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The electrochemical behaviour of steel rebars in concrete: an Electrochemical Impedance Spectroscopy study of the effect of temperature

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ABSTRACT

The effect of temperature on the electrochemical behaviour of reinforced mortar samples contaminated with chlorides was investigated using EIS. The results show an exponential dependence of the mortar cover resistivity with the temperature. This dependency was interpreted as being due to electrostatic interaction between moving ions and charged pore walls, at the gel level structure.

The corrosion rate showed a complex dependency with temperature. The Eyring equation explained the behaviour, with distinct reaction paths above and below about 30 ^{0}C, the temperature at which the electrolyte reached a pH of 12. In the presence of chlorides, the pH was lower for a given temperature.

1. Introduction

The corrosion behaviour of steel in concrete is highly dependent on the steel surface state [1] and the chemistry of the concrete cover [2,3]. The electrochemistry at the rebar-concrete interface depends on the environment in which the structure is operating, which is modulated by the concrete cover, a porous structure with calcium hydroxide-based electrolyte [4]. Thus, the corrosion behaviour of steel reinforcements is a complex phenomenon based on the interaction of multiple chemical and electrochemical variables.

The concrete cover of the reinforcements is a dynamic system whose pore structure and chemical composition changes over time [4,5] and with exposure time to the environment [6,7]. The presence of chlorides, CO_2, or sulphates is frequently cited as the main factors responsible for the onset and propagation of deterioration [7–9], i.e., cracking and/or spalling due to corrosion of the rebars. Many papers can be found in the literature describing the phenomenology of the process [10–13], the effects of individual aggressives [14], or methods for corrosion mitigation [15–18]. However, studies devoted to the influence of temperature are rather scarce [19,20], and few corrosion rate prediction models include temperature as an explicit parameter [21].

Temperature is a key factor in chemical reactions kinetics, including corrosion, obviously. However, in a recent large review on the relationship between rebar's corrosion rate and concrete resistivity [22], no citations have been found that address the effect of temperature, the focus is always on the reliability of the resistivity measurement method or the model employed [23]. As shown in the review [22], a number of linear relationships were reported to exist between resistivity and corrosion rate, but each one was limited to a specific concrete type, exposure condition, etc. No general relationship seems to exist, probably in part because temperature is not considered in such models/methods. Thus, in our opinion, a deeper knowledge of this aspect is necessary for the development of a practical inspection tool.

Therefore, the present study is focused on the effect of the temperature on both the high- and low-frequency limits of the impedance spectra obtained for steel rebars (carbon steel and different stainless steel grades). The high frequency limit is related to the conducting properties of the concrete cover, and the low frequency limit is related to the corrosion behaviour of the steel rebar [24]. Both limits experience important variations in a relatively short temperature range. These aspects will be discussed in detail in the next sections.

2. Experimental

2.1. Reinforced mortar probes

Experiments were conducted in the laboratory and in a field exposure site. A pool measuring 1.5 m x 1.5 m (base dimensions)

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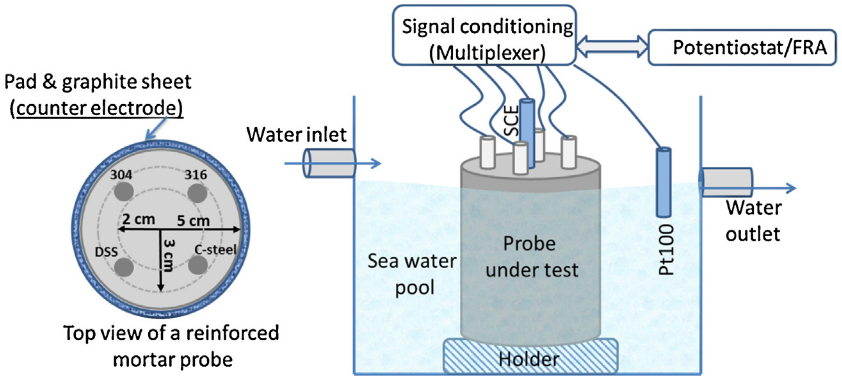

Fig. 1. Schematic representation of the distribution of the reinforcements (solid circles on the left figure) and the distribution of tested probes in the sea water pool. The locations of the reference electrode, SCE, and temperature sensor (Pt100) are also indicated, together with the electrical wiring. The counter electrode, a graphite sheet embedded in a porous pad, is placed around the test probe, as indicated in the top view cross section.

and 1.5 m high, located at the seaside under flowing seawater, where the reinforced probes being tested were submerged, was the field exposure site. In the laboratory, a small pool with seawater was employed for temperature control. A sketch of the experimental system is shown in Fig. 1.

