

Novel sensor for non-destructive durability monitoring in reinforced concrete

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ABSTRACT: Reinforced concrete is generally a durable material; however, it is also subjected to various degradation mechanisms, amongst them, corrosion of the reinforcing steel is the most common one. In this work, we present a novel sensor to be embedded in concrete and to monitor simultaneously the main parameters that lead to corrosion initiation, namely pH and chloride concentration. Instrumented mortar specimens were exposed to carbonation and chloride ingress and changes in pH and chloride concentration were continuously monitored. The results obtained show the need to monitor these two parameters simultaneously when assessing the corrosion risk and we believe the use of our sensor can strongly improve the decision-making in engineering practice.

1 INTRODUCTION

Most of the infrastructures (e.g. tunnels, garages, bridges, etc.) and public and private buildings are built in reinforced concrete; however, the durability of these structures can be seriously compromised by reinforcement corrosion (Bertolini et al. 2013). Concrete structures damaged by reinforcement corrosion have to undergo maintenance and repair in order to reach their service life; this leads to high costs. In fact, costs associated with maintenance and repair of corroding structures have a major effect on the economy of all industrialized countries (Angst 2018). The used of embedded sensors to monitor the parameters relevant for durability offers large opportunities to solve this problem. Examples of the increasing awareness of durability monitoring are the publication of the German guideline for corrosion monitoring in reinforced concrete (Dgzfp 2018) or conferences addressing this topic, such as the SMAR conference.

Various types of embeddable sensors exist to monitor parameters relevant for durability in reinforced concrete, as for example the so-called anode-ladder system or the multi-ring electrode (Raupach et al. 1997). Other interesting examples of sensors for concrete can be found in the recent review by Figueira (2017). Most of these sensors are based on monitoring corrosion current, corrosion potential, resistivity, etc. This allows obtaining information on the propagation on the corrosion front. However, reliable sensors to monitor the main parameters that lead to corrosion initiation still do not exist.

In this work, we present a sensor system composed of Ag/AgCl ion-selective electrodes (chloride sensor) and iridium/iridium oxide (IrO_x) electrodes (pH sensor). In combination with an algorithm for data evaluation, this sensor system allows monitoring simultaneously, for the first time, pH and chloride profiles in-situ and non-destructively. The data obtained allows predicting corrosion before its initiation. We believe this has major implications for the decision-making in

engineering practice and pilot projects of embedding these sensors in engineering structures are currently ongoing.

2 THEORETICAL BACKGROUND

2.1 The silver/silver chloride electrode (Ag/AgCl ISE)

The silver/silver chloride electrode (Ag/AgCl ISE) is a solid-state membrane electrode that can be used as a chloride sensor. The potential of this electrode $E_{\text{Ag/AgCl ISE}}$ is (Koryta 1972):

$$E_{\text{Ag/AgCl ISE}} = E_{\text{Ag/AgCl ISE}}^0 - \frac{RT}{F} \ln a_{\text{Cl}^-} \quad (1)$$

where R is the gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), F the Faraday constant ($96.485 \times 10^3 \text{ C} \cdot \text{mol}^{-1}$), T the absolute temperature (K), and $E_{\text{Ag/AgCl ISE}}^0$ is the electrode standard potential ($E_{\text{Ag/AgCl}}^0 = 225.6 \text{ mV vs. Ag/AgCl/sat. KCl at } 20^\circ \text{C}$ (Shreir 1994).

These electrodes showed good stability and accuracy for more than one year (Elsener et al. 2003). More detailed information can be found in the work by Seguí Femenias et al. (2016, 2015).

