

NON CONTACTING CORROSION METHOD APPLIED TO THE STEEL CORROSION RATE DETERMINATION IN DIFFERENT SOLUTIONS AND REINFORCED CONCRETE SPECIMENS.

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ABSTRACT

All the current techniques used to measure the metallic corrosion require contact with the metal. Particularly, in the case of reinforcement corrosion, this signifies the need to reach the bar that is embedded in the concrete, which may consequently result in the disruption of the integrity of the real structures. This paper explores the feasibility of using a new method for polarizing the reinforcement or any metal in an electrolyte, without the need of direct contact with it. The polarization is obtained through the induction of current from an external electrical field. The current runs through the electrolyte and the metal in parallel, depending on the electrode arrangement. The resulting Polarization Resistance calculated is termed as Inductive, $R_p = R_{pi}$. The Inductive is calculated by the model of resistances in parallel, which requires a separate measurement of the electrolyte ohmic resistance. In this study, solutions with several resistivities and concrete specimens with and without chlorides have been used. The results indicate that electrolytes of low resistivity mask the measurement, and consequently, R_{pi} could not be calculated. In electrolytes with high resistivity, such as concrete, the feasibility is found to depend on the relative values of R_e and R_{pi} .

KEYWORDS: corrosion, rate measurement, non-metallic contact.

INTRODUCTION

The measurement of instantaneous corrosion rate, proposed by Stern et al. [1], who developed the so-called Polarization Resistance or Linear Polarization, R_p technique, is based on the theory of mixed potential put forth by Wagner and Traud [2]. This method determines the corrosion current through the measurement of the slope of the polarization curve around the corrosion or mixed potential, in such a way that the polarization applied to the metal is small enough such that it cannot alter the corrosion process: $R_p = \Delta E / \Delta I$ when $\Delta E \rightarrow 0$ and $I_{corr} = B / R_p$, where B is a constant that varies from 13 to 52 mV. Thus, the R_p technique is non-destructive in nature, which has been the main reason for its rapid generalized use in numerous metal/electrolyte systems [3][4]. In particular, this technique was applied to measure the reinforcement corrosion in the 1970s [5][6].

To polarize the metal to measure its R_p (or charge transfer resistance, R_T), it is necessary to make contact with the metal, considering it as the working electrode. However, in an earlier study [7], a method that gives the R_p value without making physical contact with the metal was described. This method was termed as non-contacting method (NCCm), and was calibrated by gravimetric studies in distilled water–rebar considered as the metal–electrolyte system. In this paper, this method has been applied to different metal/electrolyte systems and concrete slabs to explore the limits of its application. Furthermore, the resulting values have been compared with those obtained by other contacting on site techniques [8][9][10].

EXPERIMENTAL

To explore the possibilities of applying this method to different electrolytes, cells that are prepared with solutions of different resistivities, in which the steel corrodes at different rates were used. Furthermore, the concrete specimens were also prepared.

Electrochemical cells

The corrosion measuring system for the NCCm employs four electrodes (Figure 1)—two counter electrodes (A and C) separated by a certain distance and two reference electrodes (REF_A and REF_C) placed between A and C.

In this study, the electrodes A and C used were graphite bars of 0.6 cm in diameter and 8 cm in length. The reference electrodes used were two Mn/MnO reference electrodes. The working electrode was a corrugated bar identical to the electrodes A and C, with an area of 5.65 cm² exposed to the solution (3 cm in length).

Two different electrode arrangements were used for the measurements, parallel or orthogonal distribution, as shown in Figure 1. The cell, parallel to the working electrode was cylindrical with dimensions of 70 mm in length and 60 mm in diameter, and the orthogonal position was tested in a prismatic cell of dimensions 160×120×40 mm.

The cells were prepared with the following solutions:

- 0.2 M Na₂CO₃ solution
- 0.1 M NaCl solution
- Tap water from Madrid
- Distilled water

Concrete elements

Two different concrete slabs were prepared, one with 3% by cement weight of chloride ions added to the mix as NaCl, and the other without chlorides. The slabs' dimensions were 160×140×10 mm. The concrete was prepared using the cement type I45/SR, with a water/cement ratio of 0.5. One steel bar of 6 mm in diameter and 120 mm in length was embedded in each slab, having an exposed area of 15.08 cm² (delimited by a plastic tape attached around the steel). The steel bar was placed on one side of the slab, leaving the rest of the specimen free of metal to measure the resistivity, as shown in Figure 2. An electric wire was connected to the bar inside the concrete, and the connection was protected with an epoxy resin.

About 24 h after their fabrication, the specimens were immersed in distilled water, and were cured in these conditions for 7 days. After 7 days, they were exposed to the laboratory conditions.

For the measurements, two stainless-steel electrodes (A and C; Figure 2) were placed at both the extremes of the rod. These electrodes were used to apply current in the range of 5–500 μA. The voltage variation was measured using two Ag/AgCl reference electrodes (REF_A , REF_C) placed between the two stainless-steel electrodes. It was observed that the distance between the electrodes, L , was always 30 mm, as shown in Figure 2.

