

# EVALUATION OF Ag/AgCl SENSORS FOR IN-SITU MONITORING OF FREE CHLORIDE CONCENTRATION IN REINFORCED CONCRETE STRUCTURES

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**ABSTRACT:** The level of free chloride concentration in reinforced concrete structures essentially determines the onset of steel corrosion initiation and further propagation. One of the well-known methods for monitoring free chloride concentration is using silver/silver chloride electrodes (Ag/AgCl). These electrodes are sensitive mainly to chloride ions and establish a certain electrochemical potential depending on the chloride ion activity in the environment. Although the functioning principles of these electrodes are well-established, their use in concrete is challenging when durability and practical engineering issues are considered. In order to be able to accurately determine free chloride content in concrete, it is important to evaluate the performance of Ag/AgCl electrodes (sensors) in strong alkaline environments i.e. those existing in non-carbonated concrete (pH~12–13.5). Furthermore the linear response of these sensors to a wide range of chloride concentrations in highly alkaline medium, as well as their sensitivity to pH changes, need a more in-depth investigation.

In this paper the response of Ag/AgCl electrodes in simulated pore solutions having different chloride concentrations and different pH values was studied. The electrodes were calibrated in cement extract solution, distilled-water and simulated pore solution. The results show that at chloride concentrations of  $> 4$  mM the effect of pH on the response of the sensors is insignificant which makes using Ag/AgCl sensors in concrete feasible i.e. this concentration is much lower than the generally reported thresholds for corrosion initiation.

**Keywords:** Ag/AgCl electrode, cement extract solution, free chloride, pH value, pore solution.

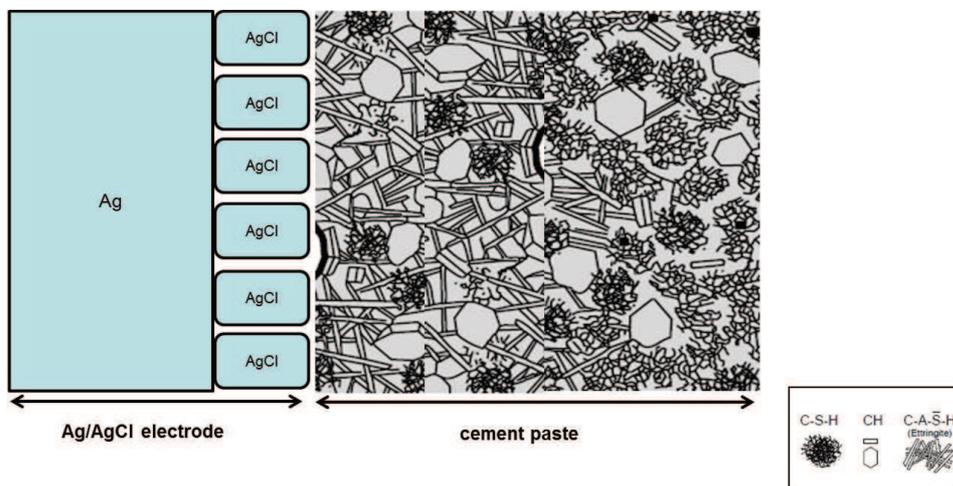
## INTRODUCTION

Corrosion of the steel reinforcement in concrete is recognized as the major problem within maintenance of civil structures. The concrete pH, usually in the range 12–13.5, provides chemical protection to the re-bars due to steel passivation. However, with time, severe corrosion problems may occur in reinforced structures <sup>[1]</sup>. Chloride ions are the major contributing factor that affects the corrosion state of the steel rebar embedded in concrete. Analysis of the chloride content in hardened cement based materials is not an easy task. The traditional way of powder drilling, dissolution in acids and chloride analysis by potentiometric titration shows quite a wide scatter <sup>[2]</sup>. Having the drawbacks of destructive techniques, attempts have been made to measure the free chloride concentration in the concrete pore solution by means of embedded ion selective electrodes. A perfect embeddable

electrode must obey several conditions: it must be stable, invariant to chemical and thermal changes in concrete, able to pass small currents with a minimum of polarization and hysteresis effects, display long-term performance, be cost effective and result from an environmentally safe manufacturing procedure [1].

Because of its good stability and easy preparation, the common Ag/AgCl electrode has been widely used as a reference electrode in electrochemistry. Solid Ag/AgCl electrodes (or commonly known as ion-selective probes) have been also developed to monitor the chloride content in model solutions or concrete structures [2, 3]. The first documented attempt to measure chloride ion activities with Ag/AgCl electrodes in hardened mortar was reported in the early 1990s [4].

