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Influence of Unsupported Concrete Media in Corrosion Assessment for Steel Reinforcing Concrete by Electrochemical Impedance Spectroscopy

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ABSTRACT

This work aims at studying the response of unsupported concrete media by Electrochemical Impedance Spectroscopy (EIS) and its influence in the results obtained for steel corrosion in reinforced concrete samples. Measurements carried out in full immersed samples correspond to a typical electrolyte media, presenting essentially a resistive behavior. Thus, rebar corrosion, which appears commonly at intermediate frequency region, can be assessed and easily interpreted.

For samples in partial dry conditions the spectra show several time-constants distributed across the entire frequency range. In the high frequency region, the time constant is ascribed to dielectric properties of the system. At low frequencies the time constant corresponds to the ionic depletion, while the time constant at intermediate frequencies result from charge separation inside the material bulk, typically of unsupported media. Interpretation of the results obtained by EIS for concrete reinforced steel in partial dry conditions cannot be fully interpreted without considering the dielectric behavior of the system.

1. Introduction

One of the most important problems in concrete durability is related to fluids uptake. Water, fog and air from the environment are the most important carriers of harmful elements. The characteristics of the pore system play a decisive role in engineering properties of concrete [1]. Moreover, concrete mechanical properties such as strength, durability and permeability are function of the material porosity [2]. High permeability causes a faster penetration of solutions, resulting in rapid concrete deterioration [3,4]. From this point of view, the interaction between harmful ions (like chlorides and sulfates) and the steel reinforcement could lead to severe corrosion threatening the whole structure.

By this reason, in the last decades, several authors have studied the reinforcement corrosion activity in concrete by Electrochemical Impedance Spectroscopy, EIS [5–10]. One of the most common environmental conditions that promote corrosion involves dry or partial dry-conditions especially, dry-wet cycles, which play a crucial role in what concerns corrosion activity. In such conditions concrete becomes an unsupported media and the obtained results are an expression of steel corrosion and concrete impedance response. Theoretical studies presented by Macdonald *et al.* [11,12] interpreted the phenomenon of EIS in unsupported media by taking into consideration that the complexity of the response must be related with charge separation inside the film bulk.

For measurements carried out in partial dry conditions, particularly associated with dry-wet cycles, the results are affected by ions, water and gases transport. This can occur by three mechanisms: permeability, diffusion and absorption [13]. These mechanisms are governed by the pore structure, which is characterized by the porosity, connectivity between pores and pore size [14], which is the main factor influencing the porosity is water-cement ratio (w/c) [15]. However, other factors, like cement type, can also affect the porosity [16]. Nevertheless, the tests to assess the permeability coefficients are long and relatively complicated [17]. EIS technique is a very suitable technique to determine concrete properties, such as permeability. Several authors have already used this non-destructive technique to reveal the microstructure of concrete [18,19].

It is well known that Fickian diffusion process is an analogue problem to Fourier heat conduction and 2nd Fick law describes the diffusion process in a transient-state. For a short diffusion times,

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that is, for the beginning of diffusion in a membrane with parallel surfaces, the profile of any specie diffusing inside the membrane is given by the following equation [20,21]:

$$\frac{c_0 - c}{c_0 - c_s} = erf\left(\frac{x}{2\sqrt{Dt}}\right) \quad (1)$$

in which D is the diffusion coefficient, t is the time, x is the distance inside the membrane bulk to the surface and c, c_s, and c_0 are the specie concentration at distance x for time t, saturation (s) and dry condition (0), respectively. To derive this equation several other conditions were considered, such as: the thickness of the diffusion layer must be much smaller than the membrane thickness, d, if diffusion occurs only at one surface side, or half the membrane thickness, if the diffusion occurs at both surfaces, and Fourier number is given by $Fo = Dt/d^2 < 0.05$; For the beginning of diffusion, $t = 0$, the concentration is residual, $c = c_0$; The concentration is maximum, $c = c_s$, at membrane surface, $x = 0$, while for $x \rightarrow d$ the concentration is residual, $c = c_0$ [22,23]. This equation was used in concrete samples by several authors [24–26]. In such conditions integration of equation 1 throughout all the membrane dimensions allows to obtain another equation that permits to determine the average diffusion coefficient for the early stages of diffusion [20,27–30]:

$$\frac{\phi_0 - \phi}{\phi_0 - \phi_s} = \frac{4\sqrt{D}}{d\sqrt{\pi}}\sqrt{t} \quad (2)$$

in which ϕ, ϕ_s, and ϕ_0 are the specie uptake for time t, saturation (s) and dry condition (0), respectively. To apply this equation to a membrane (coating, polymer, concrete, etc.) it is necessary to estimate the ϕ, ϕ_s, and ϕ_0 values using several experimental results such as impedance, gravimetric measurements, etc.