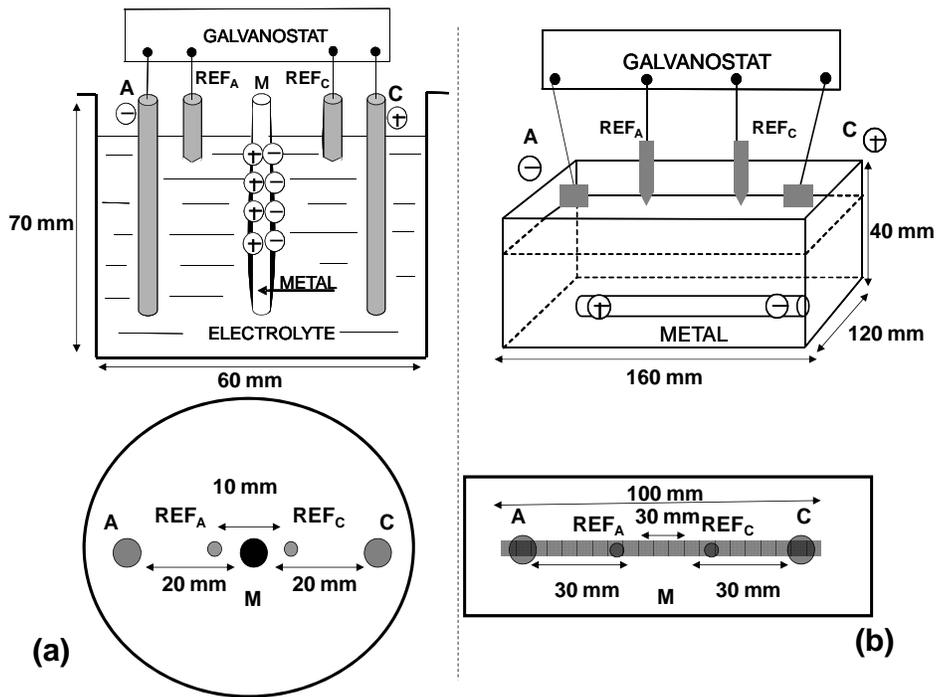


Figure 1 - Electrode arrangement for the experiments in (a) solution, with the metallic piece placed parallel to the direction of current, and (b) concrete, with the rebar placed orthogonal to the direct of current. REFA and REFC are the Mn/MnO reference electrodes.

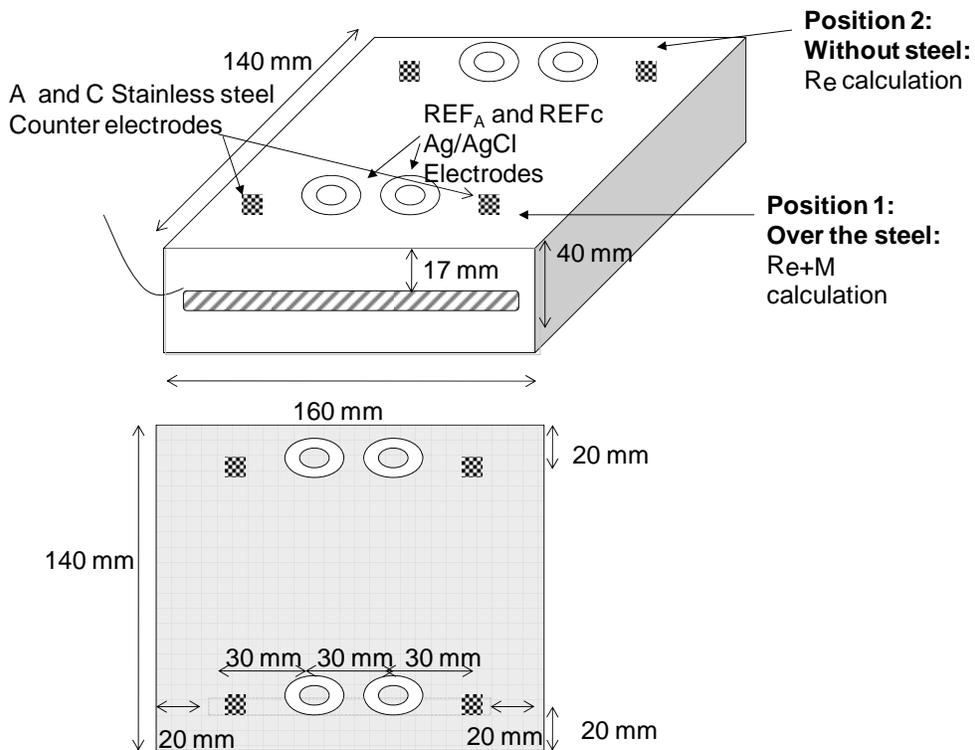


Figure 2 - Electrode arrangement for the NCCm measurement in the concrete slabs.

Calculation of R_p using NCCm

The NCCm is based on the fact that when a metal is placed within an electrical field, or when current is passed through an electrolyte containing the metal, the metal is polarized and a separation of the electrical charges that tend to oppose the external field occurs. This evidence is based on the induction phenomenon presented by materials of high intrinsic electrical conductivity.

As the R_p is the ratio between the potential and the current, the difficulty arises with respect to recording the conjugated parameter, voltage, or current, without physical contact with the electrode. However, we can overcome this difficulty by considering the fact that when a metal is inductively polarized, all the electrical charges lie on its surface, and thus, the charge transfer resistance, R_p , can be obtained directly by measuring the E/I ratio, i.e., the resistance.

The other important assumption lies on realizing the paths for the current flow. The model applied for the NCCm assumes that the current flows in parallel—one path takes the electrolyte, where the charges are carried by the ions, and the other path polarizes the metal bar (Figure 3). This indicates that only a fraction of the applied current is used in the polarization of the metal. This fraction will be logically higher, if the resistivity of the electrolyte is higher. Subsequently, an electrical analogue circuit is selected. In an earlier study, three different possible circuits were studied [7], and Figure 3 shows the one selected.

