained for ρ_{e+M} using Eq. 3 for volumetric fractions of $\gamma_e = 0.7$ and $\gamma_M = 0.3$ and several appropriate values of ρ_e and ρ_M

potential and current, that is, to derive R_p. However, early attempts were hampered by the difficulty of measuring current running through the bar without touching it. The second key aspect was to investigate whether the current detected in the metallic piece is really related to the corrosion rate.

The difficulty was overcome by realising that it is not necessary to measure both the current and the potential; what is needed is the value of the ratio $\Delta E/\Delta I$, that is, the polarisation resistance. Once the resistivity of the medium can be independently measured, the resistance of the electrolyte can be calculated using the known geometry factor k. This electrolyte resistance has to be subtracted from the overall resistance of the system comprising the electrolyte and the immersed bar. If a current is applied through the electrodes to the electrolyte without any metal, the ions in the electrolyte carry the electrical charges. However, when a piece of metal is introduced into the electrolyte, the resistivity changes because of the presence of the metallic piece, and the value measured is then lower because of the lower resistivity of the metal.

From the results of these experiments, four main aspects deserve to be commented upon: (1) the influence of the presence of a metallic piece in an electrolyte on the measured resistivity; (2) the nature of the polarisation noted in the metal when current is applied through the electrolyte; (3) the model used to calculate the electrical resistance due to the presence of the metal in the electrolyte; and (4) the relationship between this resistance, denoted by R_M (or finally R_{pi}), and the traditional polarisation resistance R_p.

4.1 Influence of the metallic piece on the measured resistance

The first question to be addressed is how the presence of a metallic piece in an electrolyte affects measurement of the electrical resistance of the system. The question is whether the R_e value measured in the presence of the metal bar is the result of the mixing of two phases (electrolyte and metallic bar) of different resistivity, or whether the applied current induces other types of phenomena and the resistance value recorded is the result of several processes.

The classical expression [11] for the case of a mix of two phases in parallel is:

$$1/\rho_{e+M} = \gamma_e/\rho_e + \gamma_M/\rho_M \tag{3}$$

The cell used in the present experiments had electrolyte and metal volumetric fractions of approximately $\gamma_e = 0.7$ and $\gamma_M = 0.3$. The resistivity of distilled water was approximately 100 Ωm after 24 h of immersion of the steel, and the resistivity of the metal was taken as 1×10^{-7} Ωm. This would result in $\rho_{e+M} = 3.3 \times 10^{-7}$. This is much smaller than the value actually measured and indicates that the resistivity of the volumetric fraction of the metallic piece is not the only contribution to the phenomenon observed.

On the other hand, Fig. 9 represents Eq. 3 for volumetric fractions of $\gamma_e = 0.7$ and $\gamma_M = 0.3$ and several values of ρ_e and ρ_M. Because of the comparatively low value of the metal resistivity, only when ρ_e is very low is an influence detected in the ρ_{e+M} value. In other words, if the metal were contributing by its volumetric fraction, a very small volumetric fraction would be enough to influence the resistivity value so dramatically as to be immediately detected. Since this behaviour was not observed, this explanation can be discarded.

4.2 Nature of the polarisation

From Figs. 2 and 4 it is evident that after the ohmic drop (step $V_0 - V_1$, primary distribution of the current) is recorded, a polarisation (step $V_2 - V_1$, secondary distribution of the current) occurs because of the metal. The nature of this polarisation can be explained by

electrostatics, which states that when a current is applied through an electrolyte, ions move towards the oppositely charged electrode, but that substances with delocalised electrical charges or of high conductivity, such as metals, are electrostatically polarised. This electrostatic separation of charges induces a polarisation, as shown in Fig. 1. In metals, this polarisation induces a current in opposition to the externally applied electrical field (this is why R_M is later termed "induced", $R_M = R_{pi}$).

From the results obtained it can be deduced that this polarization ($V_{e+m} = V_2 - V_1$) is higher when using the arrangement shown in Fig. 1b, and the current applied is also greater (Figs. 2 and 4).

A similar polarisation effect occurs in the case of stray currents in soils or when using currents to detect minerals with metallic components in soils. The presence of stray currents creates spatially distributed anodes and cathodes in the buried metals and, if they persist, corrosion with metal loss occurs in the anodic zones [1]. In the case of the induced polarisation method of geophysical prospecting, this metal loss serves to detect the existence of soil zones with metallic components [12]. However, no reports on the correct use of these phenomena for calculating the corrosion rate could be found in the literature. Unsuccessful attempts have been made [13] in which the phenomenon was not interpreted as being due to the generation of charge separation, and also in our opinion the model used was incorrect.

