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Impedance spectroscopy in reinforced concrete: Experimental procedure for monitoring steel corrosion

Part II *Polarization effect*

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An original experimental procedure is proposed to monitor the accelerated corrosion of a reinforcing steel embedded in a cement-based material by impedance spectroscopy. The principle of this procedure is based on the coupling of a constant electric field applied to accelerate the ionic transfer through cement-based material and a sinusoidal potential perturbation imposed to measure the impedance response. Preliminary tests were performed on a three-point configuration measurement using an electric field of 300 V/m typically imposed in electro-diffusion tests. Results highlighted some limitations induced by the strong value of the electric field. Then, an optimization of the procedure is suggested in order to get a convenient accelerated tool for studying the corrosion activity of a reinforcing steel embedded in cement-based materials.

1. Introduction

In a sound concrete, the reinforcing steel is both chemically and physically protected against the corrosion. However the penetration of aggressive species (chloride, carbon dioxide, sulphate, . . .) can lead to the degradation of this passive layer and to the corrosion at the reinforcing steel surface.

Various methods have been reported in the literature to assess the durability of reinforced concrete structures (gravimetric tests, potential monitoring, polarization resistance technique, cyclic voltammetry, electrochemical impedance spectroscopy). The electrochemical impedance spectroscopy is a convenient non-destructive tool for monitoring over time and characterizing the processes involved in the degradation of a reinforcing steel embedded in cement-based materials by the action of chloride ions (diffusion, corrosion) [1–5]. Its large frequency range allows data to be obtained on both the dielectric properties of the cement-based material characterizing its microstructure and the electrochemical processes that occur at the reinforcing steel surface [6–8].

One of major problems for the experiments associated to the study of the corrosion of reinforced concrete structures is that they are very time consuming. The presence of a cement-based material creates a diffusion barrier for chlorides so that much longer times is required for pitting corrosion to be initiated.

Various experiments were reported to limit the test duration by studying the corrosion on uncoated reinforcing steel (only in contact with a simulated pore solution) [9–11] or by applying an electric field to accelerate the chloride arrival at the reinforcing steel surface [12]. This last method, based on the application of a potential difference to accelerate the ionic migration within the cement-based material, is currently used in chloride electro-diffusion tests and leads to acceptable tests duration in laboratories [13]. However, this acceleration induces modifications in the studied system. Some worker have reported limitations in the use of electric fields within cement-based materials. Prince *et al.* [14] described the electrochemical aspects of the accelerated tests of chloride permeability and highlighted the voltage effect on the electrodes. Gonzalez *et al.* [15] discussed the behavior of highly polarized steel embedded in concrete. Other authors [16–18] used impedance spectroscopy for observing the microstructure changes of cement-based materials under a strong electrical field. Consequently the application of an electric field can induce some processes that invalidate the suggested conclusions about the monitoring of the impedance spectra.

Then the objective of this second part of the work is to introduce a rapid and original procedure for studying the corrosion of reinforcing steel in a cement-based material. Basically it is based on the coupling of an electric field to accelerate the chloride transfer within the cement-based material and a sinusoidal potential perturbation to monitor over time the impedance response of the reinforcing steel/cement-based material

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TABLE I Composition and characteristics of the cement-based materials

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

system. This paper highlights the limitations of such a procedure, which are generated by the presence of the constant electric field. Its influence on the studied system is discussed in order to lead to a relevant methodology for monitoring of reinforcing steel corrosion in cement-based materials.

2. Materials and experimental set-up

2.1. Materials and conservation

The specimens and their conservation are the same as those made up in the first part of this work [19]. Let us remind of the coating composition (Table I) and the steel type: a reinforcing steel plate (60 mm diameter, Fe E240).

2.2. Experimental cell and measurement set-up

Fig. 1 presents a schematic description of the measurement set-up and the experimental cell. The measurement set-up consists of a potentiostat (Solartron 1287) associated to a Frequency Response Analyser (Solartron FRA) (Fig. 1). The potentiostat applies a constant electric field that accelerates the chloride diffusion within the cement-based material. The impedance data were recorded logarithmically down in the frequency range, from 1 MHz to 5 mHz. A small sinusoidal voltage signal of 20 mV was overimposed to ensure the linearity of the response. A three-point configuration was used in the experimental arrangement: a counter electrode (large platinum mesh), a working electrode (cement-based material/reinforcing steel system) and a reference electrode system. A special reference electrode device was introduced to eliminate the experimental artifacts in the impedance spectrum at high frequencies; it associates a classical reference electrode (SCE) with a high value condenser put in parallel [19].

