

Impedance spectroscopy in reinforced concrete: Procedure for monitoring steel corrosion

Part I *Development of the experimental device*

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An original experimental protocol is devised to monitor the corrosion of a reinforcing steel embedded in a cement-based material by impedance spectroscopy. The principle of this method is based on the use of a sinusoidal potential applied to measure the impedance response. Preliminary tests were performed from a three-point configuration measurement using classical reference electrodes. Results highlighted the limitations of the introduction of such a reference electrode at high frequencies. Simulations from electric circuits suggested an explanation for these high frequency artifacts. They are mainly due to the high impedance value of the reference electrode which leads to the generation of some artifacts in the impedance response of the studied system. Finally a convenient solution is proposed to eliminate these perturbations and so obtain a suitable measurement of the impedance response of the reinforcing steel/cement based material system at high frequencies. © 2003 Kluwer Academic Publishers

1. Introduction

Reinforcing steel embedded in concrete is naturally protected from corrosion by the high alkalinity of the cement-based materials. However, the aggressive species such as chloride ions can destroy this passive layer and attack the reinforcing steel causing its corrosion. Among the various issues, early detection of corrosion initiation and propagation is of primary importance. Many electrochemical techniques have been developed to monitor the evolution of the reinforcing steel electrochemical state. The most suitable method in aqueous medium is the non-stationary method of impedance spectroscopy [1]. This non-destructive method allows the dissociation of the various relaxation times of a complex system leading to various information on the processes involved over time [2]. The large frequency range used in this method allows obtaining data both at high and low frequencies.

Since 20 years, it has been largely applied to study the microstructure of cement based-materials [3–5] (high frequency domain) and the kinetics of the electrochemical reactions on the steel surface [6–8] (low frequency domain).

Introducing a reference electrode in a three-point measurement allows to control the electrochemical potential of steel (i.e., the working electrode) and to evaluate its response. However special attention must be paid to the three-point configuration at high frequencies. At these frequencies, this configuration can generate some measurement perturbations like capacitive or inductive loops. These distortions were highlighted by various

researchers [9–13]. According to Hsieh *et al.* [10], who studied the effects of the reference electrodes in three-point configuration on solid electrolyte systems (Yttria Stabilized Zirconia System), these distortions are due to a tension divider phenomenon. Ford *et al.* [14] and Xie *et al.* [15] reported this problem on cement-based materials and assigned it to the contact surface between the reference electrode and the sample.

Then the aim of the first part of this work is to develop an experimental set-up capable of eliminating the experimental perturbations associated with the measurement configuration set-up. This first part illustrates the effects of the introduction of a reference electrode in a three-point configuration at high frequencies, which can lead to an inappropriate interpretation of the response of the system. The origins of and a feasible remedy for eliminating these artifacts are discussed.

2. Materials and conservation

The specimens were made up of a circular reinforcing steel plate (60 mm-diameter, Fe E240) and a cement paste or mortar (Fig. 1). The cement-based materials were prepared according to European standard (EN 196-1). Table I presents the composition of the cement-based materials.

The external surfaces of the specimens were covered with an epoxy resin to force the chloride ions to migrate along the specimen axis. Before being tested, the specimens were cured during 28 days in an alkaline solution. This solution (0.025 M of NaOH and

TABLE I Composition and characteristics of the cement-based materials

Material	Paste	Mortar
Deionized water/CPA CEM I 52.5 (w/c)	0.5	0.5
CPA CEM I 52.5/Sand (c/s)		0.33

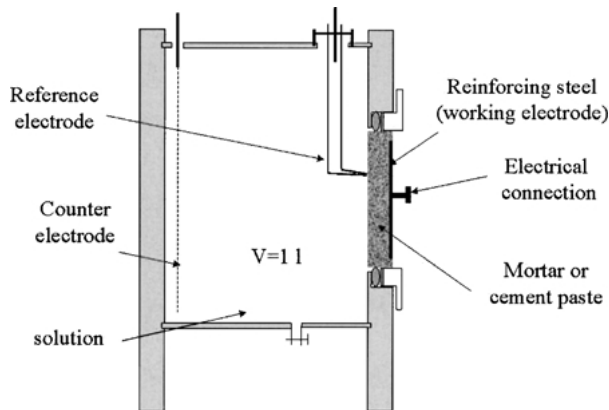


Figure 1 Schematic description of the corrosion cell.