From this circuit, the value of the Polarization Resistance of the bar is calculated as:

$$\frac{1}{R_{e+M}} = \frac{1}{R_e} + \frac{1}{R_M} \quad (1)$$

where R_{e+M} is the resistance when the metal is present in the electrolyte; R_e is the resistance of the electrolyte without the metal, and R_M is the resistance (to polarization) owing to the presence of the metal.

Thus, the R_M (also known as R_{pi}) can be subsequently calculated as:

$$R_{pi} = R_M = \frac{R_e \cdot R_{e+M}}{R_e - R_{e+M}} \quad (2)$$

If $R_e \gg R_M$, then we get:

$$\frac{1}{R_{e+M}} = \frac{1}{R_M \text{ (or } R_{pi})} \quad (3)$$

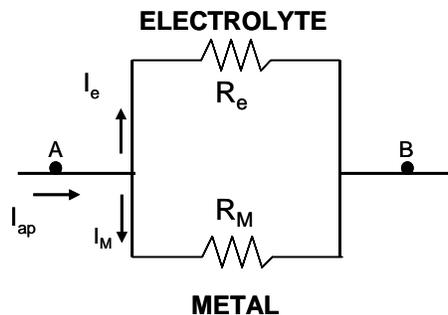


Figure 3 - Model for the NCCm interpretation proposed in an earlier study [7]

Practical procedure of NCCm

The procedure is based on measuring the difference between REF_A and REF_C (Figure 1 and 2) before and after the application of current through the electrodes A and C with a galvanostat (AUTOLAB PGSTAT30). Thus, the voltage drop between REF_A and REF_C before testing, V_0 , was measured with the bar M introduced into the solution. The current I_{ap} was observed to vary depending on the requirement of the sample measured (from 5 μA in the case of dry concrete specimens to 50,000 μA when it is applied to very conductive electrolytes), and was applied for a certain duration of time (in general, 50 s) to obtain a stable reading. Subsequently, the voltage drop between REF_A and REF_C was re-measured and referred to as V_2 . The V_{e+M} was calculated as $V_{e+M} = V_2 - V_0$. From the V_{e+M} value obtained in the previous test, it is possible to calculate R_{e+M} ($R_{e+M} = V_{e+M}/I_{ap}$).

To obtain the electrolyte resistance, R_e , it is necessary to apply a similar current step using the four-electrode arrangement, but without the metallic bar in the electrolyte (solution or concrete). In case of concrete, the four electrodes are placed in the specimen as in shown in the position 2 of Figure 2.

Corrosion Rate Measurements by contact with the metal

For verification of the NCCm reliability, the corrosion-rate measurements were carried out simultaneously using the traditional method of making electrical contact with the rebar to measure the corrosion rate. The measurement was made with the same galvanostat/potentiostat mentioned earlier. The R_p was determined by applying a linear sweep rate of 10 mV/min with a corrosion potential from -20 to +20 mV in both solutions and concrete specimens.

In the case of concrete specimens, the counter electrode was a stainless-steel mesh placed in the lower face of the concrete (under the specimen), and the reference electrode used was Ag/AgCl. In the electrolytic cells the counter electrode was one of the graphite bars (Electrode A) embedded in the solution, and the reference electrode used was Mn/MnO.

Gravimetric determinations

To calibrate NCCm, gravimetric determinations were made for the experiments carried on the electrolytic cells. The bars were cleaned and weighed before and after the end of the experiments by pickling them in an HCl solution with hexamethylenetetramine as inhibitor.

RESULTS

The results of the traditional linear polarization method are presented first, followed by the results obtained using NCCm.

Measurements obtained by contact with metal

Solutions: Figure 4 presents the values of corrosion potential, E_{corr} observed in the steels immersed in the four solutions studied. It can be observed that only the steel immersed in Na_2CO_3 presents values lesser than -300 mV (compared with Mn/MnO reference electrode). This is indicative of the low probability of corrosion in this electrolyte. With respect to the values of corrosion rate measured, only the bars submerged in the 0.2 M Na_2CO_3 solution remained passive during the test ($I_{corr} < 0.1 \mu A/cm^2$) (Figure 5). On the other hand, the rest of the steel bars were actively corroding during the test.

Concrete specimens: Figure 6 presents the E_{corr} values measured with respect to the Ag/AgCl reference electrode in both the specimens for all the experiments, while Figure 7 shows the I_{corr} values measured by traditional methods, making electrical contact with the rebar. During the first 40 days of the test, the specimen with chlorides were observed to actively corrode ($I_{corr} > 0.2 \mu A/cm^2$ and $E_{corr} < -300$ mV vs.

Ag/AgCl), while the specimen without chlorides remained passive ($I_{corr} < 0.1 \mu A/cm^2$ and $E_{corr} > -300$ mV vs. Ag/AgCl). After this time period and owing to the drying of the concrete, both the specimens showed the I_{corr} values below $0.1 \mu A/cm^2$ indicating passive state, although those values were higher in the specimen with chlorides.

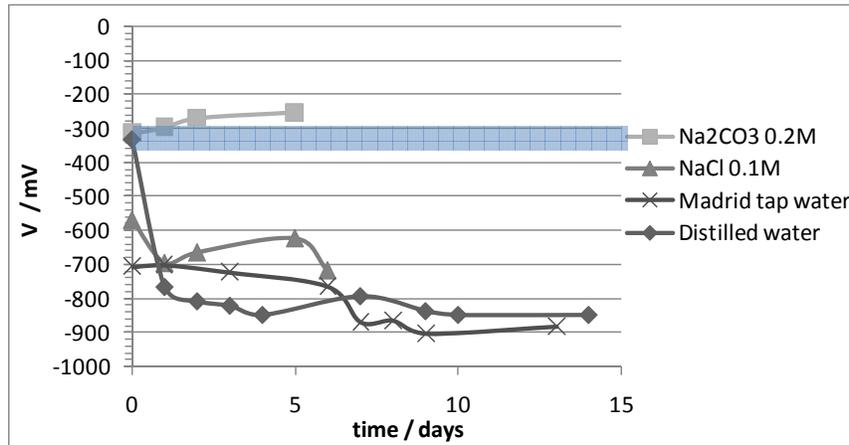


Figure 4 - Corrosion potential, E_{corr} , values versus Mn/MnO reference electrode registered on the bars immersed in different solutions.