2.2 The iridium/iridium oxide electrode (pH sensor)

Iridium/iridium oxide (IrO_x) electrodes as pH sensors. These electrodes were produced in our laboratory by thermal oxidation of iridium wires following the procedure described by Seguí Femenias et al. (2018a). The potential response E_{IrO_x} of the IrO_x electrodes is:

$$E_{\text{IrO}_x} = E_{\text{IrO}_x}^0 - \frac{RT}{F} \text{pH} \quad (2)$$

After production, these electrodes were stored in alkaline solution ($\text{pH} \approx 13.5$) for 3-4 months and then calibrated in solutions of pH ranging between 9 and 13.5), following the criteria reported by Seguí Femenias et al. (2018a).

These electrodes have been reported by Seguí Femenias et al. (2017, 2018b) to operate reliably for at least 2 years in alkaline solution and half a year when embedded in concrete. Current laboratory testing shows that the sensors work well in concrete for more than one year. More detailed information can be found in the work by Seguí Femenias et al. (2017, 2018a).

3 METHODS

Several rectangular mortar prisms were produced with embedded Ag/AgCl ISEs and IrO_x electrodes. The mortar mix proportions were always cement/water/sand 1: 0.5: 2 with CEM I 52.5, with sand size <1mm. The aim of this experiment was to monitor:

- Case 1: changes in chloride concentration during carbonation
- Case 2: corrosion during chloride ingress

For the “case 1” (Fig. 1a), the mortar samples consisted of two parts: first, mortar prisms containing 4% of admixed chlorides (by cement weight) and with 2 embedded Ag/AgCl ISEs (at the same cover depth and with one of them to be used as internal reference electrode) were produced. One hour after casting, another mortar prism was cast on the top of the previous sample with 2 embedded Ag/AgCl ISEs and 2 embedded IrO_x electrodes. The amount of admixed

chlorides was 0.5% of chlorides by cement weight. More details can be found in the work by Seguí Femenias et al. (2018b).

For the “case 2” (Fig. 1b), three Ag/AgCl ISEs, three carbon steel rods (diameter 3 mm), and three IrO_x electrodes were embedded in a mortar prism. An additional Ag/AgCl was also embedded in order to be used as internal reference electrode. Detailed information on this experiment can be found in the work by Seguí Femenias (2017).

All the samples were cured at 95%RH and 21°C for one week. Then, all the surfaces were coated with an epoxy-resin; the surface of ingress of CO₂ (“case 1”) and the surface of ingress of chlorides (“case 2”) were not coated. This ensures one-dimensional transport of corrosive agent would occur. For the “case 1”, the samples were placed in a carbonation chamber (65%RH, 21°C and 4% CO₂). For the “case 2”, the surface of ingress was put in contact with synthetic pore solution (0.2 mol·L⁻¹ KOH 0.15 mol·L⁻¹ NaOH sat. Ca(OH)₂) containing 0.5 mol·L⁻¹ NaCl. The main features of the two set-ups are shown in Figure 1. In both cases, the mentioned sensors were embedded in the mortar at different cover depths to monitor the penetration of the corrosive agent.

In both cases, the potentials of all the electrodes were monitored (time interval of 1 h) versus the internal reference electrode (Fig. 1) with a data logger. All potential measurements were evaluated with a recently developed algorithm (Seguí Femenias 2017). The output of this algorithm are the free chloride concentration and the pH at each electrode location.