0.083 M of KOH) simulates the interstitial liquid present in the porous network of cement-based materials [16] and thus ensures the specimen saturation. During the test, the specimens are exposed to this solution to which 0.5 M of NaCl were added.

3. Experimental cell and measurement set-up

Fig. 1 presents the experimental cell that is the adaptation of an existing chloride electrodiffusion cell. A three-point configuration was used: a counter electrode (large platinum mesh), a working electrode (cement-based material/reinforcing steel system) and a reference electrode (Saturated Calomel Electrode (SCE)).

The measurement set-up consists of a potentiostat associated to a Frequency Response Analyser (FRA) (Fig. 2).

The potentiostat applies a constant electric field that accelerates the chloride diffusion within the cement-based material. The impedance data are recorded logarithmically down in the frequency range, from 1 MHz to 5 mHz. A small sinusoidal voltage signal of 20 mV is

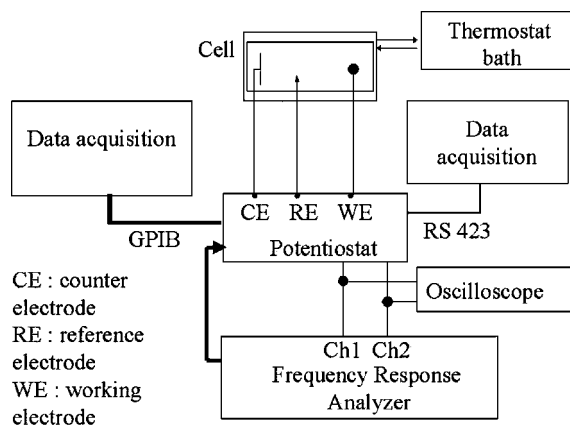


Figure 2 Schematic of the measurement set-up.

overimposed to ensure the linearity of the response. The whole device (including the potentiostat and the Frequency Response Analyzer) has an input impedance equivalent to that of an electric circuit made up of a 10 GΩ input resistance and a 50 pF internal condenser placed in parallel.

4. Results and analysis

In this first part of the work, measurements were carried out by applying a sinusoidal potential perturbation only (i.e., without additional electric field) and the impedance results were limited at high frequencies (1 kHz–1 MHz).

4.1. Preliminary results

A preliminary study used a 1 cm-width cement paste specimen to study the influence of the reference electrode type on the impedance response of the system. Typical Bode plots illustrating its impedance response with different reference electrodes (two SCE and a Mercury oxide reference electrode, respectively) are shown in Fig. 3, modulus (a) and phase angle (b) versus frequency, respectively. The response is only plotted at high frequencies. Note that, for lower frequencies than 1 kHz, measurements for the three tested electrodes are similar.

Results show that, in the 10 kHz–1 MHz frequency range, the impedance response is modified by the presence of the reference electrode. These distortions preclude any analysis of the processes involved in the HF domain (>10 kHz). To model the phenomena associated with the introduction of reference electrodes, the