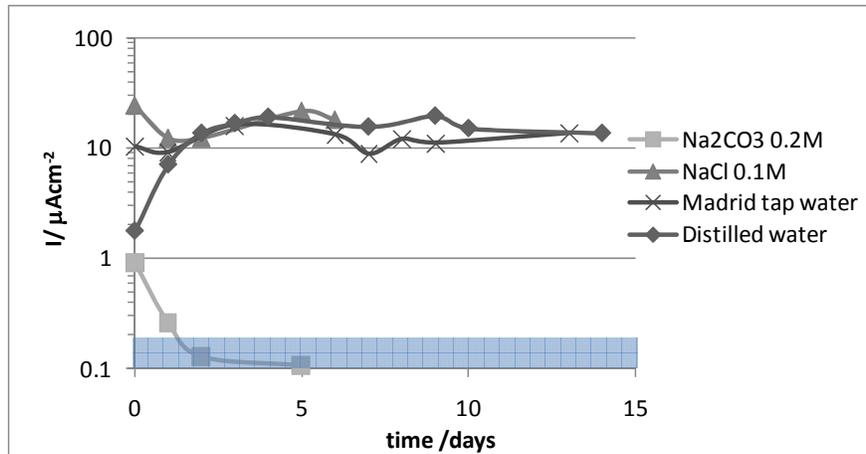


Figure 5 - Corrosion rate, I_{corr} , measurements obtained by the traditional linear sweep method in the solutions tested.

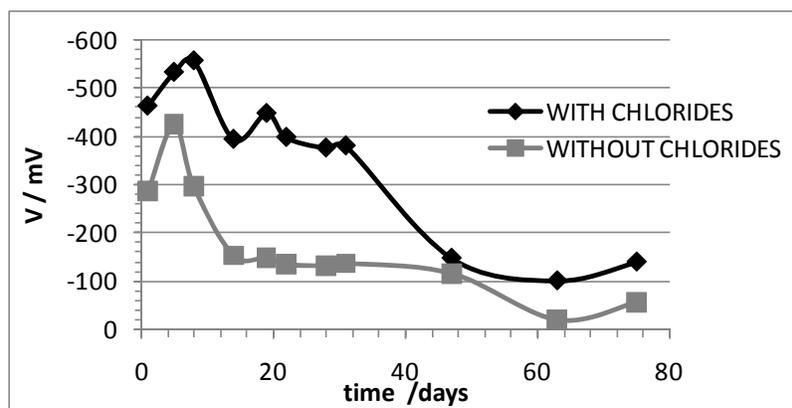


Figure 6 - Corrosion potential, E_{corr} values versus the Ag/AgCl reference electrode of the rebar registered in both the concrete specimens with and without chlorides during all the experiments.

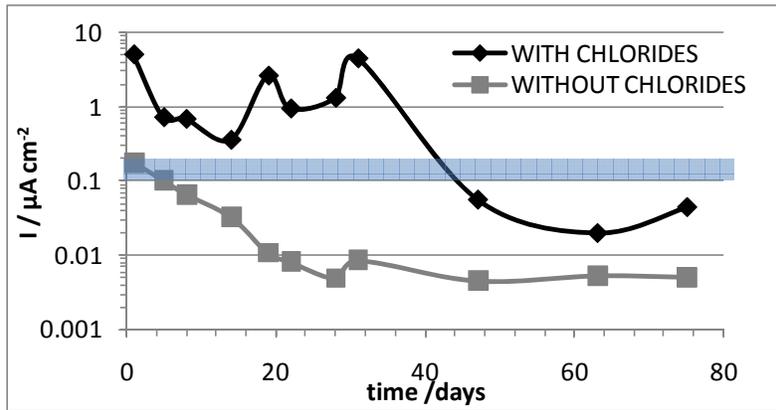


Figure 7 - Corrosion rate, I_{corr} , measured by the traditional linear sweep method (contact with the metal) in the concrete specimens.

NCCm measurements

Solutions: Figure 8 presents the resistivity calculated from the conductivity measurements made periodically on each electrolytic cell during the tests. It can be observed that the resistivity decreases strongly when salts (Na_2CO_3 or NaCl) are present in the solution, being between 0.01 and 0.2 $\text{k}\Omega\text{ cm}$ in these cases, and $>5\text{ k}\Omega\text{ cm}$ when the electrolyte is tap water or distilled water.

Figure 9 present the experimental results obtained by the NCCm, i.e., the R_e and R_{e+M} values that enable the calculation of R_M (R_{pi}). It was observed that the R_{e+M} and R_e values obtained in each solution were always in the same order of magnitude; nevertheless, differences owing to the presence of steel when measuring R_{e+M} were detected. If the electrolyte resistivity was higher, then the R_{e+M} and R_e values obtained were also higher.

In the carbonate and sodium chloride solutions, the resistivity was very low, while in the other two solutions, it was higher by several orders of magnitude. However, the values remained more or less stable during the tests.