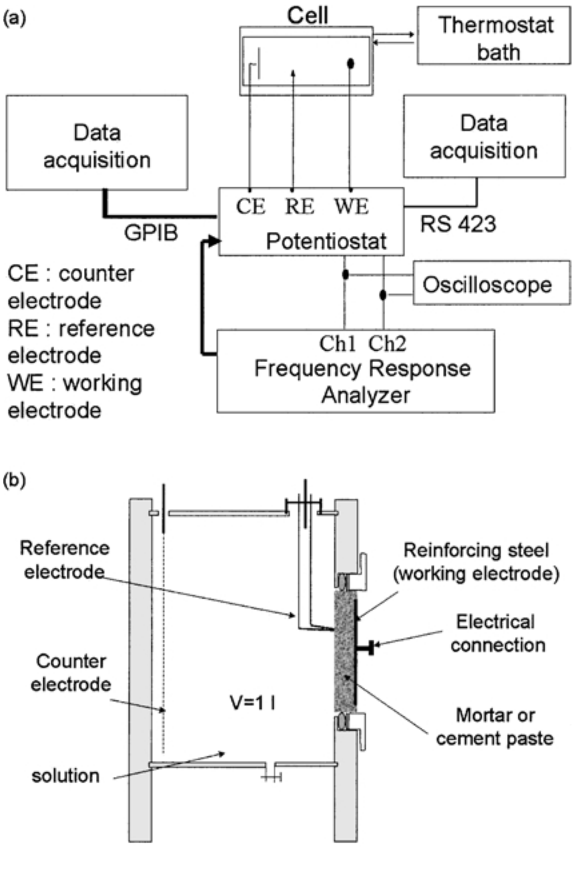

Figure 1 Schematic description of the measurement set-up (a) and of the corrosion cell (b).

The cyclic voltammograms were measured by using potentiostat at a scan rate of 1 mV/s starting from −0.5 V/OCP to +1.5 V/OCP.

3. Results and analysis

3.1. Preliminary results

Tests were conducted on a 1 cm mortar/steel disc system by applying an electric field of 300 V/m, commonly used in electro-diffusion tests [20]. Typical examples of the variations of the impedance spectra over time are shown in Fig. 2.

The Nyquist plots can be described in two parts. A first loop characterizes the high frequency domain. It is well known that the impedance response in this frequency domain is sensitive to the microstructure of the cement-based material. We show that the sample resistance increases significantly over time during the first hours of exposure (until 45 h). After this initial period, the variation is less significant. According to some previous works [16–18], this bulk resistance changes can be attributable to both thermal effects (joule heating) and microstructural changes under applied electric field. But the response in the HF domain is not the purpose of this present work.

A second loop with a very low resistive part appears at lower frequencies. No change over time is detected. Generally this part of the impedance spectrum (low frequency domain) is related to the reinforcing steel surface response dealing with the corrosion initiation [2–4]. At the end of the test (after 150 h of exposure under conditioning), a visual examination of the steel

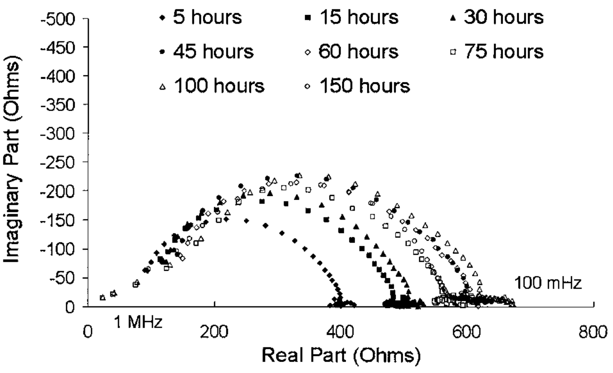

Figure 2 Impedance response of the steel/mortar system (Electric field 300 V/m).

surface highlights a corrosion development. Although the reinforcing steel passed from a passive to an active electrochemical state (i.e., corrosion initiation and propagation), the impedance response in the LF domain, which is sensitive to the electrode phenomena, does not allow distinguishing any change on the corrosion kinetics on the bar surface.

So, the objective of this study, which consists in monitoring the depassivation of the reinforcing steel cannot be reached from these experimental configuration. Consequently, a better understanding of the electric field influence on the impedance system is required.