4.3 Proposed corrosion model

4.3.1 Basis of the non-contact corrosion technique

Monteiro et al. [13] studied a circuit with R_e and R_M in series (a simple Randles circuit). However, this possibility was not considered here because in that case, in the experimentally obtained electrical response, the first potential step must be due solely to the electrolyte resistance and the second step solely to the metal polarisation resistance, which is not what has been observed for the experimental data. It has therefore been assumed that current travels in parallel through the electrolyte and the metal. Under this assumption, the responses of three electrical circuits to the application of a current step were studied. The proposed circuits are shown in Fig. 10. In these circuits, $R_{e'}$ and $R_{e''}$ represent two components of the electrolyte resistance and R_M is the metal resistance. $R_{e'}$ represents the
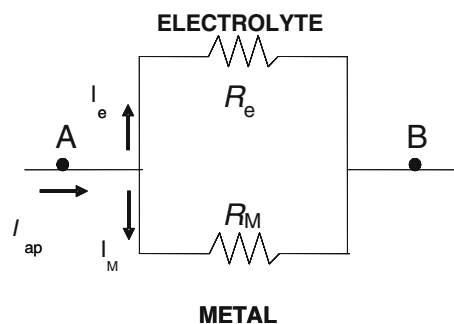

Fig. 11 Electrical model used to represent the configuration shown in Fig. 1

part of the path from the injection point (electrode) to the working electrode, and $R_{e''}$ the electrolyte path parallel to the working electrode. The capacitor associated with R_M represents the double-layer capacitance of the corrosion process. A theoretical investigation was performed using an appropriate program (5SpiceAnalysis, educational version) to obtain the model that best fits the phenomena under study considering both the resistance and capacitance values. This theoretical study on the correct model to be applied revealed that all three circuits are feasible for simulating inductive polarisation, but the most appropriate one for interpreting the experimental data is circuit 2, because it provides results which are simpler to interpret.

Under the assumption that all three circuits are feasible, circuit 2 is selected as it is the simplest and most practical. The model used for this non-contact method is shown in Fig. 11 [11], in which the current runs in parallel through the electrolyte and the bar, and two separate paths for the current are assumed: one passes through the electrolyte and the other polarises the bar. The contribution of the metallic piece to the polarisation can be calculated from the following expression:
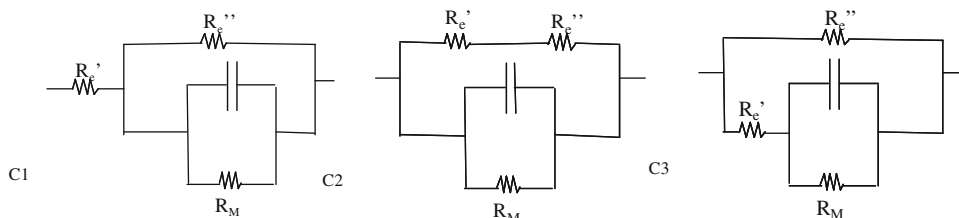
$$\frac{1}{R_{e+M}} = \frac{1}{R_e} + \frac{1}{R_M}, \tag{4}$$

where R_{e+M} is the resistance when the metal is present in the electrolyte, R_e is the volumetric resistance of the electrolyte without the metal and R_M is the resistance (to polarisation) due to the metal.

Rearrangement of Eq. 4 results in an expression for R_M:

$$R_M = \frac{R_e \cdot R_{e+M}}{R_e - R_{e+M}}. \tag{5}$$

Fig. 10 Circuits studied: C1, C2 and C3

The model (Fig. 11) has previously been published [14] and is based on the assumption that the current flows through two paths in parallel: one flows through the electrolyte, with the charges carried by the ions, and the other polarises the metal bar. This means that only a fraction of the applied current results in polarisation of the metal. Logically, this fraction will increase as the resistivity of the electrolyte increases.

The assumption that only a fraction of the total current applied is used for polarisation prevents direct calculation of R_p from I_{ap} because, although the magnitude of V_{e+M} can be measured, the fraction of the current I_{ap} used for the polarisation of the metallic bar cannot be directly measured. The only way to determine this is by measuring the electrolyte resistance directly, and subtracting its influence.

4.3.2 Graphic representation of Eq. 4

An exercise was performed to determine sensitivity of the relative values of R_e and R_M in Eq. 4, the results of which are shown in Fig. 12.

As the equivalent electrical circuit contains two resistors placed in parallel, a first immediate deduction is that when R_e is high (the inverse of R_e is very small), it can be neglected in the calculation. This logical result can be deduced from the representation of R_M versus R_{e+M} shown in Fig. 12, which represents Eq. 4.