In this study, Ag/AgCl electrodes were prepared by anodizing metallic silver in acidic environment with high chloride concentration. During the anodization process the silver wire is “coated” with AgCl packed-piled particles. This electrode, when in contact with the relevant external environment, establishes a quasi-equilibrium potential (Fig. 1). This potential depends on the chloride concentration in the environment and as long as this electrolyte concentration is maintained, the electrode potential is constant.



**Fig. 1:** Schematic representation of Ag/AgCl electrode in contact with cement paste

Some authors reported that Ag/AgCl electrodes embedded in mortar specimens are stable only for a short period, while others found good long-term stability. Consequently, these electrodes still remain a potentially interesting choice in what concerns chloride ion monitoring in reinforced concrete structures [1]. Their equilibrium potential value depends on the chloride ion activity (concentration) in the surrounding medium according to Nernst’s Law [5]. In high alkaline solution and in the presence of hydroxyl ions (as within concrete environment), silver activity near the surface (and hence electrode potential response) is determined by an exchange equilibrium, Eq.(1) [7]:



At high pH values, the AgCl membrane becomes unstable and is, partly or completely, turned into Ag<sub>2</sub>O. By continuous transformation of the electrode surface into Ag<sub>2</sub>O, a mixed potential will be developed at the electrode/solution interface. As reported in previous studies, pH has a significant influence on the potential value of the sensor at low chloride concentration and further studies need to quantify the interference of pH in order to establish a suitable calibration method for low chloride concentration environments [5]. Some authors discussed the limit of detection of the chloride ion selective electrode, due to hydroxyl ion interference, varies with pH. For the pore solution of ordinary Portland cement paste or concrete, this limit can be

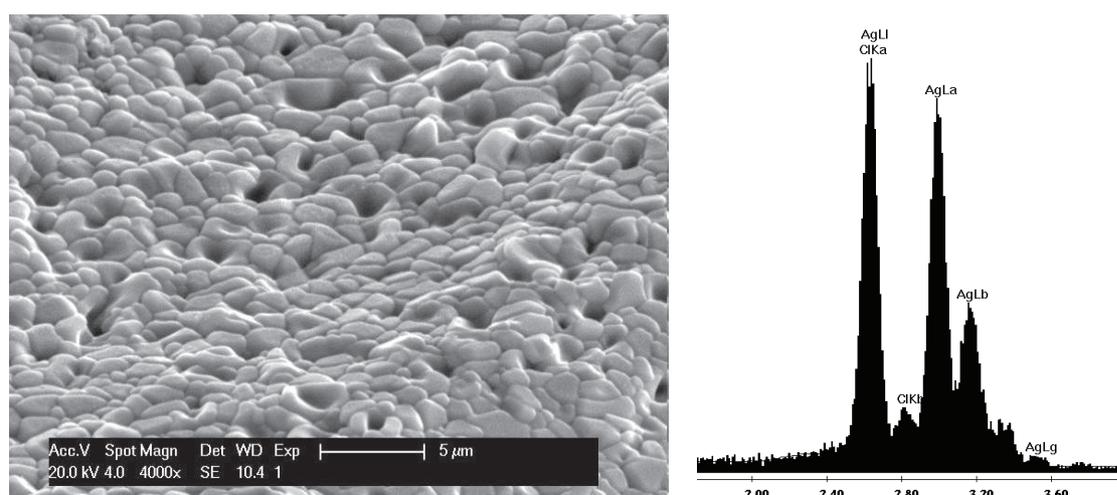
set between  $3 \times 10^{-3}$  molal, and  $7 \times 10^{-3}$  molal, i.e. just below a chloride concentration value of  $1 \times 10^{-2}$  molal. This effect can prevent the reliable measurement of free  $\text{Cl}^-$  concentrations, when these are below the corresponding limit of detection [6].

Therefore, in order to be able to accurately determine the free chloride content in concrete, it is important to evaluate the performance of Ag/AgCl electrodes (sensors) in strong alkaline environments i.e. those existing in non-carbonated concrete (pH~12–13.5) and intensely carbonated concrete (pH~7.5) [8].

In this paper the response of Ag/AgCl electrodes in simulated pore solutions with different chloride concentrations and different pH values was studied. The electrodes were calibrated in distilled water (pH=6) and simulated pore solution (pH=13.6). The range of employed chloride concentrations in the above environments allows quantification of the interference of pH and establishing a suitable calibration method for low chloride concentration environments.

## EXPERIMENT

Silver wires, 1 mm in diameter (99.99% purity) were cleaned for 2 hours in concentrated ammonia and immersed in distilled water overnight. Next, they were anodized for one hour in 0.1M HCl solution at current density of  $0.5 \text{ mA/cm}^2$  (Pt mesh served as cathode). The electrodes were stored in closed and out of direct sunlight environment until needed.