From these experimental results, it is plausible that the influence of the electric field is not limited to low frequencies measurements. The impedance spectra are modified over time exposure. We attributed these changes to a thermal effect and microstructural changes as suggested in literature [16–18]. However, a more thorough study is required to explain the electric field effect on impedance response at high frequencies and to confirm the conclusions suggested from these observations.

First, let us limit the following discussion to the impedance response at low frequencies in the aim of carrying out a relevant experimental set-up that allows the corrosion monitoring of reinforcing steel surface coated with a cement-based material.

3.2. Behavior of steel under an electric field effect

The electrode potential governs the electrochemical reactions that occur on the electrode surface. So, for the experimental conditions suggested in this paper, the knowledge of this potential is essential to control the electrochemical reactions during the tests. According to Pourbaix diagrams [21], from a given anodic potential threshold, the electrode surface is prone to electrolysis reaction. In our pH (about 12–13), pore solution (0.025 M of NaOH and 0.083 M of KOH) and chloride ions conditions (0.5 M of NaCl in solution), the transformation of the chlorides to hypochlorites can occur. However, according to Prince *et al.* [14], the electrolysis reaction must be the first one to take place on the reinforcing steel surface.

Typical polarization curve for an uncoated reinforcing steel immersed in a simulated interstitial solution (NaOH: 0.025 M, KOH: 0.083 M) shows two stages (Fig. 3):

- the first one, called passivation domain, has its potential between −0.5 V/SCE with +0.5 V/SCE, and a low current density,
- and the second one with upper potential values (> +0.5 V/SCE) and higher current density.

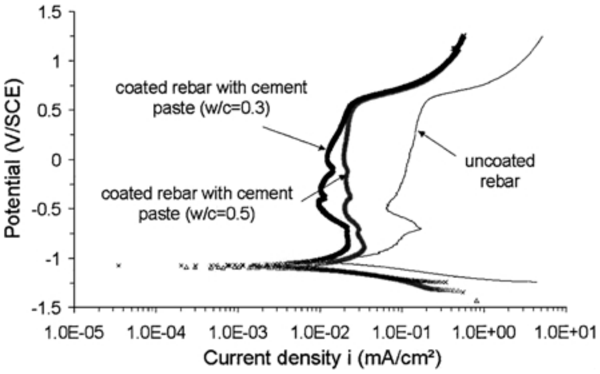

Figure 4 Polarization curve of the reinforcing steel. Influence of the cement-based material coating.

A visual observation of the steel surface during the cyclic voltammograms allows emphasizing the formation of micro-bubbles when the anodic potential reaches +0.5 V/SCE. The increase of the current density during this second stage seems to be induced by the electrolysis process of water (Equation 1) with an oxygen release.

$$4OH^- \rightarrow 2H_2O + O_2 \uparrow + 4e^- \qquad (1)$$

In a similar way, polarization tests were performed to study the case with a cement-based material coating on the steel surface. The results (Fig. 4) reveal no significant alteration of the polarization curves. The comparison with the previous results on an uncoated reinforcing steel (Fig. 3) shows that only the passive currents values are modified. This is the direct consequence of the ohmic fall in the cement-based material and the reduction of the active surface due to the solid phase of the cement-based material.

Fig. 5 shows the voltammograms obtained by repeating the above experiments with NaCl addition: 0.1 M,

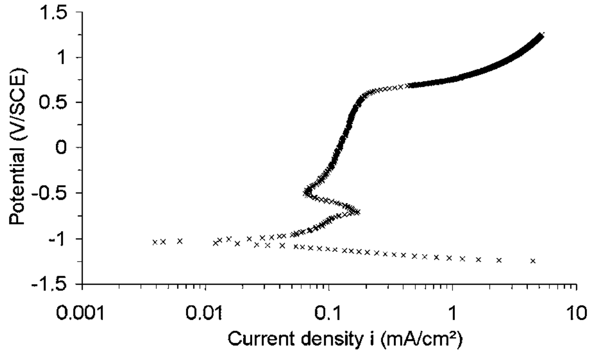

Figure 3 Polarization curve of the uncoated reinforcing steel in alkaline solution with NaOH-KOH used to simulate the pore solution of a cement-based material at 30°C (experimental conditions).