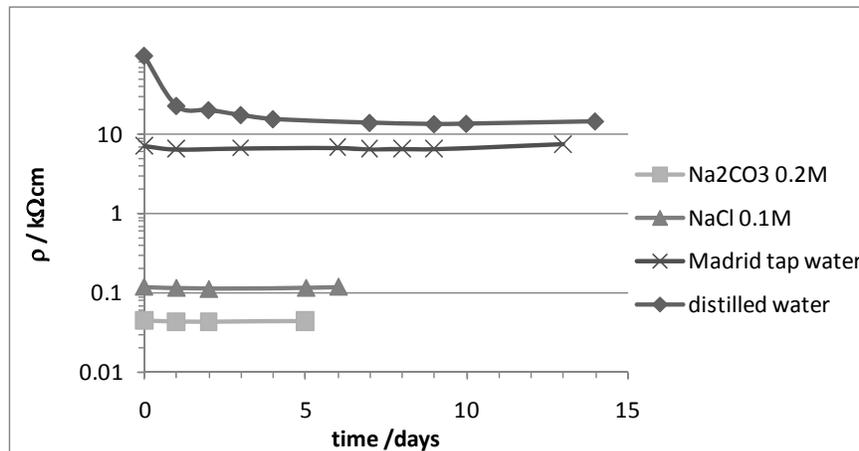


Figure 8 - Resistivity values measured in the different solutions during the experiment.

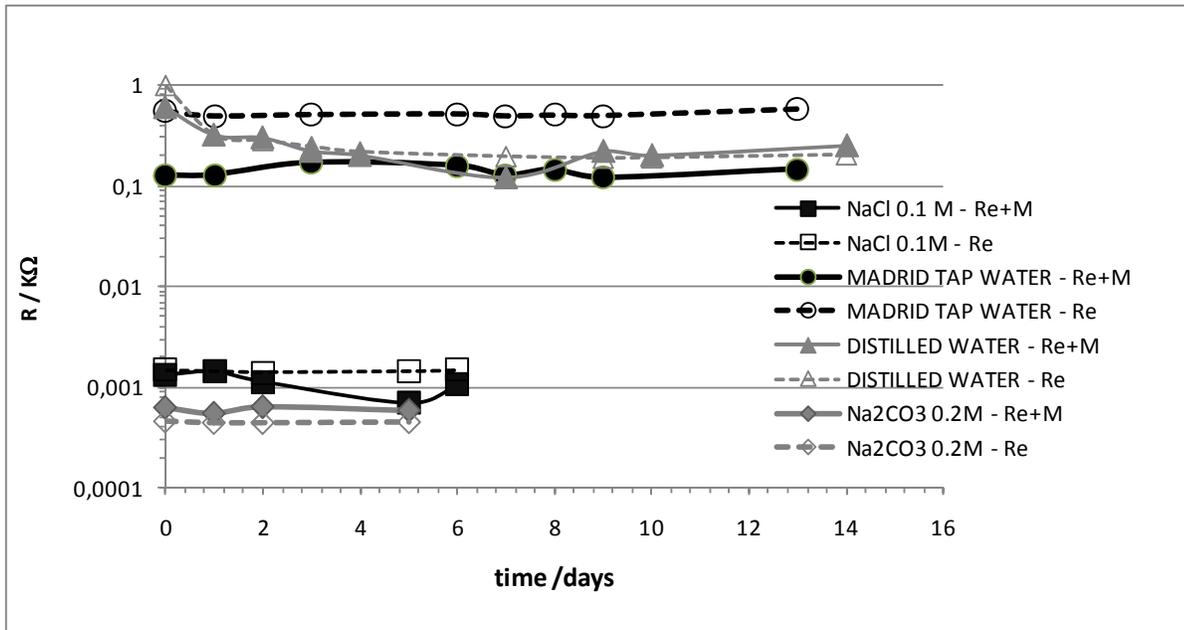


Figure 9 - R_e and R_{e+M} registered using NCCm in different solutions.

Concrete specimens: Figure 10 presents the resistivity values measured in both the specimens (with and without chlorides) during the experiments using the so called Wenner or four points method [11]. During the first 8 days, the resistivity was observed to decrease owing to the water immersion of the specimens. Subsequently, when the specimens were maintained under laboratory conditions, the resistivity of both the specimens increased as the concrete dried, reaching values $>200 \text{ k}\Omega \text{ cm}$, in the case of the specimen without chloride.

Figure 11 present the results obtained with respect to the R_e and R_{e+M} values that are in the same order of magnitude, but differ owing to the presence of the steel embedded in the concrete when measuring R_{e+M} . In both the cases, the values increased steadily during the experiment owing to the progressive curing and hardening of the concrete.

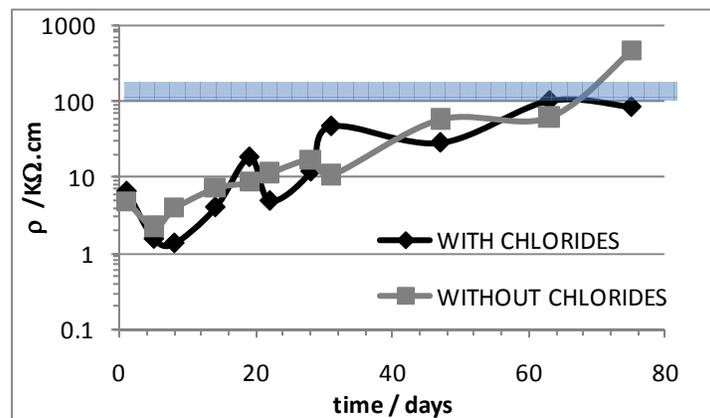


Figure 10 Resistivity values obtained in both the concrete specimens with and without chlorides during all the experiments.