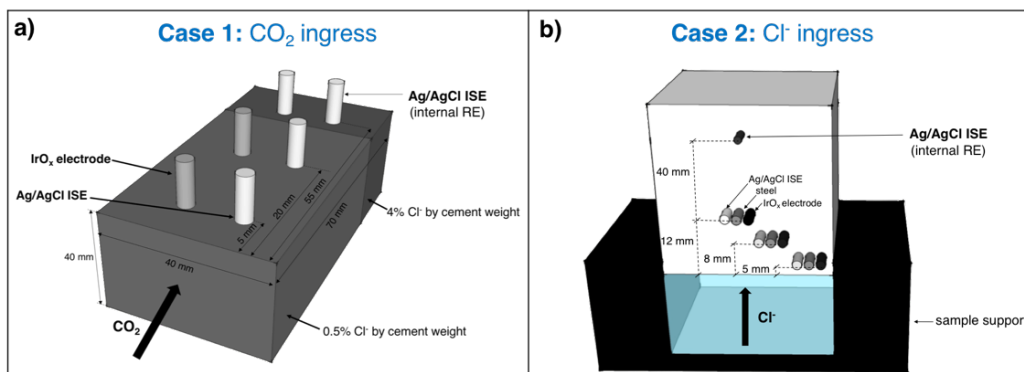


Figure 1. Representation of the set-ups used to monitor (a) chloride concentration and pH with embedded Ag/AgCl ISEs and IrO_x electrodes respectively (b) chloride concentration, corrosion state and pH with embedded Ag/AgCl ISEs, steel rods, and IrO_x electrodes respectively. All the surfaces were coated with epoxy resin with the exception of the surface of ingress of CO₂ (a) and chlorides (b).

4 RESULTS AND DISCUSSION

4.1 Monitoring of changes in chloride concentration during carbonation (case 1)

Chloride concentration and pH are the parameters that play dominating roles in corrosion initiation (Bertolini et al. 2013). Additionally, the interaction between these two parameters must also be considered; the risk of corrosion increases as the ratio of chloride to hydroxyl ion concentrations increases. In this regard, a common threshold value to trigger corrosion is Cl⁻/OH⁻ = 0.6 (Hausmann 1967).

The chloride concentration in the pore solution increases because bound chlorides are released when the concrete is carbonated (Reddy et al. 2002); thus, increasing the risk of corrosion initiation. This is shown by means of a representative example. Fig. 2a shows the measured free chloride concentration at a depth of 5 mm as a function of time of exposure in the carbonation chamber. During this time, the pore solution pH decreased from 13.6 to about 12.3. Fig. 2b shows the logarithm of the measured Cl^-/OH^- ratio as a function of the pore solution pH in the same specimen, together with the critical ratio Cl^-/OH^- of 0.6 usually considered critical for corrosion initiation. The carbonation front (pH 9–10) typically determined in practice by means of the phenolphthalein spraying method is also shown (dashed vertical line) in the graph. The amount of admixed chlorides was here 0.5% by cement weight.

The free chloride concentration increased about 1.5-fold when the pH decreased from 13.6 to about 12.3 (Fig. 2a). This results in a marked increase in the Cl^-/OH^- ratio (Fig. 2b); for a pH decrease down to ≈ 12.3 , the ratio Cl^-/OH^- is about 13, much above the value considered critical for corrosion initiation. This shows the relevance of pH monitoring: damage due to carbonation is usually only considered when the pore solution pH has decreased down to 9 (Bertolini et al. 2013) but we show that pH drops down to 12 can already be considered critical. It should also be noted that the amount of admixed chlorides (0.5% by cement weight) is similar to the allowable chloride contents stipulated in the standards (Trejo et al. 2016). Thus, a decrease of about 1 pH unit (from 13 to 12) results in a significant risk of corrosion initiation even for amounts of admixed chlorides not considered critical. From Fig. 2b, it can be seen this pH decrease is usually not detected in practice; this is because usually the traditionally used pH-indicator spraying method only allows measuring pH drops down to 9–10 (Yu et al. 2010). Thus, the corrosion risk in this case would be underestimated.