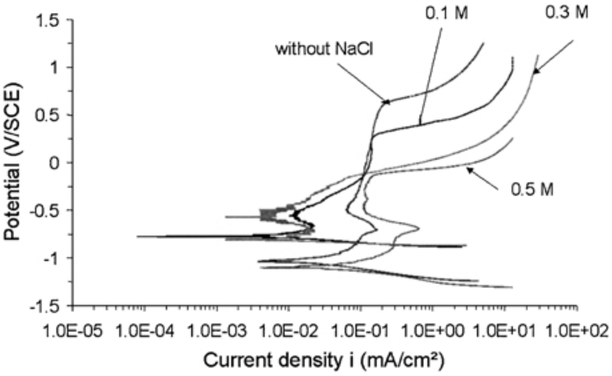

Figure 5 Polarization curve of the uncoated reinforcing steel in alkaline solution with NaOH-KOH (legend indicates the added NaCl concentration).

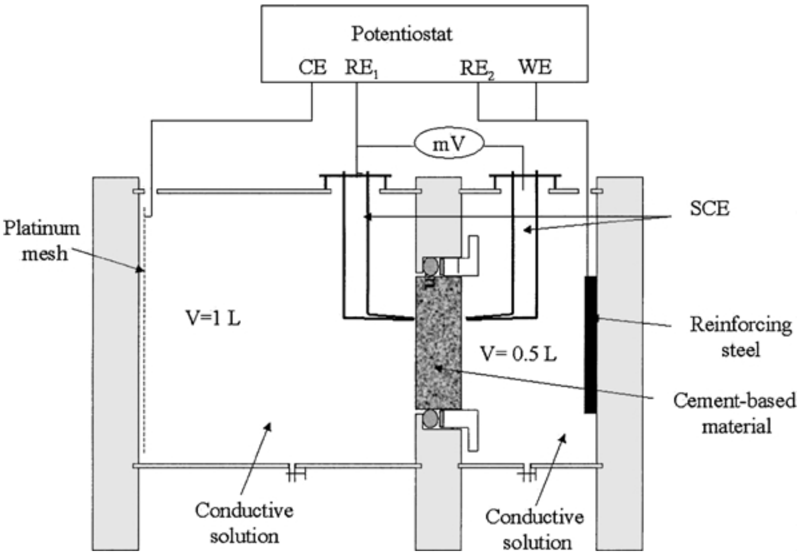

Figure 6 Experimental cell carried out to estimate the electric field at the specimen's sides.

0.3 M and 0.5 M, respectively. A limited passive region appears in case of reinforcing steel immersed in the chloride solution. The voltammograms indicate that the more the chloride concentration is high, the more the potential threshold decreases. The rapid increase of the current density before reaching the anodic potential from which the electrolysis process takes place (+0.5 V/SCE) for the specimens exposed to NaCl can be attributed to a chloride-induced iron dissolution process. When the chloride concentration at the vicinity of the steel reaches a significant value, chlorides tend to be adsorbed preferentially at the electrode surface leading to iron dissolution. We noted by a visual observation of the steel surface the presence of corrosion products during these polarization tests above this potential threshold.

These results (Figs 3, 4 and 5) show that the value of the electric field is an important factor to monitor the corrosion process by impedance response measurements. The application of a high electrical field (300 V/m) generates a high anodic polarization at the reinforcing steel surface. The information given by the impedance diagrams are in agreement with that deduced from the polarization curves. At its high anodic polarization, an active electrolysis process of water occurs at the steel surface: the impedance response is a demonstration of this very fast anodic process associated with high current. In this impedance response, the passive film response is short-circuited. Even if chlorides are in a sufficient concentration for the breakdown of the passive film, the measured impedance at low frequencies remains mainly governed by the electrolysis process and the corrosion due to chlorides will be masked.

As suggested by the series of polarization curves (Figs 3, 4 and 5), the solution for avoiding the electrolysis process at the steel surface consists in limiting the anodic potential value of the reinforcing steel (below +0.5 V/SCE). Then we have to define the effective electric field if the anodic polarization of the electrode reaches the limit value of +0.5 V/SCE.

3.3. The real value of the imposed electric field

An experimental device simulating our experimental configuration was carried out in order to get the true electric field applied between the two faces of the cement-based material (Fig. 6). The reinforcing steel and the cement-based material were separated by a high conductive solution in order to limit the potential fall between the steel and the cementitious material. The experimental results are presented in Fig. 7. Two distinct trends were observed:

– in the passive regime (potential < +0.5 V/SCE), the current density remains low and the electric field value remains below some 50 mV (area I),

– in the second domain (> +0.5 V/SCE), the electric field value increases strongly with the increase of the anodic potential (area II).