**Fig. 2:** SEM micrograph and EDS analysis of AgCl layer deposited at  $0.5 \text{ mA/cm}^2$  current density

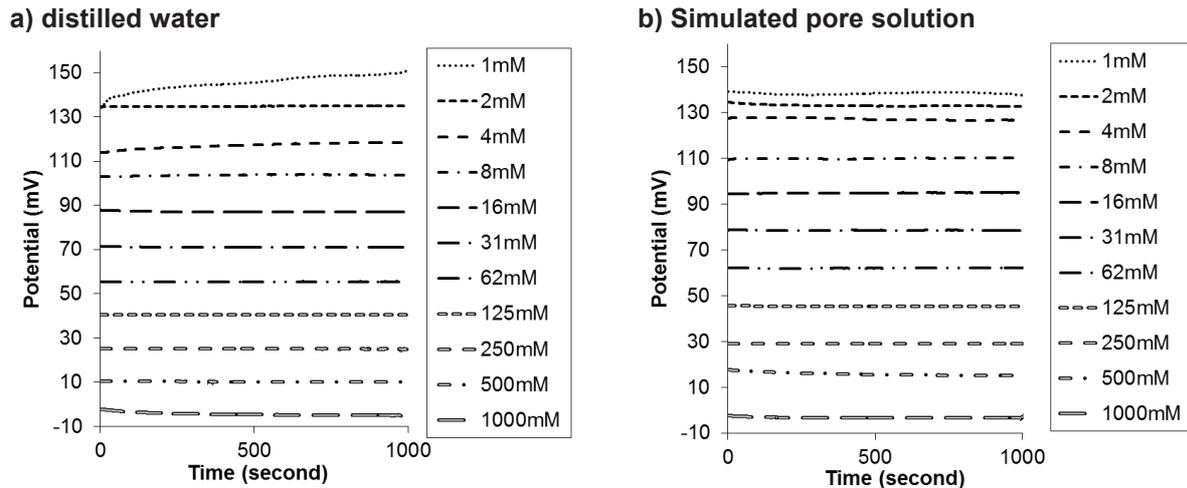
Electrical connection for further tests was made through welding of the anodized silver wire to a copper wire; the non-anodized and welded zones were insulated by epoxy resin.

Fig. 2 shows the surface morphology of a Ag/AgCl electrode, anodized in 0.1 M HCl. Scanning electron microscopy (SEM) observations show the uniformly packed and piled particles, deposited on the silver substrate; Energy dispersive x-ray analysis (EDS) confirms the presence of AgCl through the observed Ag and Cl peaks in the EDS pattern. The electrode (sensor) potential was measured in distilled water (pH~6) and in simulated pore solution (0.63 M KOH+0.05 M NaOH+Sat.  $\text{Ca}(\text{OH})_2$  in the presence of various chloride concentrations.

## RESULTS

Fig. 3 shows the fast response of the sensors to the various levels of  $\text{Cl}^-$  concentration in

different solutions, establishing stable potential values. This is essentially a potentiometric measurement: when exposed to solutions with various amounts of  $\text{Cl}^-$  ions, the Ag/AgCl electrode responds in a few seconds and reaches a constant potential depending on the  $\text{Cl}^-$  concentration in less than 1 min. The final potential increases (becomes more anodic or positive) with decreasing  $\text{Cl}^-$  ions concentration and more negative (more cathodic) with increasing chloride concentration. These potential changes follow fundamental principles and Nernst law, but are also determined by the ease of the electrochemical process i.e. the response of the sensor is also influenced by the morphology and microstructural properties of the AgCl layer, shown in Fig.2 (the dependence of sensor response on AgCl layer properties is not subject to this work)



**Fig. 3:** Potential response of Ag/AgCl electrode in solutions with various amounts of  $\text{Cl}^-$

As can be observed (Fig.3) the type of solution determines slightly different response of the Ag/AgCl sensor under the same chloride ion concentration. For instance, for 1 mM  $\text{Cl}^-$  concentration, the sensor potential in distilled water presents 13.1 mV higher value, compared to the potential reading in simulated pore solution. This decreased potential values in simulated concrete pore solution, which has a notably higher pH value (13.5) than distilled water (pH of 6.0), is mainly due to the interference from hydroxyl ( $\text{OH}^-$ ) ions. This deviation at low chloride contents could be attributed to the formation of  $\text{Ag}_2\text{O}$ ,  $\text{AgOH}$  or  $\text{Ag}(\text{OH})_2$ . When the chloride ion concentration increases to 1000 mM, the potential of the sensor in simulated pore solution is a slightly higher (1.9 mV) than that in distilled water and simulated pore solution, containing 1007 mM chloride concentration. Therefore, the influence of pH on the potential of the sensor in 1000 mM chloride concentration is different from those in 1 mM chloride solution so the potential variation is less significant at higher chloride concentrations. This interference has seldom been quantified before for the case of concrete pore solution.