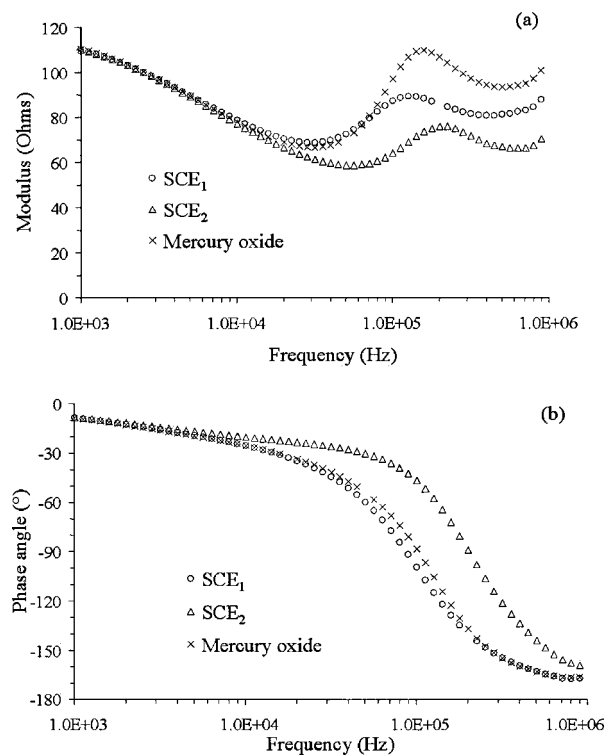


Figure 3 Influence of the reference electrode type. Two SCE (called SCE1 and SCE2) and one Mercury oxide electrode (Hg/Hg₂ SO₄) were tested: (a) Modulus and (b) Phase angle.

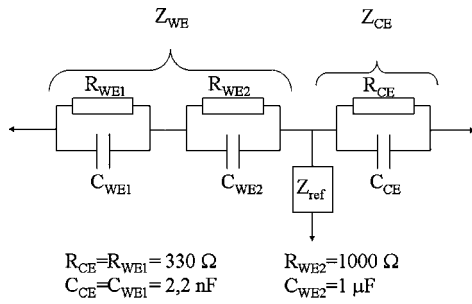


Figure 4 Equivalent electric circuit simulating the reinforcing steel/cement-based material system.

response of an electric circuit made up of resistances and condensers was studied. The elements of the circuit were selected to simulate the impedance response of a reinforcing steel/cement-based material system. This simplified electric model is composed of three elements whose numerical values are specified in Fig. 4 [9]:

- Z_{WE} represents the equivalent impedance of the system made up of the reinforcing steel and the cement-based material (Working Electrode). It is composed of two RC elements ((R_{WE1}, C_{WE1}) associated with the cement-based material and (R_{WE2}, C_{WE2}) associated with the reaction phenomena which take place on the steel surface). This last element includes a high resistance value and a condenser value around $1 \mu F$ [2]. As a consequence, its response will not be presented in the following graphs in the frequency domain studied in this first part of the work,

- Z_{CE} simulates the counter-electrode (CE) impedance,

- Z_{ref} corresponds to the reference electrode impedance. A large range of resistance value (from 10Ω to $100 k\Omega$) was studied. An equivalent circuit associating a $10 k\Omega$ resistance and a $1000 \mu F$ condenser placed in parallel was also tested.

Fig. 5 shows the influence of the reference electrode impedance on the impedance response of the equivalent circuit. As previously observed in the experimental measurements, the impedance response is strongly influenced by the value of the reference impedance in the $10 kHz$ – $1 MHz$ frequency domain. This result shows the relevance of the method to model the experiment. Moreover, an increase of the reference electrode impedance value leads to an increase of the associated distortions. In addition, the coupling of a high resistance value ($10 k\Omega$) and a high condenser value ($1000 \mu F$) has a similar effect to a low-value resistance and allows to eliminate the influence of the reference electrode on the whole impedance of the system. Fig. 6 plots versus frequency:

- the input impedance of the measurement set-up (association of the FRA and the potentiostat),
- the threshold value based upon tolerable deviation particular to the instrument employed (a value of 1% from true impedance is proposed, as suggested by Hsieh *et al.* [9]),
- and the impedance values of the electric elements used to simulate reference electrode.

