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The effect of long-term atmospheric aging and temperature on the electrochemical behaviour of steel rebars in mortar

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ABSTRACT

This study describes changes in the electrochemical properties of carbon steel reinforcement bars embedded in mortar after their exposure to a mild atmosphere for 15 years. The development of an oxide layer was followed using electrochemical impedance spectroscopy. The samples were also subjected to a temperature cycle that allowed an electrical equivalent model to be developed in order to understand the electrochemical behaviour. This study concluded that the oxides layer plays a key role in the corrosion process by supporting the cathodic reaction. The oxide layer was identified in the frequency range of 10 kHz–1 Hz, and it grew rapidly during years 3–10 of atmospheric exposure. The aged oxide layer was also damaged by temperature cycling, which decreased the barrier effect.

1. Introduction

Reinforced concrete is the material most commonly employed in civil construction thanks to its unique cost to mechanical performance ratio. Although reinforced concrete elements and structures are expected to last for several generations, everyday experience shows that this is not true. Repairs actions are often necessary after only a few years.

The chemical stability of the steel reinforcements depends on the formation of the passivation layer, which confers the stability that is key for durability. The passive layer degrades in low pH environments (which occurs in carbonated concrete) and in the presence of chlorides (which are typical of marine environments).

Although carbonation and chlorides are the main factors that affect the durability of reinforced concrete structures, the exposure conditions must also be considered for reliable lifetime predictions. Wetting/drying cycles and temperature are among the most relevant environmental factors involved.

The present communication aims at reviewing recent literature on the effects of temperature on both the concrete cover and the passive layer in order to introduce new data on electrochemical impedance spectroscopy (EIS) measurements performed on samples that have been exposed for up to 15 years outdoors in our laboratory.

Regarding the passive film, its comprehensive characterization has been the focus of many studies over the recent decades. A large number of these reported studies included a passivation assessment in simulated pore solutions [1–12]. This specific experimental procedure has

allowed researchers to precisely control the variables affecting the performance of the passive layers. Thus, the pH value, electrolyte composition, or chloride content are the main factors traditionally discussed in the literature. Valuable information concerning the corrosion resistance of these films could be obtained, mainly by focusing on the determination of the critical chloride content for pitting nucleation [3,5,7,8]. On the other hand, some other important achievements have also been attained concerning the thickness, chemical composition and structure of the passive films developed under a variety of experimental conditions [4,6,9–11,13]. The main inconvenience of performing the analytical experiments in an aqueous electrolyte is the length of the testing period. Typically, testing times shorter than a few days are used, and no long-term studies can be completed in practice. Reinforced concrete specimens must be considered in order to execute a bone fide long-term analysis [14–16]. In this particular system, special attention must be paid to the electric field distribution, especially when performing measurements in the high frequency domain [17,18].

The influence of the surrounding environmental temperature is a neglected issue in reinforced concrete durability studies. A few researchers have included this parameter as a factor influencing the corrosion performance. The simulation model developed by Pour-Ghaz et al. [19] has shown that an increased corrosion rate occurs with discrete temperature increments, but no subsequent changes in the passive layer were reported. Andrade et al. [20] studied the corrosion performance of concrete structures exposed to real atmospheric conditions (including daily and seasonal temperature cycles), but, again, no

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precise correlation with the rebar passive state has been discussed. Deus et al. [21] found modifications in the composition of the passive layer, namely, an increased oxidation level along with an increased hydroxide content as the temperature increased. This revealed the major influence that temperature has on the film protection ability. In another recent study by these authors, changes in the chemistry of the pore's electrolyte were found to be linked to the temperature variations that ultimately influence the properties and performance of the developed passive layers [22].

The present paper describes the influence of the artificially controlled temperature cycles on the physical properties of the passive layer that naturally develops on steel rebars in reinforced mortar samples exposed for 15 years to the atmosphere. The effects of the aging process are also discussed here by comparing the sporadic measurements that have been recorded over that period.

Among the analytical methods commonly used to characterize the passive layers, electrochemical impedance spectroscopy has been demonstrated to be a suitable tool for the non-destructive assessment of the passive layers [15,16,22,23]. The choice of an appropriate equivalent model is a critical step for successfully interpreting of the data obtained in this study. In this sense, a circuit based on the transmission line model originally developed by Macdonald for the analysis of porous layers [24] was found adequate for the study of other conducting films [25,26], and has been adapted for use in the present study.

2. Experimental

2.1. Preparation of the samples

The samples were prepared as described previously [27] using cement CEM I 52.5R, and the water/cement and sand/cement ratios were 0.5 and 3, respectively. Sand ϕ was equal to 0–6 mm. Mortar samples were cast in a cylindrical shape with a carbon steel bar, where ϕ was 8 mm. The samples were then placed in the centre, as depicted in Fig. 1. The results presented here correspond to two specimens.