Figure 12 also shows how R_e can influence the R_{e+M} value in accordance with Eq. 4. When the metal is passive, R_M is high and its inverse is relatively small, so R_e dominates the result. However, when the metal is active, R_M is small and the influence of R_e on the total response R_{e+M} is negligible. In the experiments performed for this study, cases were found for which a negative value was obtained for R_M because the resistance of the electrolyte, R_e, was less than R_M.

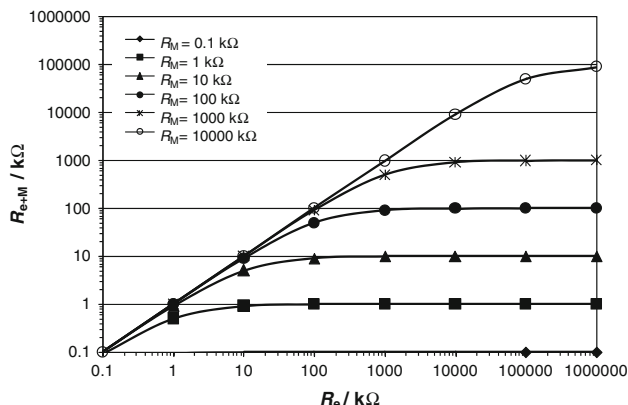Therefore, in conductive electrolytes, a very small part of the total current is used to induce polarisation of the immersed metal. This complicates application of the method to metal/electrolyte systems in which the resistivity of the electrolyte is comparatively small. However, for cases such as concrete, for which the resistivity is comparatively high, its application is promising, and a simplification of the type shown in Eq. 6 can even be used:

$$\frac{1}{R_{e+M}} = \frac{1}{R_M} \tag{6}$$

In other words, R_M (equivalent to R_p) can be deduced directly from R_{e+M} without separate measurement of the electrolyte resistance. Some preliminary tests were carried out on reinforcement concrete using this approach and the results will be published in a future paper.

4.4 Relation between R_M (R_{pi}) and R_p

Assuming that the electrical equivalent circuit is as shown in Fig. 11, it is now feasible to calculate R_M from the results shown in Fig. 8. Values of R_M calculated using Eq. 5 and R_p calculated using the traditional method (with metallic contact between the potentiostat and the metal) and their variation over 14 days are shown in Fig. 13. Gravimetric calibration of the electrochemical techniques used to determine the corrosion rate is shown in Fig. 14.
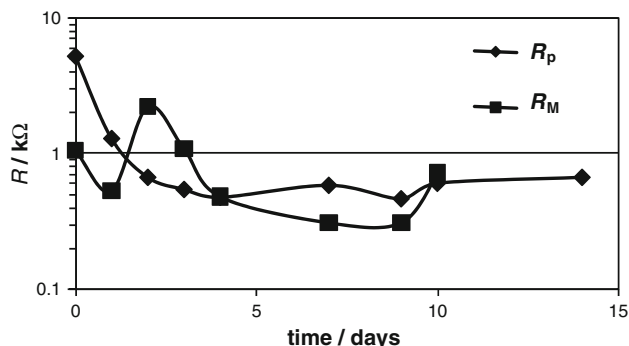

Fig. 13 Comparison of R_p and R_M values obtained in distilled water and their variation over time

Fig. 12 Graphical representation of Eq. 4: theoretical variation of R_{e+M} as a function of R_e for different values of R_M.
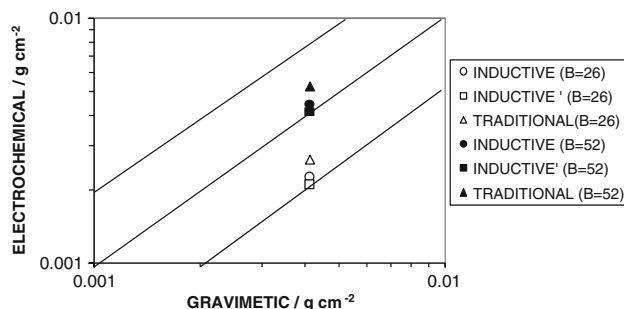

Fig. 14 Comparison of the electrochemical losses over 14 days calculated using R_p and R_M values and gravimetric measurement of the steel bar submerged in distilled water at the end of the experiment

Table 1 Gravimetric weight loss

Initial weight (g)	Final weight (g)	Weight loss (g)
17.7716	17.7482	0.0234

Quite good agreement is observed between the inductive and traditional electrochemical techniques, and between the electrochemical and gravimetric methods. The greatest weight loss for steel suffering from corrosion occurs when B in Eq. 2 is taken as 52 mV. This agreement indicates that Eq. 4 is a good representation of these phenomena and can be applied to calculate the corrosion rate of a metallic piece immersed in distilled water using the non-contact method described here. The magnitude of the weight loss obtained after removing the bar from the cell is presented in Table 1.

