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Sensor for oxygen evaluation in concrete

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Abstract

This paper includes results from a research work carried out for developing and optimising a sensor to measure the limiting current of oxygen reduction in concrete.

Platinum, stainless steel and carbon steel materials were tested as working electrodes in saturated $Ca(OH)_2$ solution. Linear correlations were obtained between the limiting currents of oxygen reduction and the oxygen concentration in solution.

The measurements of the limiting current density due to oxygen reduction have been made in concrete specimens with a sensor consisting of platinum and stainless steel, as working electrodes, graphite, as a counter electrode, and activated titanium, as a reference electrode, under different conditions of water and oxygen accessibility to the concrete. The results show that this sensor detects oxygen content variations in the interstitial solution of the concrete, providing qualitative information about the evolution of oxygen availability in concrete.

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1. Introduction

The implementation of a maintenance strategy together with the adequate monitoring procedures is considered as essential to prevent the premature corrosion of reinforcements and its consequences on the durability of concrete structures.

Sensors and associated monitoring systems can provide a realistic assessment of the service life of a structure giving information about both a spatial distribution and a temporal change in concrete cover properties, and concerning the reinforcement state [1].

The oxygen transport is one of the different measures that must be considered in the assessment of cover zone quality [1]. Vennesland [2], in a study dedicated to the evaluation of maintenance methods at Gimsøystraumen Bridge, points out this determination as the most conclusive one of the electrochemical monitoring methods used.

In submerged structures, for which the degree of saturation will generally be very high, the rate of steel corrosion is primarily controlled by diffusion of dissolved oxygen through the concrete cover [2–4]. The availability of oxygen at the reinforcement steel surface, as well as the mechanism and kinetics of oxygen reduction can thus be considered as essential factors for the corrosion of steel in concrete.

Significant attention has been paid to the subject of oxygen transport in concrete [2,4–8]. The oxygen transport evaluation using electrochemical techniques is based on the assumption that when a sufficiently negative potential, within a limited potential domain, is applied to the working electrode, the only cathodic reaction is the reduction of oxygen and, then, the oxygen transport may be recorded as an electrical current.

There are also some articles that address the mechanism and kinetics of oxygen reduction on iron, in alkaline solutions [9–14]. These papers propose an oxygen reduction mechanism on iron that involves the mediation of surface Fe(II) sites, formed by reduction in the passive film, which act as adsorption centres promoting the oxygen reduction reaction.

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Although the generalized opinion that the absence of oxygen in the vicinity of iron interrupts the corrosion, recent studies have disclosed that other reduction reactions will be able to assure its progression [4,15,16]. Alonso et al. [4] reported that once corrosion has been initiated, this process might be developed with a certain activity, even if there is a lack of oxygen.

Other research studies have been devoted to the cathodic reduction of oxygen in alkaline solutions simulating concrete and in concrete [17–19], reporting its influences on the reinforcement steel corrosion.

Considering the role of oxygen reduction on the reinforcement steel corrosion and the stated importance of monitoring systems, the main objectives of the present study are to develop and to evaluate a sensor to be used for monitoring the oxygen availability in concrete. When integrated in a corrosion monitoring system, this sensor would be able to provide complementary information about the main cathodic reaction and also concerning the external factors that may limit it.

2. Experimental

2.1. Studies performed in solution

Potentiodynamic tests were performed to study the influence of the working electrode material on oxygen reduction. Platinum (wire of $0.45 \, cm^2$), AISI 316 stainless steel ($l = 13$ mm, diameter $= 10$ mm) and low carbon steel ($l = 13$ mm, diameter $= 10$ mm) were tested as working electrodes. Platinum was used as a counter electrode and the reference electrode was a Hg|HgO (0.1 M KOH) XR400, from Radiometer Copenhagen. The potentials were converted to the Standard Hydrogen Electrode (SHE) scale.