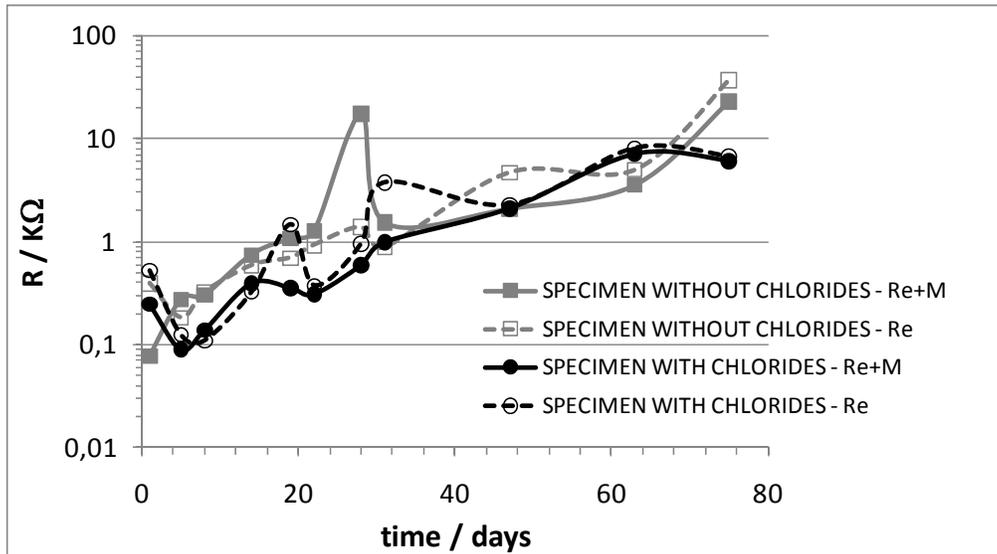


Figure 11 R_e and R_{e+M} registered using NCCm in the concrete specimens with and without chlorides.

DISCUSSION

The R_{pi} , also known as R_M in this study, can be calculated using equation (2), or using equation (3), when $R_e \gg R_M$. If R_e is lower, then the sensitivity of the expression becomes lesser, as the term $1/R_e$ becomes higher. In other words, the proportion of current passing through the electrolyte is relatively high and almost no current is spent in the metal polarization. Subsequently, when the metal corrodes (smaller R_{pi}), if the resistivity is low, then equation (2) may not be sensitive. On the contrary, when R_e is high, the term $1/R_e$ becomes small, and equation (3) can be applied. This shows that it is the proportion of R_e/R_M that indicates the sensitivity of the technique. If R_{e+M} is larger than R_e , then R_M becomes negative and the technique cannot be applied.

These deductions were confirmed in most of the **conductive solutions**, where, in the case of the carbonate solution with very low resistivity, negative values of R_{pi} were obtained, whereas values far from the real ones were obtained in the case of the NaCl solution. Figure 12 presents these behaviours, where the evolution of R_p and R_M (R_{pi}), either calculated from equation (2) or the simplification equation (3), are represented. As indicated in the figure, the closer values to R_p are observed in the case of distilled water, where the resistivity is high enough to have a negligible influence on the value of R_{e+M} .

These facts are coherent with the polarization resistance determination, for which it is necessary to remove the effect of the electrolytic resistance to obtain the correct value of the R_p . This is usually achieved through the positive feedback of the potentiostats. When the removal of the electrolytic resistance cannot be achieved electronically, then it is the ratio of R_e/R_p that controls the feasibility of the correct measurement. The same constraint exists in the non-contacting corrosion tests, but with the limitation that the electrolyte resistance cannot be electronically removed.

This was also verified when plotting the gravimetric and electrochemical losses, and the comparison is given in Figure 13. The figure demonstrates that the gravimetric loss is in agreement with the electrochemical ones as well as the values obtained from the traditional R_p , in the case of distilled water, while the case of tap water being an intermediate one. In other solutions, only the traditional R_p is observed to be in agreement with the gravimetries.