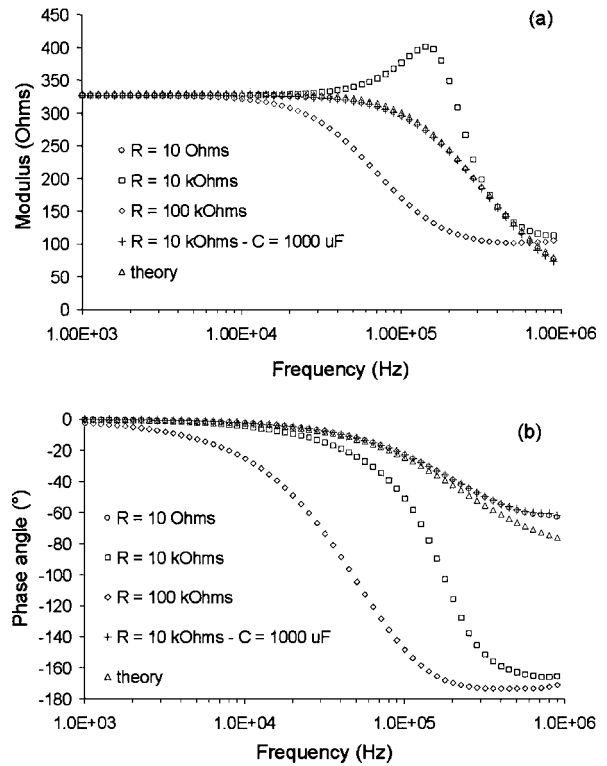


Figure 5 Influence of the reference electrode impedance value on the impedance response of the equivalent electric circuit presented on Fig. 4: (a) Modulus and (b) Phase angle—(legend indicates Z_{ref} value).

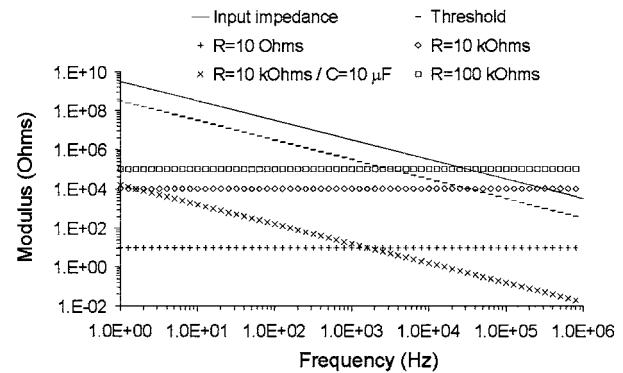


Figure 6 Input impedance modulus of the measurement set-up (Potentiostat + FRA), the 1% threshold and the modulus impedance value used as reference electrode to measure the impedance response of the equivalent electric circuit.

Distortions on the system impedance response appear when the magnitude of the reference electrode impedance exceeds the threshold.

4.2. Experimental device proposed

In their study on YSZ (Ytria-Stabilized Zirconia) system and other solid electrolytes, Hsieh *et al.* [9, 10] put measurement distortions in three-point configuration down to a voltage divider effect, which introduce errors on modulus and phase angle of impedance response. For such a measurement configuration, the relationship between the measured impedance Z_{mes} and the true impedance Z_{real} is [9]:

$$Z_{mes} = r Z_{real} \quad (1)$$

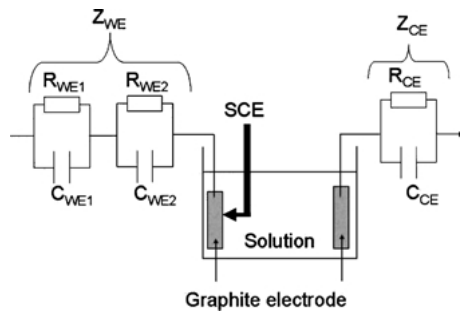


Figure 7 Experimental set-up used to estimate the impedance response of the equivalent electric circuit with a SCE reference electrode.

In this case, the r value is defined by the following expression:

$$r = \frac{Z_{\text{input}}}{Z_{\text{input}} + Z_{\text{ref}}} \quad (2)$$

where Z_{ref} is the reference electrode impedance and Z_{input} , the input impedance of the measurement apparatus (FRA + Potentiostat).

By considering three measurement configurations, Hsieh *et al.* [9] show that the r value can be also deduced using a combination of these three impedance spectra:

$$r = \frac{Z_{2\text{pts}} + Z_{\text{LO}} - Z_{\text{HI}}}{Z_{2\text{pts}}} \quad (3)$$

where $Z_{2\text{pts}}$, Z_{LO} and Z_{HI} are the impedance responses for three different measurement configurations.

An experimental study was conducted to calculate value of r parameter by using the SCE reference electrode in a three-point configuration (Fig. 7). The r value is deduced from Equation 3. The test circuit is described in Fig. 4. A conductive solution was used to ensure a good current transfer between the counter-electrode and the working-electrode. Graphite sheets were used to ensure the electric contact between the solution and the test circuits.