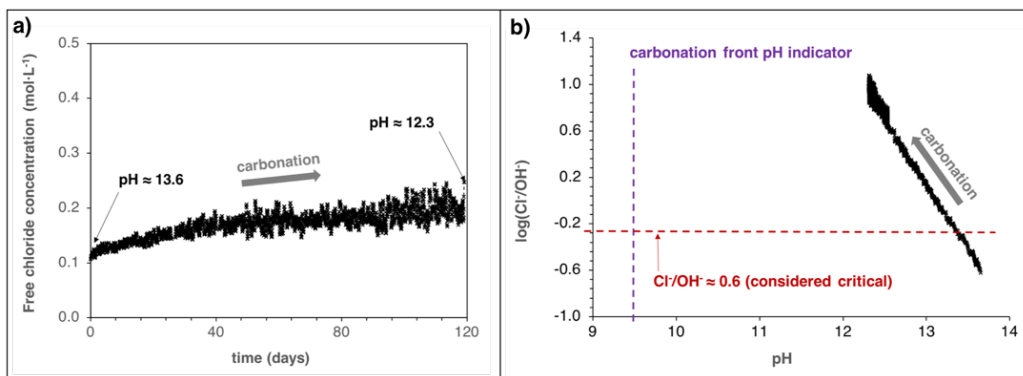


Figure 2. (a) Measured free chloride concentration as a function of exposure time in the carbonation chamber. The initial and final measured pH are also indicated in the graph. (b) Logarithm of the measured Cl^-/OH^- ratio as a function of the pore solution pH. In both cases, the results correspond to the sample samples and for the sensors embedded at 5 mm depth. The amount of admixed chlorides was 0.5% by cement weight.

4.2 Corrosion monitoring during chloride ingress (case 2)

Fig. 3 shows the measured steel potential and Cl^-/OH^- ratio as a function of chloride concentration at 5 mm (a) and at 12 mm (b), together with the critical ratio $\text{Cl}^-/\text{OH}^- = 0.6$ considered critical for corrosion initiation (Hausmann 1967). In both cases, the measured pH was higher than 13 (Seguí Femenias et al. 2018b).

The measured steel potential decreased from about -100 mV (vs. Ag/AgCl/sat. KCl) to about -400 mV (vs. Ag/AgCl/sat. KCl) for chloride concentrations higher than $1 \text{ mol}\cdot\text{L}^{-1}$ (Fig. 3a). Such potential decreases at these chloride concentrations are usually related to active corrosion (Bertolini et al. 2013); this is also in agreement with the measured Cl^-/OH^- ratio, which is much above the value Cl^-/OH^- considered critical for corrosion initiation.

Fig. 3b shows that the steel potential was relatively constant for chloride concentrations below $0.6 \text{ mol}\cdot\text{L}^{-1}$. This is in agreement with the measured Cl^-/OH^- ratio that was always below 0.6 (value considered critical (Hausmann 1967)); it is thus assumed that no corrosion occurred. In order to show the relevance of pH changes, the Cl^-/OH^- ratio was also calculated assuming that the pH had decreased down to 13 and 12.5 (empty markers in Fig. 3b). Under these circumstances the risk for corrosion initiation would be high, as the calculated Cl^-/OH^- ratio increased up to 6 and 16 respectively at $0.5 \text{ mol}\cdot\text{L}^{-1}$. This situation is likely to occur in practice for structures that have been exposed to CO_2 ingress for several years and thus a certain degree of carbonation may have taken place.

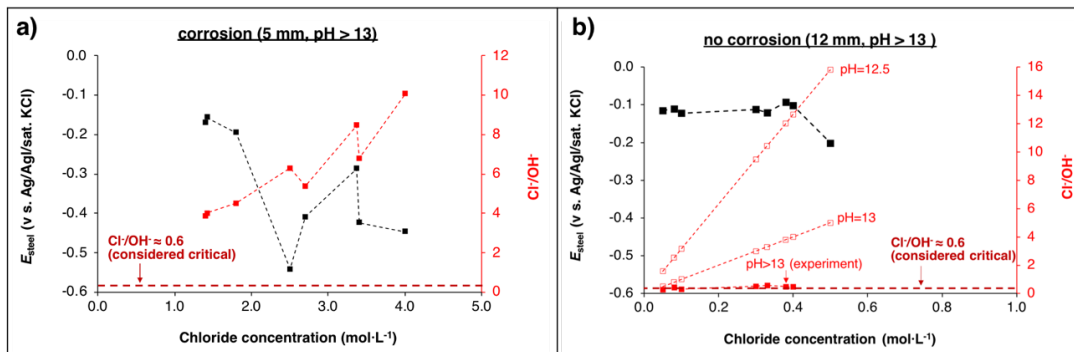


Figure 3. Steel potential and measured Cl^-/OH^- ratio as a function of the chloride concentration at 5 mm (a) and 12 mm depth (b). In both cases, the measured pH was higher than 13 (Seguí Femenias et al. 2018b). In (b), The Cl^-/OH^- , calculated assuming that the pH had decreased down to 13 and 12.5, is also depicted (empty markers).