This work aims at studying the response of unsupported concrete media by EIS and its influence in the results obtained for reinforcing steel corrosion in concrete samples.

2. Experimental

Six different concrete mixtures were designed with the aim of covering a range of water-cement ratio (w/c) typically encountered in reinforced concrete and considering the type of cements most commonly used. Limestone coarse aggregates and natural silica sand were used. Characteristics of the concrete mixes are summarized in Table 1. The mixing time was about 5 minutes. More details about the concrete mixes and mixing procedures can be found elsewhere [32]. The tests were performed in small cylinders (150 mm diameter and 50 mm tall) sawn from larger ones (150 mm diameter and 300 mm tall). The original specimens were removed from molds at 24 hours and kept in tepid (20 °C) water for 7 days.

The 300 mm tall cylinders were sawn in slices of 50 mm which were coated with a double layer of adhesive aluminum in their molded (curved) surface. In the conditioning period, between the end of curing and permeability testing, which occurred after 28 days, all specimens were kept in a laboratory chamber at 20 °C and 60% RH. The specimens were kept in the conditions of the conditioning period between the end of the permeability tests and EIS tests.

Air permeability was assessed, using a test method developed by Torrent [33], which presents a good correlation with oxygen permeability assessed by Cembureau method [34], the latter of which is recommended by RILEM TC 116-PCD [35] and considered as "reference test" by RILEM TC 189-NEC [36] to characterize gas permeability. Compared to Cembureau, the Torrent method has the advantage of being faster, since gas permeability is assessed in a non-steady state. The principle of the test is to create a certain degree of vacuum in the test chamber using a vacuum pump and then cut the connection between the vacuum pump and the test chamber and measure the rate at which pressure increases in the latter. This makes it possible to calculate air permeability coefficient kT associated with this method [37].

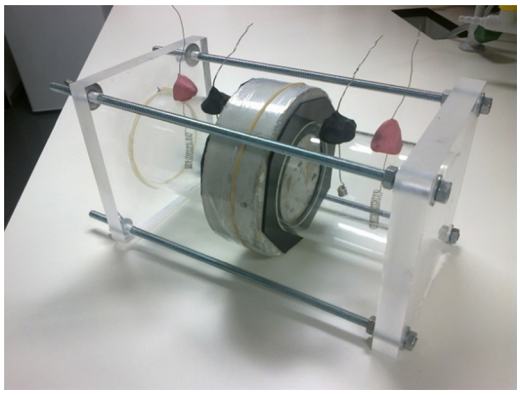

Fig. 1. Picture of a four electrodes arrangement cell used for the saturation tests.

The saturation tests were performed using a 1% sodium chloride (NaCl) solution in the two-compartment cell and using a four-electrode arrangement. The concrete sample was held between the compartments, with two smaller platinum electrodes working as pseudo-reference electrodes and two larger platinum electrodes acting as counter electrodes (fig. 1). To avoid the short-circuiting of the current by the surrounding environment rubber washers were used on both sides between the container and the samples. The transversal area exposed to the electrolyte was 50.12 cm^2, while 176.71 cm^2 was the total transversal area of the samples. The ratio between the total area and the exposed one was 3.5.

For the drying tests, a two electrode arrangement cell was used, in which two plates of stainless steels (316L), with 100 cm^2 each and the ratio between the total area and the exposed one was 1.77, were compressed against the sample flat faces, operating each one simultaneously as counter and reference electrode (fig. 2). For the saturation tests the EIS measurements started about 30 seconds after full-immersion and were carried out until saturation occurs, that is, until low frequency impedance were stabilized, between 14.5 hours and 145 hours depending of samples type. The samples were kept in immersion during at least 1 week to guarantee that full-saturation condition was achieved for all of them. Afterwards, samples were removed from solution and assembled in the two-electrode arrangement cell. The EIS drying tests started about 2 minutes after samples were removed from solution. These tests were performed continuously during 120 hours to 180 hours until the samples dryness imposes difficulties for EIS measurements and spectra stabilization occurred.

The EIS measurements were conducted using a Zanher Zennium Electrochemical Workstation. The frequency range used at the

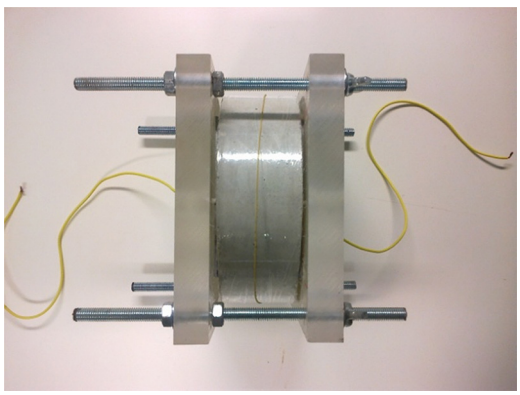

Fig. 2. Photograph of a two electrodes arrangement cell used for the drying tests.