Fig. 8 points out the influence of the electric field on the impedance response in the LF domain. The impedance responses of a steel/cement-based material system under various electric field (without electric field, 5 V/m and 300 V/m, respectively) were compared. A high electric field strongly modifies the impedance spectra due to its influence on the electrochemical

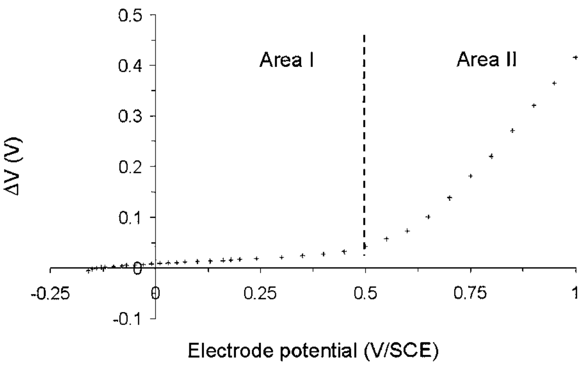

Figure 7 Potential difference between the two faces of the cement-based material versus the anodic potential value applied at the reinforcing steel.

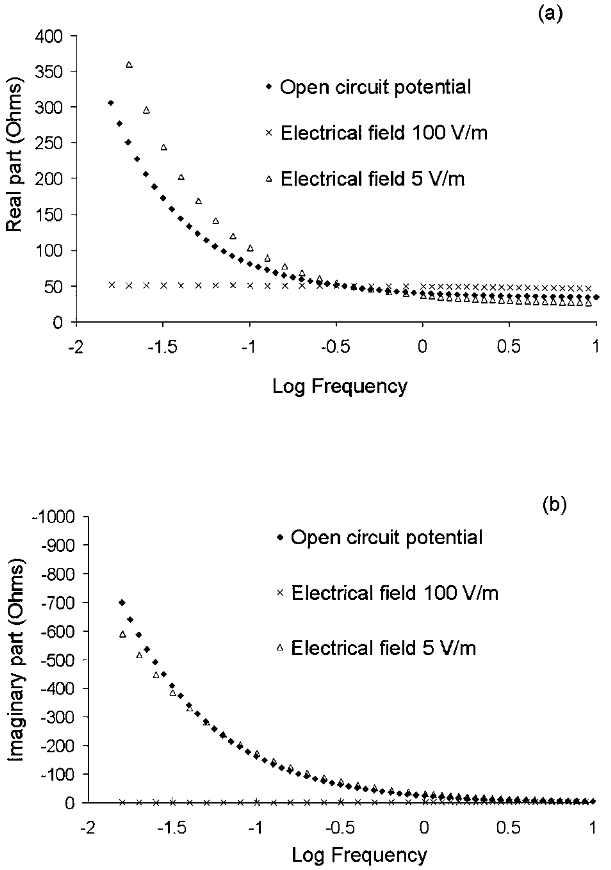

Figure 8 Influence of the electric field value on the impedence response of the specimen. (a) Real part versus Log(Freq.). (b) Imaginary part versus Log(Freq.).

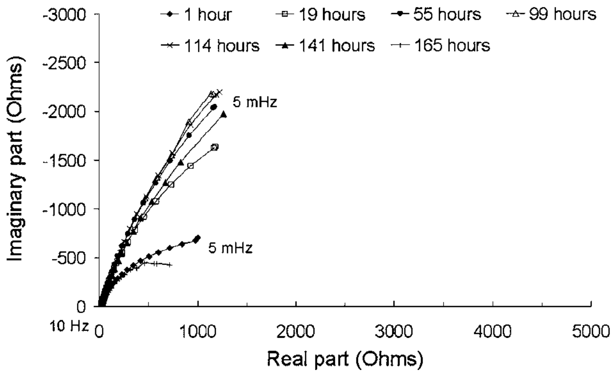

Figure 9 Evolution of the impedance response of the specimen (cement paste $w/c = 0.5$) versus time.

processes that occur at the electrode surface (electrolysis reaction). This reaction masked the other electrochemical processes, which can take place (passive reaction, anodic oxidation of iron).

However, this influence becomes negligible when the electric field value remains below 5 V/m. In this case, the impedance response proposes a similar evolution to that obtained without electric field at rest potential (noted as Open Circuit Potential in Fig. 8).