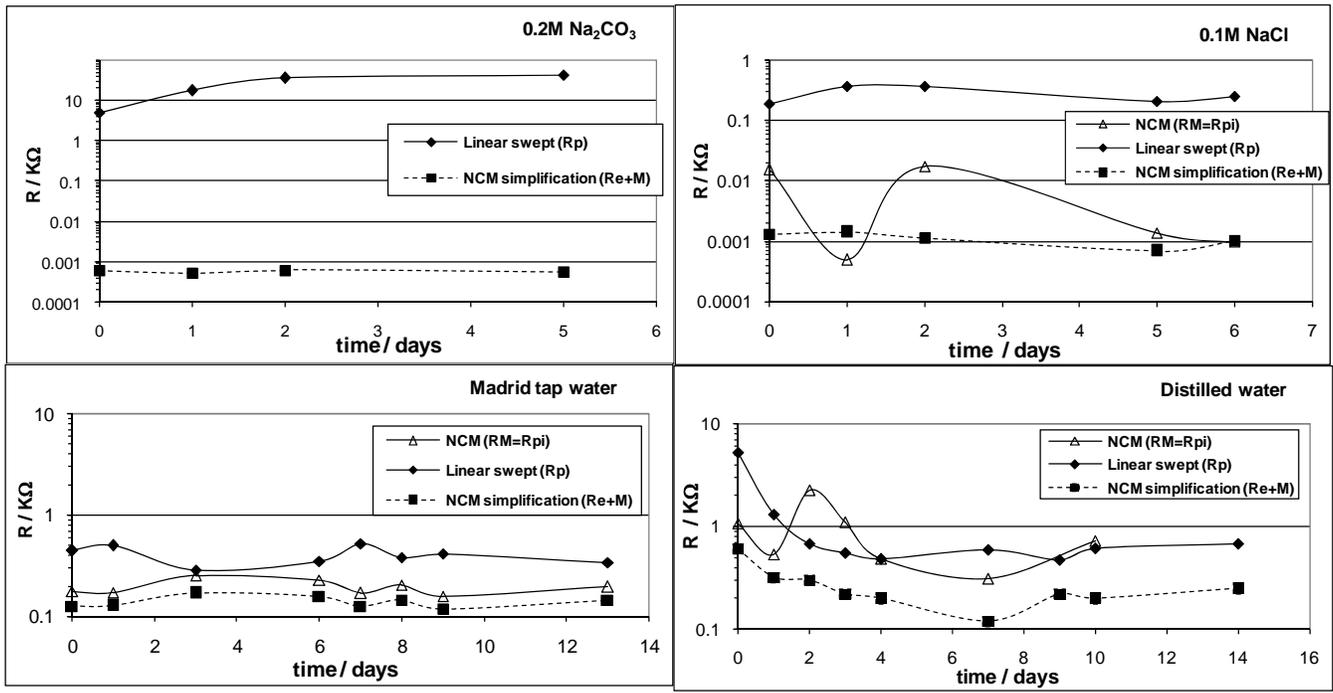


Figure 12 Evolution of $R_M \cong R_{pi}$ (equation 3 – simplified NCCm), R_M (equation 2), and R_p , with time.

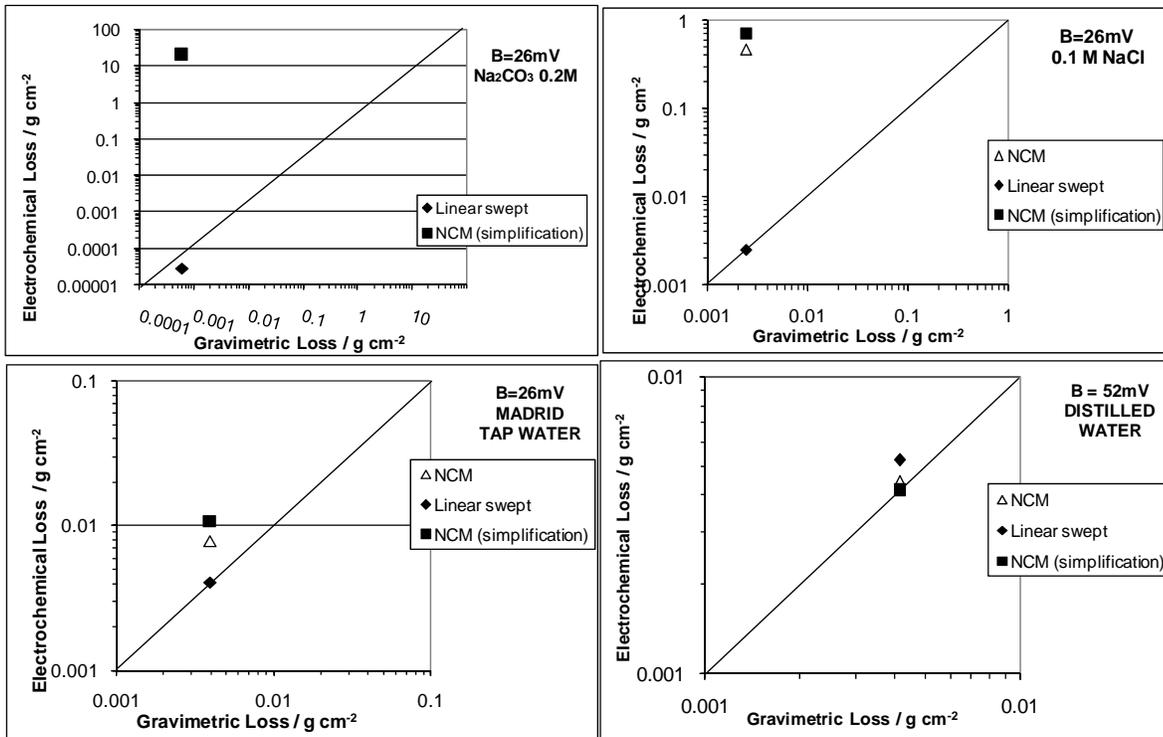


Figure 13 Gravimetric calibration of the results obtained using NCCm applied to the different electrolytic cells.

With regard to the **concrete specimens**, the limitation arises not only owing to the low resistivity, but also because of the high value of R_p in passive state. Figure 14 presents the R_M (R_{pi}), R_{e+M} , and R_p values obtained in the concrete specimens. The R_M values have been calculated using equation (2). When $R_e < R_{e+M}$, equation (2) gives a negative value for R_M . In those cases, the R_M values have not been represented. Furthermore, from the figure, a good correlation between R_M (R_{pi}) and R_p in the specimen

with chlorides can be observed. However, in the specimen without chlorides, the R_M and R_p are observed to be of the same order of magnitude and R_M becomes negative. Nevertheless, at the end of the experiment, when the concrete resistivity is $>100 \text{ k}\Omega \text{ cm}$, the R_M gives positive values. In most of the measurements made in the specimen without chlorides, R_M remains negative.