4.3 Implications of the results

Simultaneous monitoring of both pH and chloride concentration is essential for reliably assessing the corrosion risk. On one side (“case 1”), the amount of free chlorides dissolved in the pore solution can markedly increase during carbonation of cement paste due to the release of bound chlorides. This can lead to conditions considered critical for corrosion initiation, even if the amount of admixed chlorides was considered allowable according to the standards (Trejo et al. 2016). On the other side (“case 2”), it has been shown that even for cases where corrosion is not taking place during chloride ingress, the risk of corrosion can become significant if the pore solution pH decreases only by 1 unit (for example, from pH 13.5 down to 12.5). This is likely the case for existing structures that may present a certain degree of carbonation. However, a pH drop down to 12.5 is usually not detected in practice; usually only pH drops down to 9-10 are detected (pH-indicator spraying method). The risk of corrosion would be thus underestimated as the material would be considered “uncarbonated”.

The situation described above is similar in laboratory research: studies on the increase of chloride concentration due to a decrease of pore solution pH are usually carried out for “fully carbonated”

concrete (pH 9). As an example, Fig. 4 shows the ratio of free chloride concentration after and before carbonation (Cl^- free, carb. and Cl^- free, uncarb. respectively) as a function of the total amount of admixed chlorides. Our results, when the pore solution decreased down to 11 and 12.3 (Seguí Femenias et al. 2018b), are also shown.

Fig. 4, shows that the free chloride concentration may increase by a factor of as much as 2.4 upon carbonation (down to pH 9) of the cement paste. This results in a significant increase in the corrosion risk. Nevertheless, it is important to note that a pH decrease by 1 or 2 units (pH drop down to 12.3 or 11) already leads to an increase of chloride concentration higher than 1.5-fold and thus a high risk of corrosion. However, this situation is usually not studied. This is because, among other reasons, a method for reliably monitoring pH and chloride concentration in concrete non-destructively and simultaneously did not exist.

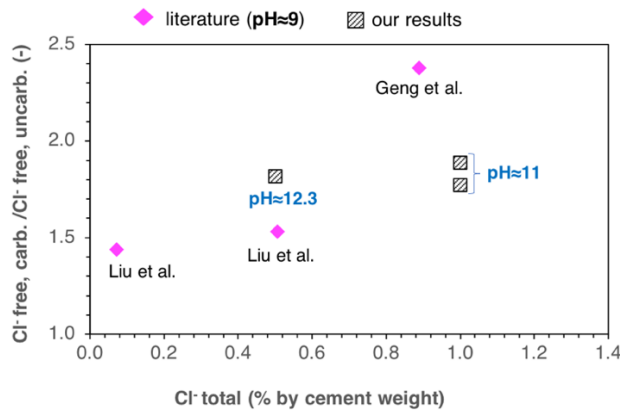


Figure 4. Ratio of free chloride concentration after and before carbonation as a function of the total admixed chloride content. The results shown correspond to literature data reported by Liu et al. (2016) and Geng et al. (2016) when the pore solution pH decreased down to ≈ 9 . Our results, when the pH decreased down to 11 and 12.3, are also shown (Seguí Femenias et al. 2018b).