4. Discussion—Optimized procedure

Preliminary results show that the electric field used to accelerate the chloride diffusion (300 V/m) generated electrochemical processes preventing the corrosion characterization through the monitoring over time of the impedance response. Fig. 8 shows that the electric field had to be limited to a value of 5 V/m to prevent the electrolysis process that masks the other electrochemical processes in the impedance response. As a consequence, this limited value requires reducing the coating thickness to 1 mm to remain in a suitable duration of laboratory tests. In order to preserve the material representativeness and homogeneity, this last modification implies a new experimental constraint: the nature of the coating tested is now limited to a narrow sample group.

From these comments, a complete procedure was performed on a cement paste specimen ($w/c = 0.5$) for monitoring corrosion of reinforcing steel embedded in a cement-based material in contact with a NaCl alkaline solution. The experimental procedure was tested. This study was limited to the low frequency domain (<1 Hz). The impedance spectra (Fig. 9) show a loop with a significant dimension and changes over exposure time. Until 55 h, an increase of the diameter of this loop was observed. It was followed by a stabilized response and finally, after 141 h, a decreasing phase.

At the end of the test, the visual inspection of the sample surface highlighted the presence of cracks with some corrosion products.

The variation of the response at low frequencies is due to the electrochemical reactions that occur on the steel surface. These latter depend on time exposure.

A simplified equivalent circuit model, such as Randles circuit [4], was applied to fitting the low frequency impedance response. The R_P value was plotted versus time (Fig. 10).

During the first hours, the electric field induces an anodic polarization of the reinforcing steel (Fig. 7). Under these potential and pH conditions, the steel is placed in a passive region, supporting a stable oxidized form (Fig. 3) [21, 22]. The formation of this adherent surface film slows down the corrosion rate of the reinforcing steel. This explains the evolution over time of the polarization resistance. The increase of the R_P resistance characterizes the growth of this passive layer over time. After a given time, the system becomes thermodynamically stable and R_P reaches a plateau. During this two periods (increase and plateau), the chlorides migrate within the cement-based materials. When chlorides reach the reinforcing steel surface in a sufficient quantities (which corresponds to the threshold value for

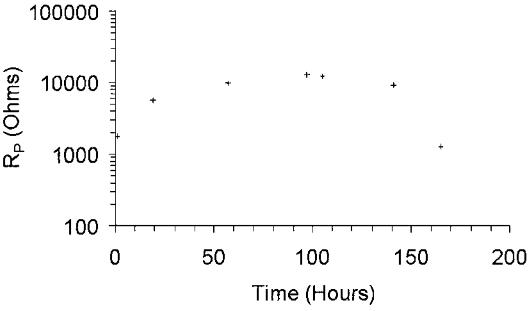

Figure 10 R_P resistance for specimen (cement paste $w/c = 0.5$) as a function of exposure time.

passivity breakdown), the passive film is broken and the corrosion process is initiated by pitting. That leads to a modification of the electrochemical process at the reinforcing steel surface (anodic oxidation of steel with oxygen reduction) and explains the drop of the "polarization" resistance.

The results obtained show the relevance of this suggested procedure. However a more thorough study is planned to analyze the responsible phenomena for the evolution over time of the polarization resistance (SEM observations, EDX analysis, . . .). Other types of coatings will be studied. This part will be the subject of a future paper.

5. Conclusion

In this paper we have introduced an original test procedure to monitor rapidly the corrosion of reinforcing steel in cement based materials. It is based on the adaptation of an electro-diffusion cell and on the use of the impedance spectroscopy. The work points out the special attention that needs to be paid with accelerated testing. The application of a significant electric field introduces modifications on the system response. At high frequencies it leads to microstructural changes and thermal effects [16]. In this frequency range, a more thorough study is required to confirm these comments.

The electric field had also an influence on the impedance response at low frequencies. This frequency domain characterizes the electrochemical processes that occur on steel surface. In accelerated conditions, if the electric field applied is over 5 V/m, the electrolysis process is the main reaction which occurs. It short-circuits the others electrochemical processes, which can take place in the same time on the electrode surface. Consequently the depassivation by chlorides will not be able to be detected.

From the experimental results, an optimization of the procedure is suggested. The electric field has to be limited to a value of 5 V/m. New tests performed from these experimental conditions showed the relevance of the proposed procedure.

Our experimental set-up is now well suited for studying the processes involved in the corrosion of reinforcing steel in cement-based materials. The objectives of the next step will aim to apply this experimental procedure for determining the chloride threshold responsible for the corrosion initiation.

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