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Multiprobe chloride sensor for in situ monitoring of reinforced concrete structures

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Abstract

In situ monitoring of the chloride content is one of the most important procedures in preventing and controlling chloride-induced corrosion in reinforced concrete structures. Thus, the development of chloride sensors is of paramount importance for the continuous monitoring of concrete structures. The sensors must present long lifetime and reliability and operate in a wide range of chloride concentrations.

The present work aims at developing and testing a sensor based on Ag/AgCl electrodes for in situ monitoring of chloride ions in reinforced concrete structures. Although these electrodes are widely used in analytical experiments due to their sensitivity to the chloride ion, little is known on their behaviour during exposure to alkaline environments, such as those existing in concrete.

The multiprobe sensor presented in this work was tested in mortar and concrete specimens, revealing good stability. The results reveal that the Ag/AgCl sensor presents good sensitivity in a wide range of chloride concentrations.

Keywords: Chloride sensor; Concrete; Reinforcing steel; Corrosion

1. Introduction

Corrosion of reinforcing steel is a major cause for degradation of concrete structures, especially when exposed to carbon dioxide or chloride ions. Accumulation of corrosion products at the steel–concrete interface originates internal stresses that frequently lead to cracking and ultimately to delamination of the concrete cover. Further, the corrosion process leads to substantial reduction of the cross-section of the rebars and, therefore, to deleterious effects on the mechanical properties of the overall structure.

Chloride-induced corrosion is a particularly insidious problem, since it leads to localized attack that can result in severe security problems on the reinforced concrete structures and require expensive repair works. The best way to avoid the corrosion-induced damage is through prevention, including monitoring of the aggressiveness of the environment. This makes the assessment of the chloride content in the concrete a sensible method for monitoring structures at risk. The procedure usually involves drilling the concrete at various depths for collection of powder samples that are then submitted to chemical attack and chemical analysis for quantification of the total chloride content. This procedure, although well-established, is destructive and time-consuming, and requires periodical repetition. The use of in situ probes for continuous monitoring is in its essence a much more straightforward procedure. They require embedding in the structure before the concrete casting stage, but readings and assessment of the chloride concentrations would be practically instantaneous, thus making the whole process a very simple one.

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Ag/AgCl electrodes are widely used and commercially available as selective chloride electrodes. They consist of a silver wire coated with a conversion layer of silver chloride (AgCl). Under these conditions the equilibrium at the surface is

$$\mathrm{Ag} + \mathrm{Cl}^- \leftrightarrow \mathrm{AgCl} + \mathrm{e}^- \tag{1}$$

and, the equilibrium potential is given by Nernst equation

$$E = E_0 - 2.3\frac{R \cdot T}{n \cdot F}\log(\mathrm{Cl}^-) \tag{2}$$

where E_0 stands for standard equilibrium potential, R for the universal perfect gas constant, T for the temperature, n for the number of electrons involved and F for Faraday's constant.

Although the principles are well-established, there are major requirement for concrete applications that need to be fulfilled by this electrode, namely the stability and lifetime in alkaline environments such as those existing in concrete (pH ≅ 12–13), as well as the linear response to a wide range of chloride concentrations. The use of Ag/AgCl electrodes to determine the chloride content in solutions simulating the concrete interstitial electrolyte has been described in the literature [1–4]. Atkins et al. [3] discussed the effect of temperature and the presence of bromides in seawater in the potential readings. Literature [4] also reports that Ag/AgCl electrodes embedded in mortar specimens are stable only for short periods (less than three months). In spite of the doubts risen in literature, Ag/AgCl electrodes still remain a potentially interesting choice in what concerns chloride ion monitoring in reinforced concrete structures.

The present work aims at developing and testing a chloride sensor based on anodized silver wires for use in concrete structures. The sensor was tested at different concrete depths and in a wide range of chloride concentrations.