Regarding the calculation using equation (3), the $R_{e+M} = R_M$ values are observed to be closer to the traditional R_p values in the specimen with chlorides, but in both the specimens, the agreement can be considered satisfactory.

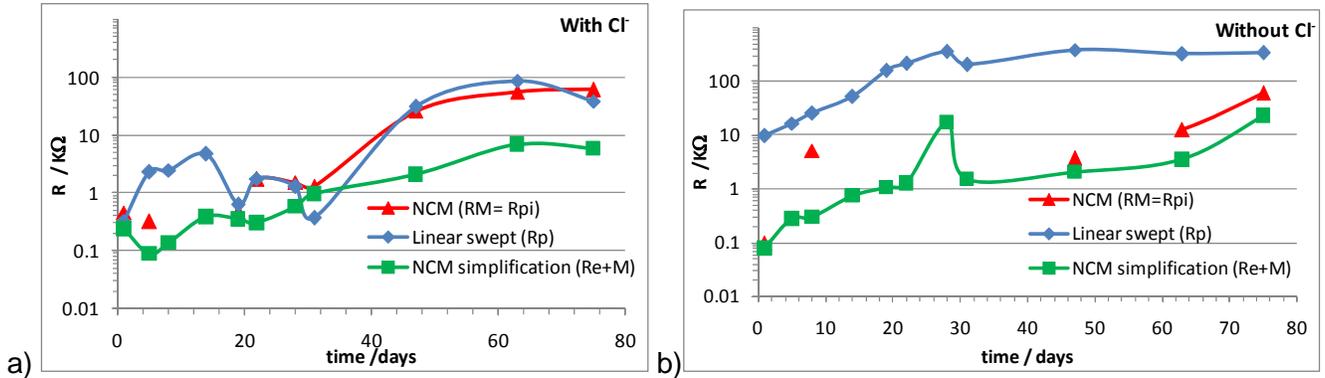


Figure 14 R_p , R_M , and R_{e+M} results registered in the concrete specimens: a) with chloride, and b) without chloride.

General comparison of R_p and $R_M(R_{pi})$

The main objective of this work was to study the limits of determination to the polarization resistance using the NCCm, which is presented in Figure 15, where traditional R_p values are compared with the R_M (R_{pi}) ones, obtained by means of equation (2).

The cases in which the agreement can be considered satisfactory are when the resistivity of the electrolyte is higher than the polarization resistance, i.e., for the tap and distilled water, and when there are chlorides in the concrete specimens. These are the cases in which the metal corrodes and R_M (R_{pi}) is lower than R_e . Conductive ($\rho < 5 \text{ k}\Omega \text{ cm}$) solutions or passive bars in concrete with low resistivity produce values far from the accordance, or even negative when the metal remains passive.

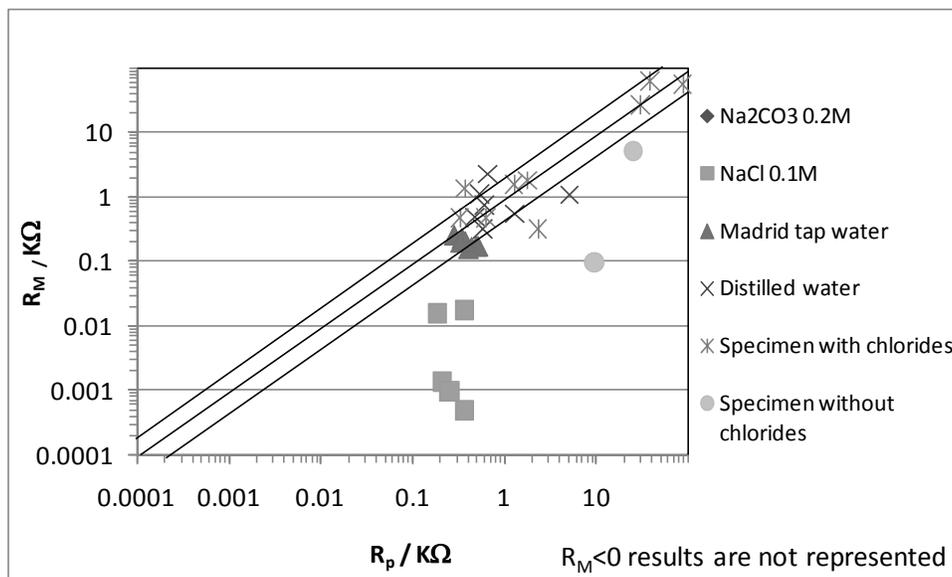


Figure 15 Comparison of R_p and $R_M \cong R_{pi}$ in all the electrolytes and concrete specimens studied.

CONCLUSIONS

The main aim of this study was to explore the limits of application of the non-contacting equations proposed for the R_{pi} calculation through non-contacting corrosion method. The experimentation carried out provided the following conclusions:

- 1) It has been confirmed by means of verifying the agreement in some tests between the electrochemical and the gravimetric losses that the calculation of the polarization resistance, R_p , is feasible through the polarization induced by an external field, without electrically touching the metal. This technique has been named non-contacting corrosion method, NCCm.
- 2) The limits of application deduced indicates that the technique is not applicable when the resistivity is much lower than the R_p and when the steel is passive, unless the resistivity is high. Also is worthy to mention that the comparison between the NCCm (by calculating $R_M = R_{pi}$ through equation 2) and the traditional contacting method provided similar results in the case of active steels immersed in electrolytes of high resistivity. However, negative R_M values were also obtained through this expression when the concrete present low resistivity. The wrong results obtained in this condition could be due to a change in the equivalent circuit that represents the system. More complex circuits are under study for a better understanding of the process.

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