4.4 Application in practice

With our sensor, we expect to significantly improve and refine condition assessment in reinforced concrete structures. By placing the sensors at different depths, profiles on the corrosion risk initiation can be obtained at different times and thus, our sensor system can act as an early warning for corrosion initiation. Additionally, it should also be noted that higher rates of corrosion have been observed in presence of chlorides and carbonation compared to when these two corrosion factors act separately (Gonzalez et al. 2013). Thus, information obtained by using these sensors in corroding structures can shed light on the corrosion rate under different exposure conditions, i.e., partially carbonated concrete exposed to chloride ingress.

In order to promote the use of our sensors in practice, two pilot projects are currently ongoing. The first pilot project consists of embedding our sensor system in a bridge in Cuba exposed to seawater. Here, the splash zone of the bridge is the most critical area as higher concentration of chlorides are typically found (Bertolini et al. 2013) and thus this will be the main location where our sensors are installed. Additionally, it should be noted that a significant part of this bridge is built with LC3 cement; this is an OPC blended cement and thus prone to higher carbonation rates compared to pure OPC (Ho et al. 1987, Skjolsvold 1986). The second pilot project consists of

embedding our sensor system in a parking garage in Austria; in this case, exposure to chlorides is expected on the lower part of the building walls due to the use of deicing salts. Additionally, the construction material consists of a newly developed quaternary blended cement for Switzerland (OPC blended with limestone, fly ash and, burn oil shale) and thus potentially prone to high carbonation rates (Ho et al. 1987, Skjolsvold 1986)

Fig. 5 shows a schematic representation of the locations for embedding our sensor system in the bridge in Cuba (a) and in the parking garage in Austria (b).

At this moment, it should be noted that the sensors are connected through wires to externally installed data loggers for data acquisition and transmission. However, it is known that wired-connections may represent a weak point in the structure and can promote the penetration of aggressive agents. For this reason, current research is focused on obtaining a wireless device that monitors and transmits the sensors responses.

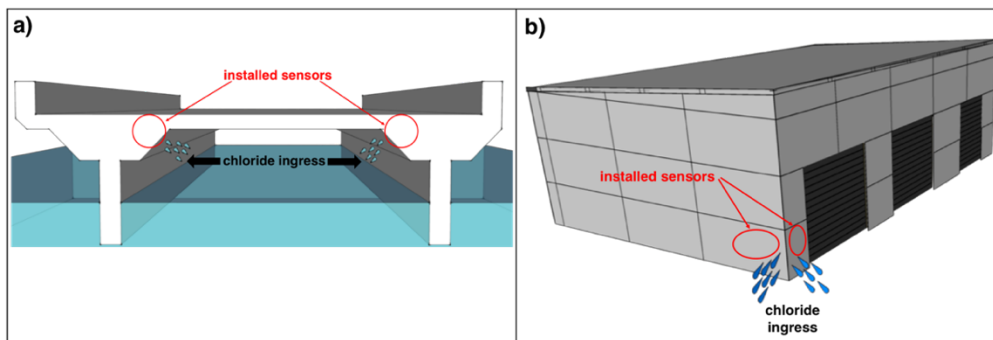


Figure 5. Ongoing pilot projects of applying our sensors in structures: (a) a bridge in Cuba exposed to seawater and (b) a parking garage in Austria exposed to deicing salts. In both cases, the sensor installation is planned for the first half of 2019 and the material used consists of OPC cement blended with supplementary cementitious materials. (schematic illustration)

5 CONCLUSIONS AND OUTLOOK

In this work, we present a novel sensor that can be embedded in concrete in order to monitor pH and chloride concentration changes. The results obtained show that during carbonation of cement paste, chloride concentration increases due to the release of bound chlorides, which significantly increases the risk of corrosion. During chloride ingress, it has been shown that a decrease of 1 pH unit or less can have an important impact on the assessment of the corrosion risk. It is concluded that in many cases, the risk of corrosion would be underestimated if only pH or chloride concentration were monitored. We thus believe that the use of our sensor may provide useful information for engineers in the decision-making. Pilot projects are currently ongoing.

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