2. Experimental procedure

2.1. Preparation of the chloride sensor

Polished silver wires were cleaned by immersion in a solution of NH_4OH (10 vol.%) for 6 h, washed with distilled water and anodized for 30 min in 0.1 M HCl solution at room temperature under a current density of 2.0 mA/cm^2, according to the procedure described in the literature [5]. The oxidised Ag wires (sensors) were welded to a conductive copper wire and a set of five sensors were mounted in a mould into which an epoxy resin was cast. The sensors had various lengths in order to minimize the result of geometrical effects on the diffusion of chloride ions (Fig. 1).

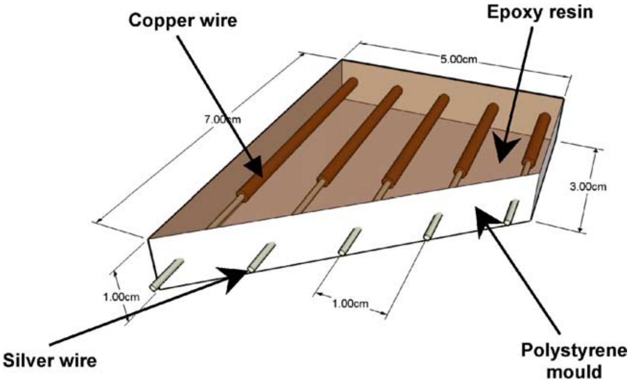

Fig. 1. Scheme of the multiprobe chloride sensor.

2.2. Calibration in solution

The Ag/AgCl sensors were calibrated in aqueous NaCl solutions of different concentrations and compared with determinations made using a commercial selective electrode (Consort®).

The response of the sensors under alkaline environment was tested in saturated $Ca(OH)_2$ solutions with NaCl concentrations ranging from 100 to 50 000 ppm. Calibration curves were obtained at different temperatures: 5, 15 and 50 °C.

2.3. Tests in mortar samples

Cylindrical mortar samples having a water/cement (w/c) ratio of 0.6 were prepared, using commercial Portland cement, sand and distilled water. These samples were cured for one week in a moisture saturated environment. The multiprobe sensor was embedded in the mortar samples. A deposit containing the 0.5 M NaCl solution was mounted on the top of each sample, according to the scheme depicted in Fig. 2. Three identical mortar samples were prepared, one of them being exposed to pure water (blank specimen).

2.4. Tests in concrete specimens

A mix with 0.5 w/c ratio was prepared according to Table 1. The dimensions of the concrete specimens were as follows: height = 1 m, wide = 0.26 m and depth = 0.08 m. A 400NR steel mesh was embedded in the concrete

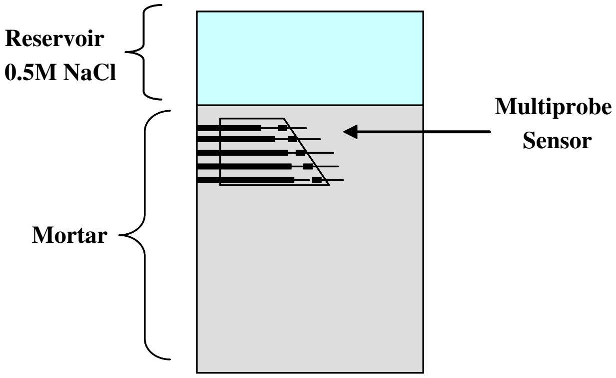

Fig. 2. Scheme of the probe sensor embedded in the mortar samples.

Table 1
Concrete composition

Cement CEM II 32.5 (kg/m^3)	360
Sand (kg/m^3)	631
Aggregates I (kg/m^3)	488
Aggregates II(kg/m^3)	731
Water(kg/m^3)	180
w/c	0.5
Sodium Chloride (kg/m^3)	14.7

specimens. The diameter of the steel bars was 0.01 m and the distance between the bars was 0.1 m. The concrete cover was 0.03 m.

The probes were embedded in the concrete specimens at the rebars level. These samples were cast and cured for two weeks, then painted with epoxy paint, leaving only one exposed side. These samples were periodically submitted to water spray.

All the potential readings were obtained using a saturated calomel electrode (SCE) as reference.