According to the literature, it was shown that in conditions of the same chloride concentration the potential of Ag/AgCl electrode in simulated pore solution containing NaCl is always more positive than that in pure NaCl solution [7]. However, in the current study the potential of Ag/AgCl electrodes in distilled water with 1 mM and 2 mM was more positive than the corresponding potential in simulated pore solution. This indicates that the high pH affects the sensor behavior at low chloride concentration.

To investigate the effect of pH on the potential of the sensor at different chloride concentrations, simulated pore solutions with different pH (7.0, 9.0, 12.6, 13.6) and chloride concentrations (1 mM, 2 mM, 4 mM, 16 mM, 62 mM and 250 mM) were prepared and the potential of the sensors was measured in these solutions. In order to prepare the solutions at

different pH, and chloride concentrations but with similar ionic strength (to minimize the effects due to the presence of ions other than hydroxyl ions), concentrated nitric acid was added drop-wise to the solution to adjust the pH at the relevant values. After pH adjustment, the potential of the sensor in the solutions was recorded.

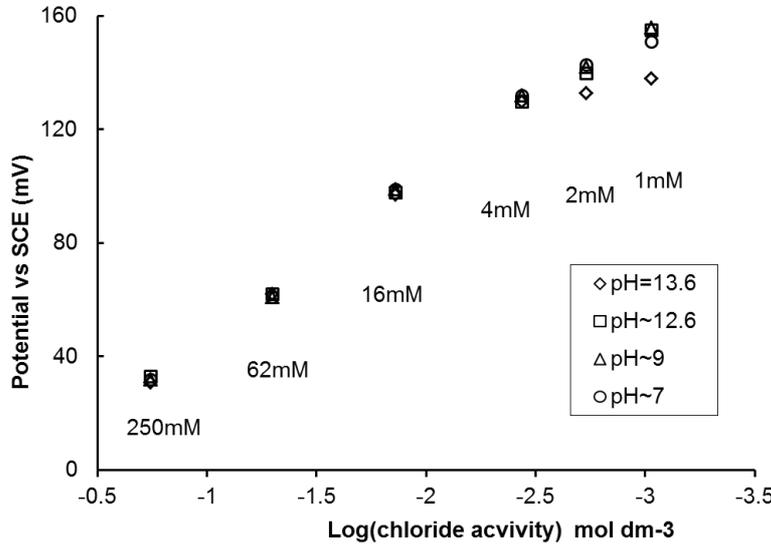


Fig. 4: The effect of pH on the response of the sensor

Fig. 4 shows the pH sensitivity is lower at higher chloride concentration. At low chloride concentration the potential difference between the solutions with different pH is larger than the potential difference at higher chloride concentration. In the case of 1 mM and 2 mM the difference between the maximum and the minimum potentials is about 18 mV and 10 mV, respectively. At 4 mM chloride concentration there is only 2 mV difference between the highest and lowest potential of the sensor. At higher chloride concentrations the effect of pH on the response of the sensor is less than 1 mV which is insignificant. Therefore, in solutions with chloride concentration lower than 4 mM, the effect of pH on the response of the sensor is not negligible. Therefore, the Ag/AgCl electrodes (sensors) can be used to determine chloride concentrations in cement-based materials with high accuracy at chloride concentration higher than 4 mM. Considering pH of 12.6 as the maximum value results in higher accuracy at low chloride concentrations and the difference between the maximum and the minimum potential of sensor at 1 mM and 2 mM chloride solutions decreases to 5 mV and 3 mV, respectively. Consequently, pH has a significant influence on the response of the sensor when a pH increase from 12.6 to 13.6 is relevant (12.6 – 13.6 being the pH range for pore solution in concrete environment).

These results indicate that (ideally) the chloride-content should be determined along with simultaneous detection of pH values, especially when low chloride concentrations are concerned. The performance of the Ag/AgCl sensors in embedded conditions (cement paste, mortar and concrete specimens) is an on-going investigation, focusing on sensor readings' interpretation and defined field application.

## CONCLUSIONS

The following conclusions can be drawn from the present investigation:

- At 1000 mM chloride concentration, the solution composition has a minimum effect on the response of the sensor.
- The pH has a significant influence on the potential value of the sensor at chloride concentration lower than 4 mM.
- The pH value should be simultaneously detected in order to precisely determine the chloride content in concrete with low or minimal chloride concentration.

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