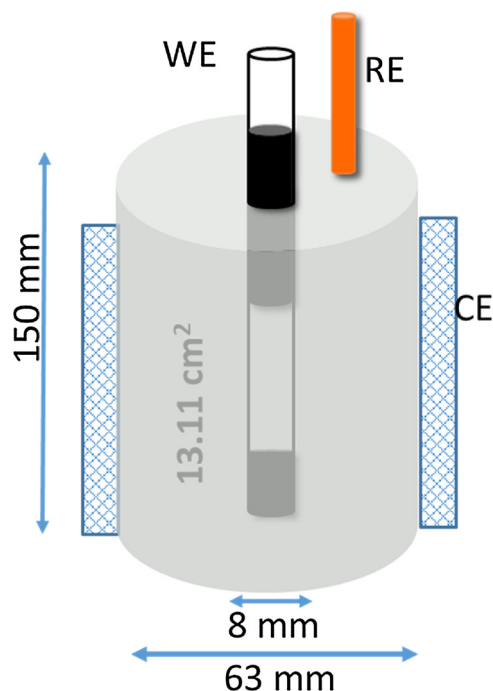


Fig. 1. Schematic view of the electrochemical cell arrangement. The active surface of the rebar, (13.11 cm^2) is defined in the central part by epoxy coating, as illustrated. The counter electrode, a graphite sheet, surrounds the mortar, and the reference electrode is placed on top.

After 28 days of curing, the samples were exposed for 15 years in a mild rural-marine atmosphere that could be classified according to the ISO 9223:2012 [28] as S1 and P0 in terms of chloride and SO_x depositions, respectively. However, the wetness time was long (classified as T5). The ambient temperature ranged from 5–15 °C during the winter and 15–30 °C in summer.

2.2. Electrochemical measurements

Electrochemical measurements, corrosion potential (E_{corr}) and electrochemical impedance spectroscopy (EIS) were taken periodically during the 15-year exposure period using different potentiostat models, Metrohm- Autolab® or Eco Chemie®. The cell arrangement is represented in Fig. 1 and has been described elsewhere [18,27]. The working electrode (WE) was the rebar studied, the counter electrode (CE) was a flexible graphite sheet surrounding the mortar cylinder and the reference electrode (RE) was a saturated calomel electrode (SCE). The ionic contact between the RE and CE with the mortar was assured by the use of a wet pad. These measurements were performed at room temperature.

After 15 years of natural weathering, the effect of temperature on the electrochemical parameters was studied. To do this, the mortar cylinders with CE and RE were introduced in a double-wall thermo-regulated baker that had a large enough diameter to let a 2–3 mm layer of water for ionic contact between the CE and mortar. The RE element was maintained external, at ambient temperature, and connected through a wet pad. The temperature of the circulating bath varied at steps of 5 °C, and the electrochemical measurements were taken after a minimum of 24 h to ensure thermal equilibration at the rebar level [21,29]. For this series of measurements, an Autolab® PGSTAT204 was employed. The temperature was controlled using a Lauda® Brinkman Ecoline Recirculating Chiller RE 415 thermostat.

2.3. Surface examination

Following temperature cycling, one of the reinforced specimens was broken so that the exposed surface and a cross section of the rebar could be examined by light and electron microscopy. For light microscopy, an Olympus GX71/GX51 Inverted Metallurgical Microscope was employed. For scanning electron microscopy (SEM) and energy dispersive X-ray (EDX), an Electroscan JSM-54 model JEOL 5410 equipped with an energy dispersive X-ray detector Link ISIS 300 was used.

3. Results and discussion

3.1. Characterisation of the oxide layer

Upon extraction from the mortar, the rebar had the appearance of uncorroded steel with only a slight rust colour (Fig. 2A). However, a cross section revealed the presence of an approximately 28 μm thick homogeneous oxide layer (Fig. 2B–C). Considering that magnetite and hematite (with densities 36.4% and 34% less than that of iron, respectively) are the main products of corrosion, the 28 μm thick oxide layer corresponded to about 18 μm of rebar thickness loss (i.e., an average of $1.2 \mu\text{m y}^{-1}$ or $0.1 \mu\text{A cm}^{-2}$, assuming the Fe/Fe^{2+} process involves $1 \mu\text{A cm}^{-2} = 11.6 \mu\text{m y}^{-1}$). The range of 0.1 – $0.2 \mu\text{A cm}^{-2}$ is commonly considered to be the threshold value between passivity and active corrosion [30]. Thus, the observed oxide scale corresponded well to a situation of passivity, which was expected for the mild atmospheric conditions of exposure, but approached the limit usually considered for active corrosion [30].

This structure of the oxide scale is very convenient for the discussion that follows because the entire surface seemed to have a homogeneous reactivity, and no parallel paths for current flow due to preferential dissolution had to be considered.

The chemical analysis of the oxide layer presented in Fig. 3 also

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