3. Results and discussion

3.1. Tests in solution

The calibration curves obtained in saturated $Ca(OH)_2$ solutions contaminated with different amounts of chloride ions at different temperatures revealed a linear response (Fig. 3), with a correlation coefficient of 0.99, and in good agreement with those obtained with the commercial selective electrode. The slope of the curves slightly increased with temperature, being identical to the theoretical expected ones, as presented in Table 2.

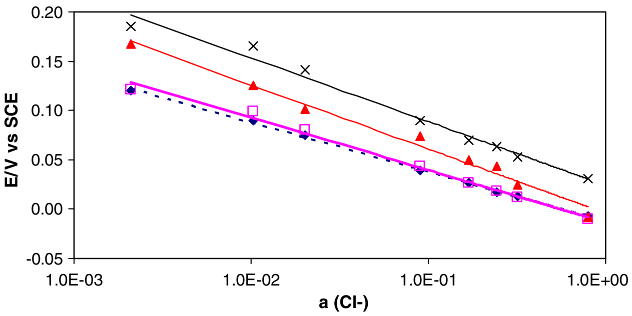

Fig. 3. Calibration curves obtained in saturated $Ca(OH)_2$ solutions with various amounts of chloride ions at different temperatures: (◆) 5 °C; (□) 15 °C; (▲) 50 °C and (×) commercial electrode, 15 °C.

Table 2
Theoretical and experimental slopes from calibration curves depicted in Fig. 3

Temperature (°C)	Theoretical slope (V)	Experimental slope (V)
5	−0.055	−0.050
15	−0.057	−0.053
50	−0.064	−0.065

3.2. Tests in mortar

For the mortar specimens exposed to distilled water, the potential was practically constant and showed little variation among the several probes (Fig. 4). In contrast, when ingress of Cl$^-$ occurred from the solution, a potential decay occurred at some stage of the process (Fig. 5). The time necessary for the potential drop was naturally shorter for the probes closer to the surface as they revealed by the progression of the chloride diffusion front. The values from the curves were used to obtain the chloride profiles (Fig. 6). The chloride content at each concrete depth increased with

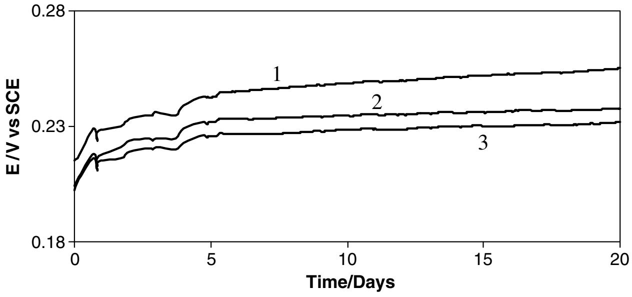

Fig. 4. Potential readings for the multiprobe sensor, at different distances from the steel rebar, embedded in mortar samples exposed to distilled water.

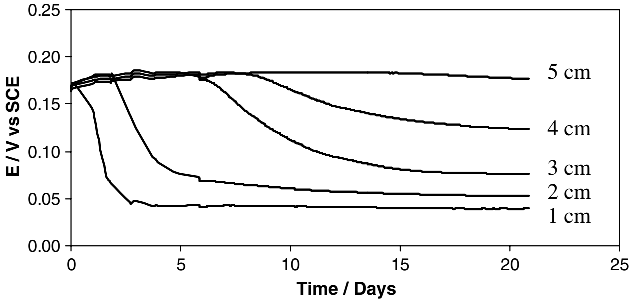

Fig. 5. Potential readings for the multiprobe sensor embedded in mortar samples exposed to NaCl 0.5 M.

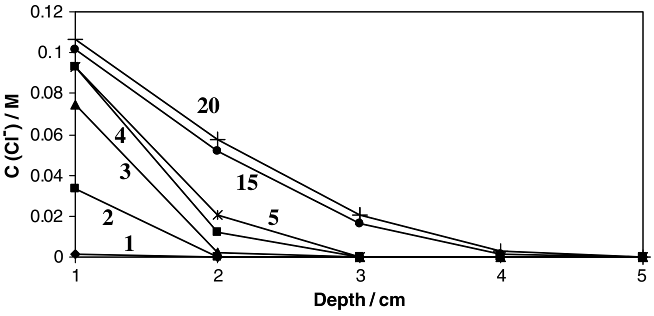

Fig. 6. Chloride profiles in a mortar sample exposed to 0.5 M NaCl. Time, in days, for chloride diffusion indicated in the plot.