Fig. 8 plots impedance data for the three measurement configurations. The difference between Z_{HI} and Z_{LO} highlights the negative effect introduced by the use of the reference electrode on the measured response (in the absence of voltage divider effect, HI and LO configurations should propose the same impedance spectra).

According to Figs 5 and 6 and Equations 1 and 3, to get the measured impedance close to the real impedance of the system, Z_{ref} must be negligible in comparison with the input impedance Z_{input} (r must converge to unity). However, measurements show that, in the frequency range varying from 25 kHz to 1 MHz, the reference electrode impedance (calculated from r parameter) is significant in comparison with the input impedance of the measurement apparatus (Fig. 9).

5. Application and discussion

To avoid these distortions, a solution consists in reducing the reference impedance value. The test performed on electric circuits described in Fig. 4 showed that the coupling of a high value condenser to a high value re-

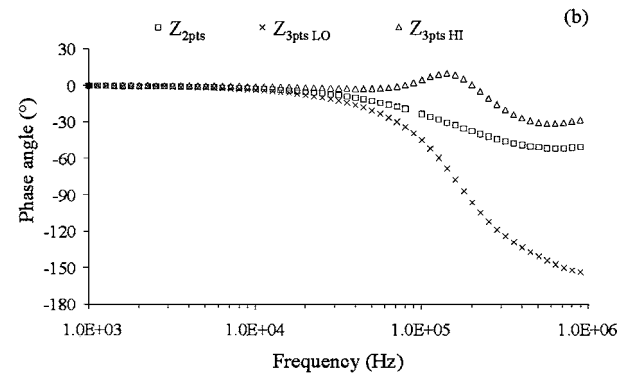
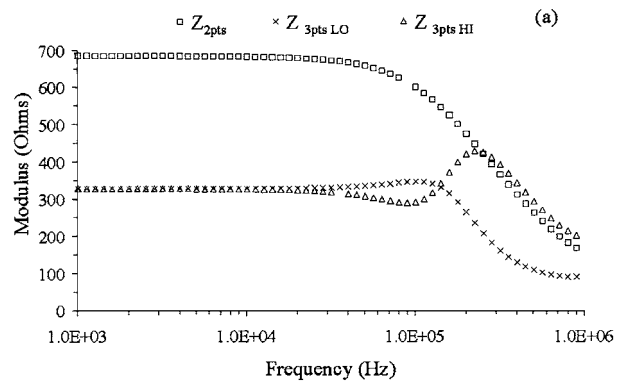


Figure 8 Impedance response of the equivalent electric circuit in the three points measurement configuration proposed by Hsieh *et al.* [9]: (a) Modulus and (b) Phase angle.

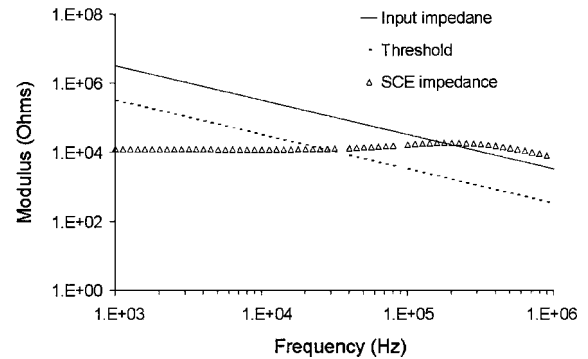


Figure 9 Modulus of the SCE impedance.

sistance allowed to reduce strongly the reference electrode impedance at high frequencies and eliminate its influence on the impedance response measurement. So, from these observations, a particular device was proposed. It associates the SCE reference electrode placed

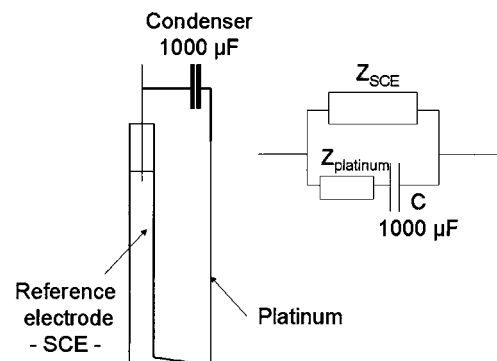


Figure 10 Corrected system schema.