In this paper then it is assumed that R_M (finally referred to as R_{pi}) is equivalent to R_p, as estimated using electrode contact, and therefore the corrosion current i_{corr} can be calculated from R_M using the Stern–Geary relation [2]. The reason why the resistance R_M (R_{pi}) is equivalent to the traditional R_p is not yet clearly understood and further studies are required to provide the complete scientific basis. The theoretical basis can be linked to the fact that currents generated in the metal due to the separation of charges are linearly related to the induced voltage, fulfilling the premise of the linear polarisation method [15]. If the currents are linearly related to the induced voltage, then their ratio can be considered as a polarisation resistance, which will depend on the state (passive or corroding) of the metal.

A linear relation between applied current and induced voltage can be derived from the relation presented for the total current in Fig. 6. It seems reasonable to accept that the linear relation that holds for low polarisation when current is directly applied to the metal should also hold when the current is induced by an external electrical field. In other words, provided that the induced polarisation remains low, the relation between polarisation and current, from now on termed the contactless corrosion technique, could be used to measure the corrosion rate for electrolytes with high resistivity and where access to direct metallic contact is difficult. The resistance, referred to here as R_M, can then be termed induced polarisation resistance, R_{pi}, to distinguish it from the traditional R_p.

5 Conclusions

The following conclusions can be drawn:

1. Experimentally it has been verified that a piece of metal can be polarised in an electrolyte when a current is applied externally through electrodes that are not in direct contact with the metal.

2. Induced polarisation is linearly related to the electrical resistance measured through two additional reference electrodes (the four-electrode method) and a linear relation is observed between the applied current and induced potential change.

3. It is thus feasible to calculate the polarisation or charge transfer resistance, R_p, of a metal in an electrolyte through the shift in potential induced by application of an external current without electrically touching the metal. This polarisation resistance is referred to as R_{pi} to distinguish it from the traditional R_p.

4. The equation proposed for calculation of R_{pi} is: R_M $(R_{pi}) = R_e R_{e+M}/(R_e - R_{e+M})$, where R_e is the electrical resistance or voltage drop due to the electrolyte for the same electrode arrangement without the metallic component, R_{e+M} is the electrical resistance measured when the metal is in the electrolyte, and R_M (R_{pi}) is the traditional R_p. This equation is derived by assuming that the current runs in two parallel paths (electrolyte and metal) through the cell. An equivalent electrical circuit is also proposed.

5. The method developed here is termed the contactless corrosion method. It is based on the fact that when a metal is placed within an electrical field or a current is passed through an electrolyte containing the metal, the metal is polarised and develops electrostatic separation of electrical charges, which generates a current opposing the external field. The phenomenon can be achieved using either direct or alternating current, or by placing the metal in a magnetic field.

6. Finally, if R_e is much higher than R_{pi}, then, the corrosion rate can be obtained directly from the resistance calculated from the voltage drop $V_2 - V_0$, that is, from the R_{e+M} value.

References

1. Evans UR, Hoar TP (1932) Proc R Soc A 137:343
2. Stern M, Geary AL (1957) J Electrochem Soc 104:56
3. Wagner C, Traud W (1938) Z Elektrochem 44:52
4. Hoar TP (1967) Corros Sci 7:341
5. Mansfeld F (1973) J Electrochem Soc 120:515
6. Gabrielli C, Keddam M, Takenouti H et al (1979) Electrochim Acta 24:61
7. Andrade C, González JA (1978) Werkst Korros 29:515
8. Feliú S, González JA, Andrade C et al (1989) Corros Sci 29:105
9. Castellote M, Andrade C, Alonso C (1999) Adv Cem Res 11(2):63
10. Castellote C, Andrade C, Alonso C (2001) Cement Concrete Res 31:1411

11. McDonald JR (1987) Impedance spectroscopy emphasizing solid materials and systems. Wiley, New York
12. Orellana E (1974) Prospección geoleléctrica por campos variables. In: Biblioteca Técnica Philips. Editorial Paraninfo, Madrid
13. Monteiro PJM, Morrison F, Frangos W (1998) ACI Mater J 95:704
14. Andrade C, Martínez I, Alonso C et al (2001) J Constr Mater 51:263
15. Feliú S, González JA, Andrade C et al (1989) Mater Struct 22:199