For the potentiodynamic studies, a Solartron system (SI 1287 interface, SI 1260 frequency response analyser) was used. Negative potential scans at $0.5 \, mV \, s^{-1}$ were carried out from the open circuit potential to -0.90 V and -1.07 V, respectively, with platinum (Pt) and with carbon (CS) and stainless steel (SS) working electrodes. The experiments were conducted in an electrochemical cell (ASTM G5) filled with an unstirred saturated aqueous solution of $Ca(OH)_2$, pH 12.6, at 25 °C. According to Page and Treadaway [20], this solution may be taken as an approximate electrolyte to concrete pore solution. The levels of O_2 in the solution were reduced in a controlled way by bubbling N_2 through the solution in the cell before each electrochemical experiment. A galvanic WTW oxi 330 oxygen sensor with a cellox 325 probe was used for the measurements of the oxygen concentration in the solution.

2.2. Studies performed in concrete

A sensor was prepared consisting of either platinum ($l = 20$ mm, diameter $= 0.5$ mm) or stainless steel ($l = 26$ mm, diameter $= 6$ mm) as working electrodes, graphite ($l = 30$ mm; diameter $= 12$ mm) as a counter electrode, and activated titanium (wire of $l = 26$ mm) as a reference electrode ($E_e = +0.143$ V (SHE)) [21]. The electrode materials were connected to a cable of four electrical conductors and inserted into a plastic mould. Araldite and epoxy resin were used to isolate the contacts and to define the working areas of the electrode materials.

Concerning the reference electrode, the use of activated titanium has been reported for this purpose [1,21] and previous experiments in solution have been quite satisfactory concerning its reproducibility and stability [22].

The sensors were embedded in concrete prisms ($10 \times 10 \times 12$ cm), which were prepared with concrete made of cement type I, with a cement content of $300 \, kg \, m^{-3}$ and a water to cement ratio of 0.5, were cured for seven days in a chamber with a degree of humidity of $95 \pm 5\%$. The sensors (I, II and III) were set to provide a concrete cover thickness of 15 mm with respect to the working electrode materials.

The concrete prisms with the embedded oxygen sensors were then submitted to the exposure conditions given in Table 1, in order to evaluate the performance and also the durability of the sensor in concrete under different oxygen access conditions.

To evaluate the influence of chloride, one of the sensors was immersed in a 10% NaCl aqueous solution and compared with another one that was kept during the same period immersed in distilled water. Before the electrochemical measurements, both sensors were submitted to similar conditions at room temperature. The concrete prisms were previously immersed for 10 days in dearated water (C6) and then dried for seven days in a chamber at 60% RH (C7).

For the electrochemical experiments, a PC4 Gamry system equipped with a potentiostat was used. The cathodic currents were determined potentiodynamically and the electric resistance of concrete by electrochemical impedance spectroscopy (EIS). Automatic ohmic compensation was applied during the potentiodynamic measurements.

Potentiodynamic scans at $1 \, mV \, s^{-1}$ were performed from open circuit potential to -0.90 V (Ti$_A$) and -1.20 V

Table 1
Exposure conditions of concrete prisms

Conditions	
C1	Immersion in dearated distilled water at room temperature ($T = 20 \pm 2$ °C) for 18 days
C2	Drying in a chamber at room temperature ($T = 20 \pm 2$ °C; RH $= 65 \pm 5\%$) for 2 days
C3	Drying in a dearated atmosphere for 12 days at room temperature followed by 6 days at 40 °C, and by 1 day at room temperature ($T = 20 \pm 2$ °C)
C4	Immersion in dearated distilled water at room temperature ($T = 20 \pm 2$ °C) for 42 days, after a 12-month drying period in a chamber at RH $= 60\%$ and at room temperature ($T = 20 \pm 2$ °C)
C5	Exposure to the laboratory atmosphere ($T = 20 \pm 2$ °C; RH $= 65 \pm 5\%$) for 3 days, after a 7-month immersion period in water at room temperature ($T = 20 \pm 2$ °C)