in parallel with a platinum wire (weak resistive and non-reactive in chloride environment) and a high condenser value ($1000 \mu\text{F}$), as described in Fig. 10. The condenser reduces the impedance of the reference system in the HF domain and does not modify the intrinsic properties of the SCE electrode which role is to measure and

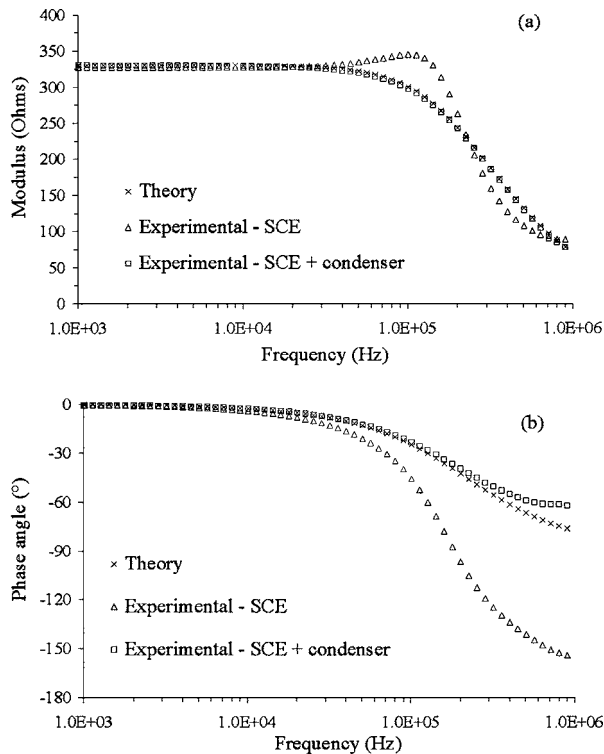


Figure 11 Impedance response of the tested equivalent electric circuit—Comparison between measurements with the SCE only and measurements with the SCE and the condenser: (a) Modulus and (b) Phase angle.

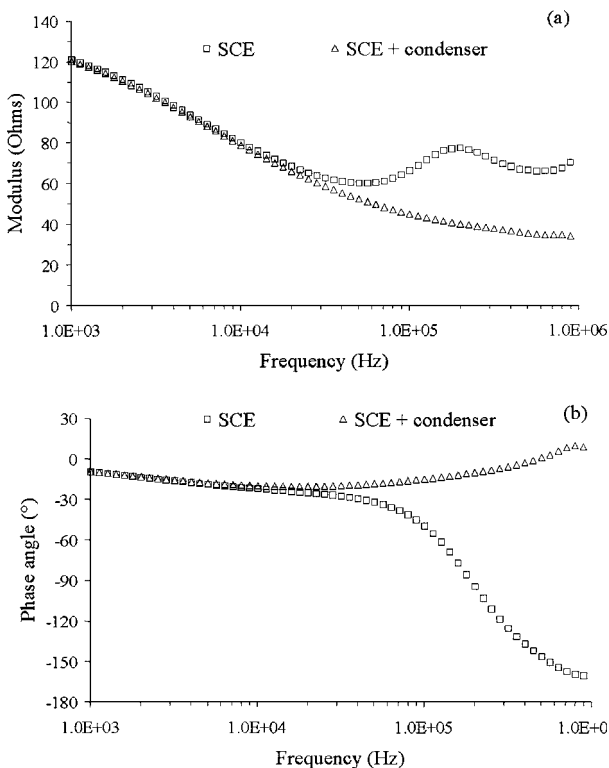


Figure 12 Impedance response of the reinforcing steel/cement-based material system—Comparison between measurements with the SCE only and measurements with the SCE and the condenser: (a) Modulus and (b) Phase angle.

control the electrochemical potential of the reinforcing steel.

