

The importance of chloride sensors stability in monitoring ageing phenomena in concrete structures: Ag/AgCl electrodes performance in simulated pore-water environment

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Abstract: One of the reported problems associated with the performance of Ag/AgCl electrodes in alkaline environment, as concrete pore water, has been their poor stability. Open circuit potentials are typically observed to be stable for a time period of a few minutes to some days depending on the thickness and microstructure of the sparingly soluble AgCl and the subsequently developed mixed potentials at the electrode/solution interface. In this paper the open circuit potential of the chloride sensors were monitored over time in simulated pore solution with and without chloride and their electrochemical response recorded via electrochemical impedance spectroscopy (EIS). The alterations in response of the sensors can be denoted to transformation of the AgCl layer to Ag₂O in chloride-free high pH environment as in concrete pore water. Recovery of the AgCl layer takes place in chloride-containing medium, where establishing of sensor stability is determined by the chloride concentration.

Keywords: Chloride sensor, open circuit potential, electrochemical impedance spectroscopy

1 Introduction

One of the most common issues within ageing infrastructure is steel corrosion in reinforced concrete. Among others, the level of (free) chloride concentration in the vicinity of the steel reinforcement is an important parameter as far as corrosion initiation and propagation are concerned. The traditional techniques for measuring the free chloride content in concrete require destructive sampling and thus cannot be used for continuous monitoring of the free chloride content. In addition, in these techniques the amount of chloride will be measured in the concrete volume under investigation instead of localized measurement, which leads to inaccurate results in the case of concentration gradients [1, 2]. The drawbacks of destructive techniques raised the attempts to measure the free chloride concentration in the pore solution using embedded ion selective electrodes [2, 3]. Silver/silver chloride (Ag/AgCl) electrodes are sensitive to chloride ions and ideally exhibit a certain electrochemical potential that depends on the chloride ion activity in the solution [1]. Although the principles of Ag/AgCl electrodes are well-established, the stability and durability of these electrodes in high alkaline environments such as those existing in concrete (pH~12–13) are of great importance and need to be fulfilled. Otherwise, the application in concrete environment is not feasible [4, 5].

As reported, the potential of Ag/AgCl electrodes (ion-selective (ISE), membrane ones) decreases with time upon immersion in solutions of high pH, in the absence of chloride. This can be attributed to the “damage” of the ISE membrane through the formation of silver oxides or silver hydroxide [5]. Previous studies showed that in high pH solutions with chloride, the potentials are almost stable over 6 months with only ± 1.5 mV changes, whereas in the absence of chloride, the potential of the Ag/AgCl electrodes (chloride sensors) were less stable and decreased over time [7]. On the other hand, the relation between the chloride activity and electrode potential is logarithmic, i.e., the potential changes sharply at chloride concentrations close to zero even with a minimum variations in chloride concentration. As further discussed by Angst et al. [7], after 6 months immersion in chloride-free solution, the sensors were removed and placed in potassium hydroxide (KOH) solutions with the same alkalinity, but containing 0.5 M sodium chloride. In the case of 0.01M and 0.1M KOH they responded to the chloride concentration correctly and almost immediately. However, in the case of 1M KOH, the sensors

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approached the stable potential within a few hours. The authors concluded that the formation of silver oxide is fully reversible [7]. Similarly, other studies [6] report that Ag/AgCl electrodes demonstrate lower potentials when the pH is above 12 and approach the potential of silver/silver oxide at pH of 14.

In this paper the variation in the potential of Ag/AgCl electrodes was monitored in simulated pore solutions (pH~13.6). Meanwhile, the electrochemical response of the sensors was monitored via electrochemical impedance spectroscopy (EIS) in an attempt to correlate electrochemical phenomena to possible changes in the microstructure of the chloride sensors within treatment.

2 Experiments

Silver wires of 1 mm in diameter (99.99% purity, as received) were placed for 2 hours in concentrated ammonia and subsequently immersed in distilled water overnight. Then the wires were anodized for one hour in 0.1M HCl solution at a current density of 0.5 mA/cm² (relevant procedure for the anodization regime as reported in [8]); platinum mesh served as a cathode. After anodization a brown-black AgCl layer was formed over the silver substrate. The anodized silver wire was welded to a copper wire and the non-anodized and welded zones were protected with an epoxy resin. Two series of tests were performed. In the first series, the sensors were immersed in simulated pore solution (SPS) (0.63M KOH+0.05 M NaOH+Sat. Ca(OH)₂) with pH of 13.6, free of chloride, over 115 days. The open circuit potentials (OCP), versus saturated calomel (SCE) reference electrode, were measured over time. In the second series the sensors were treated in SPS free of chloride for 4 days before immersion in SPS with 1000 mM and 125 mM chloride concentrations. OCP and EIS measurements were performed in these solutions. The EIS measurements were performed by superimposing an AC voltage of 10 mV amplitude (rms) in the frequency range of 50kHz (1kHz) to 0.01Hz, using Autolab, Metrohm, NL.