Carbon steel, B 400S, and two austenitic stainless steels, AISI 304 and AISI 316, were employed as reinforcements, together with a duplex stainless steel, SAF 2205. Ribbed rods (ϕ= 10 mm) were employed. The nominal composition is given in Table 1. The rebars, with a lateral surface of 30 cm^2, were buried in mortar probes, after being degreased with acetone. In the figures given here, the steels will be labelled as CS, 304, 316, and DSS for the B 400S, AISI 304, AISI 316, and SAF 2205, respectively.

The mortar samples were prepared using Ordinary Portland Cement, CEM-I-52.5-R, with a water-to-cement ratio = 1:2 and a cement-to-sand ratio = 1:3. The probes were cast in cylindrical moulds to produce testing probes of 10 cm in diameter and 20 cm in height, and cured in a 100% RH atmosphere at 22 $\pm 2\,^0$C for at least one month before being transferred to the test sites (seaside pool or laboratory at 100% RH).

The geometry of the probes and the positioning of the electrodes in the reinforced probes have been described elsewhere [25]. The sole difference in the present case is that the steel rebars for field exposure were not placed at the rotation axis of the mortar cylinder because four rebars were embedded per cylinder, as shown in Fig. 1.

The results reported here correspond to 1.2 years for laboratory exposure and 3.3 years for the seaside site.

2.2. *Alkaline solution*

For the tests conducted in solutions, a 0.1 M NaOH solution simulating the pH of concrete interstitial electrolyte was employed. NaCl was added in some tests to simulate a contaminated electrolyte.

Only the cross section of a SAF 2205 rod was employed. The surface was polished with SiC paper abrasion down to grade 1200, followed by rinsing in ethanol and distilled water.

2.3. *Cement paste*

As was done with the mortar samples, cement paste samples were prepared using Ordinary Cement Portland CEM-I-52.5-R according to the composition, specifications, and conformity criteria of the EN 197-1:2000. The water-to-cement ratio employed was 0.5. The mix was cast in square-base prism moulds measuring 16 cm x 4 cm x 4 cm, demoulded after 24 h, and stored in a 100% RH atmosphere for at least one month prior to further manipulation.

Cubic samples 4 cm on a side were cut from the prisms. Each sample was saturated either with deionised water or with a 1 M NaCl solution, following the ASTM C1202 standard [26]. The saturated samples were then covered with polyethylene film to avoid lixiviation and immersed in the same filling solution, conditioned at the desired temperature. Impedance measurements of the samples were taken 24 hours after immersion using square-shaped copper electrodes, following the contact method procedure described elsewhere [27]. Measurements were taken for each sample in the three orthogonal directions to check for reproducibility.

2.4. *Electrochemical equipment*

The electrochemical data, corrosion potential and electrochemical impedance spectra, EIS, were collected in the laboratory, in a three-electrode electrochemical cell configuration using a potentiostat Ecochemie PGStat 30. The reference electrodes were the saturated calomel, SCE, in all cases. An external salt bridge was employed when necessary to keep the reference electrode at constant (room) temperature. The cell configuration for the reinforced mortar samples is shown in Fig. 1.

The EIS measurements were performed at the corrosion potential, from 10 kHz down to 1 mHz, seven frequencies per decade and 10 mV rms amplitude of the sinusoidal wave.

For the high frequency measurements, an Agilent 4294A apparatus was employed, which allows the measurement of capacitances in the 10^{-15} F range. The practical frequency window used was 50 MHz down to 100 Hz, in a two-electrode configuration, as described elsewhere [27].

Table 1
Nominal composition of the steels tested, w/w %.

Steel	C_{max}	Si_{max}	Mn_{max}	P_{max}	S_{max}	Ni	Cr	Mo	N
AISI 304	0.08	1	2	0.045	0.030	8.00-10.50	18.00-20.00	–	–
AISI 316	0.08	1	2	0.045	0.030	10.00-14.00	16.00-8.00	2.00-3.00	–
SAF 2205	0.03	1	2	0.030	0.015	5	22	3.2	0.180
B 400S	0.24	–	–	0.055	0.015	–	–	–	0.013