time and globally the profiles were according to the evolution expected from Fick's law for transient diffusion (Eq. (3)):

$$\frac{C(x,\ t) - C_{\mathrm{i}}}{C_{\mathrm{s}} - C_{\mathrm{i}}} = 1 - \operatorname{erf} \frac{x}{\sqrt{4 \cdot D \cdot t}} \tag{3}$$

in which $C(x,t)$ is the chloride content at depth x at time t, C_{i} the initial chloride content on the exposed surface, t the exposure time, x the depth, D the chloride diffusion coefficient and erf the error function. Fitting of the experimental results (Fig. 6) using Eq. (3) indicated a diffusivity, $D = 2 \times 10^{-12}$ m s^{-2}. This value is close to those found in literature [7].

3.3. Tests in concrete

Fig. 7 depicts the evolution of the potential for sensors embedded in reinforced concrete specimens as indicated in Table 1. The readings started 80 days after casting of the specimens. The potential readings were reasonably stable. The evolution observed in Fig. 7 showed that the sensor can be used in concrete specimens, revealing reasonable stability. The data depicted in Fig. 7 was converted into chloride concentrations (Table 3) and revealed a concentration lower the one determined from the initial mixture. This can be explained by the complexation of part of the chlorides with the cement hydration products, leading to the formation of Friedel's salt, and to a decrease in the free chloride content.

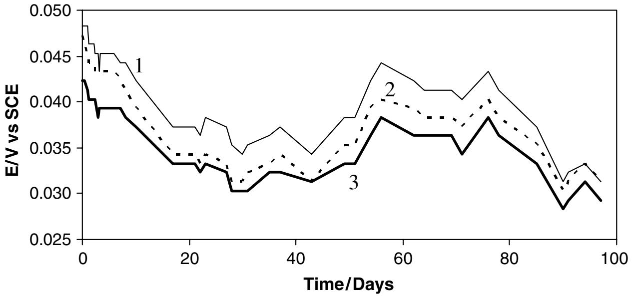

Fig. 7. Evolution of the potential for chloride sensors embedded in concrete samples.

Table 3
Chloride content predicted using the sensor and real content added to the concrete mix

Distance (cm)	$[\mathrm{Cl}^-]_{\mathrm{med}}$ (M)	$[\mathrm{Cl}^-]_{\mathrm{real}}$ (M)
1	0.16	0.25
2	0.18	
3	0.20	

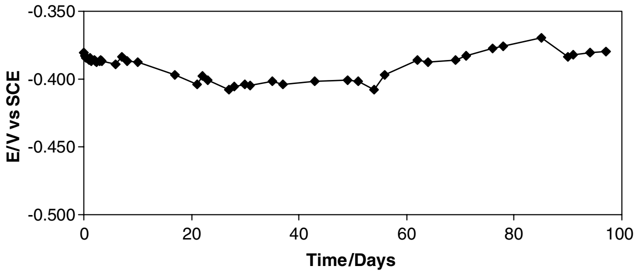

Fig. 8. Evolution of the potential for steel rebar embedded in concrete.

The open circuit potential of the rebars embedded in the concrete sample was also measured. The open circuit potential values are in the range −0.375 V to −0.475 V, being characteristic of corrosion activity, as expected, since chlorides were added to the concrete mix (Fig. 8).

4. Conclusions

A multiprobe chloride sensor was tested in solution and also in mortar and in concrete samples. A linear response was found in saturated calcium hydroxide solution, for a wide range of chloride concentrations.

The sensor allowed determination of chloride concentration profiles in mortar specimens that approximately followed Fick's law for transient diffusion. The effective chloride diffusivity was estimated as 2×10^{-12} m s^{-2} for the mortar specimens.

The tests made using concrete specimens revealed reasonable stability for the duration of the experiment. Nevertheless, the question of the lifetime of the probe requires further testing.

Acknowledgement

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