In a first application, tests were performed on electric circuits (Fig. 7) by substituting the SCE electrode for the corrective device described in Fig. 10. The impedance spectra (Fig. 11) are similar to the theoretical responses given by considering the known values of the different elements of the electric circuit. Distortion effects observed previously have disappeared in the HF domain. In a second application, the corrector device was then applied in our experimental cell (Fig. 1). Fig. 12 presents the impedance responses of the reinforcing steel/cement-based material system. Good reproducibility is observed in the entire high frequency domain (1 kHz–1 MHz). These results highlight the relevance of the suggested solution.

6. Conclusion

An experimental procedure, based on the adaptation of an electro-diffusion cell and on the use of the impedance spectroscopy method, is developed to monitor in a non-destructive way the corrosion of a reinforcing steel embedded in a saturated cement-based material by chlorides.

The preliminary results showed that the use of a classical reference electrode (SCE, mercury oxide) in a three-point configuration for measuring the impedance of a steel/cement-based material system requires special attention. It generates some experimental perturbations at high frequencies. Simulations on electric circuits (from resistive elements) have led to the identification of the origins of these artifacts. They are due to the high-value impedance of the reference electrode. A convenient solution is proposed to eliminate these perturbations and obtain a reproducible response, essential for a correct exploitation of the impedance spectra at high frequencies. The solution consists in associating a platinum wire of low value diameter ($100 \mu\text{m}$) and a $1000 \mu\text{F}$ condenser placed in parallel to the classical reference electrode.

The results obtained using this original set-up show the relevance of the proposed device. The experimental set-up is now well adapted to characterize the processes at high frequencies involved in the corrosion of reinforcing steel in cement-based materials.

As for the low frequency domain, it will be the purpose of the second part of the work. Let us just indicate that the aim is to accelerate the corrosion process by accelerating the chloride diffusion within the cement-based material coating; i.e., by applying an electric field.

References

1. J. R. MACDONALD, in "Impedance Spectroscopy: Emphasizing Solid Materials and Systems" (John Wiley & Sons, New York, 1987).
2. J. T. S. IRVINE, D. C. SINCLAIR and A. R. WEST, *Adv. Mater.* **2**(3) (1990) 132.
3. C. A. SCUDERI, T. O. MASON and H. M. JENNINGS, *J. Mater. Sci.* **26** (1991) 349.
4. S. J. CHRISTENSEN, R. T. COVERDALE, R. A. OLSON, S. J. FORD, E. J. GARBOCZI, H. M.

- JENNINGS and T. O. MASON, *J. Amer. Ceram. Soc.* **77**(11) (1994) 2789.
5. W. J. MCCARTER, *J. Mater. Sci.* **31** (1996) 6285.
 6. D. G. JOHN, P. C. SEARSON and J. L. DAWSON, *Brit. Corr. J.* **16**(2) (1981) 102.
 7. GU PING, FU YAN, XIE PING and J. J. BEAUDOIN, *Cem. Conc. Res.* **24**(2) (1994) 231.
 8. GU PING and J. J. BEAUDOIN, *Adv. In Cem. Res.* **10**(2) (1998) 43.
 9. G. HSIEH, S. J. FORD, T. O. MASON and L. R. PEDERSON, *Solid State Ionics* **91** (1996) 191.
 10. G. HSIEH, T. O. MASON and L. R. PEDERSON, *ibid.* **91** (1996) 203.
 11. D. D. EDWARDS, J. H. HWANG, S. J. FORD and T. O. MASON, *ibid.* **99** (1997) 85.
 12. S. CHECHIRLIAN, P. EICHNER, M. KEDDAM, H. TAKENOUTI and H. MAZILLE, *Electroch. Act.* **35**(7) (1990) 1125.
 13. G. E. LAGOS, N. BONANOS and B. C. H. STEELE, *ibid.* **28**(11) (1983) 1581.
 14. S. J. FORD, T. O. MASON, B. J. CHRISTENSEN and R. T. COVERDALE, *J. Mater. Sci.* **30** (1995) 1217.
 15. XIE PING, GU PING and J. J. BEAUDOIN, *ibid.* **31** (1996) 144.
 16. O. AMIRI, A. AÏT-MOKHTAR, A. SEIGNEURIN and A. AMMAR-B, in Proceedings of XV^{ème} Rencontres Universitaires de Génie Civil, Strasbourg (1997) p. 259.

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