Figure 1 shows the morphology of the AgCl layers, formed on the Ag substrate after anodization in 0.1M HCl (Fig. 1a) and the relevant EDS spectrum (Fig.1b), confirming the deposited layer as silver chloride.

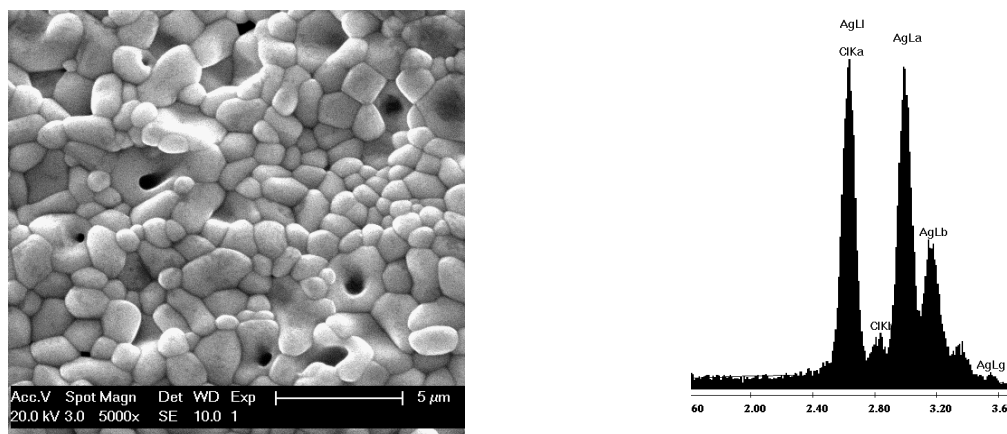


Figure 1 SEM top view of AgCl layer deposited over the silver substrate (left); b) EDS of deposited AgCl (right)

3 Results

3.1. Time dependency of the potential of the sensor in alkaline solution

Three replicate sensors were immersed in an open to air, chloride-free simulated pore solution (SPS) and their open circuit potentials (OCPs) recorded for 19 days. As shown in Fig. 2, the potential of these sensors decreased from an average value of 137 mV at the start of immersion to approx. 100 – 110 mV after 19 days. As aforementioned, in the absence of chloride and in high

pH environment (pH of 13.6 hereby employed), silver hydroxides form and further transform to silver oxides (Ag_2O). The continuous formation of Ag_2O shifts the potential of the sensors to more negative values, arriving at the recorded potentials of ~ 100 mV (Fig.2), which is according the Nernst equation and solubility constants for the $\text{Ag}/\text{Ag}_2\text{O}$ interface in conditions of close to room temperature and pH ~ 14 .

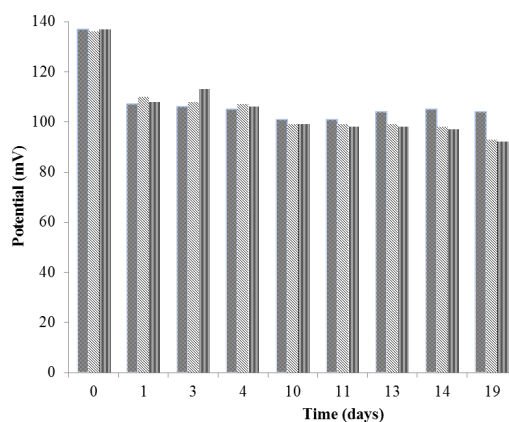


Figure 2 Potential stability of the electrodes in simulated pore solution without chloride over time

3.2. The effect of chloride concentration on the response of the sensors

In this test series, the effect of pre-conditioning of two replicate sensors in chloride-free SPS solution was monitored when chloride was added to the original solutions. When the sensors were exposed to the chloride-free SPS medium, silver hydroxide forms, transforms to silver oxide and OCP values shift cathodically (Fig.3). The result is as previously commented and observed for the series of three replicate sensors (Fig.2), i.e. within immersion OCP values were in the range of 130 – 140 mV (start, Fig.3) and after 4 days of immersion established around 110 mV (day 4, Fig.3). The next step was “contamination” of the solutions with chloride: two chloride concentrations were employed – 1000 mM and 125 mM. The test was executed as follows: after 4 days of immersion in Cl-free SPS, the solution was adjusted to contain 1000mM chloride concentration and the response (OCP) of the sensors were recorded over time of 5 min to 1h (Fig.3). As expected, a cathodic shift of potential was immediately observed and OCP values stabilised around -6mV (which is the expected level of OCP relevant to the activity of Cl-ions in this solution, [8]).

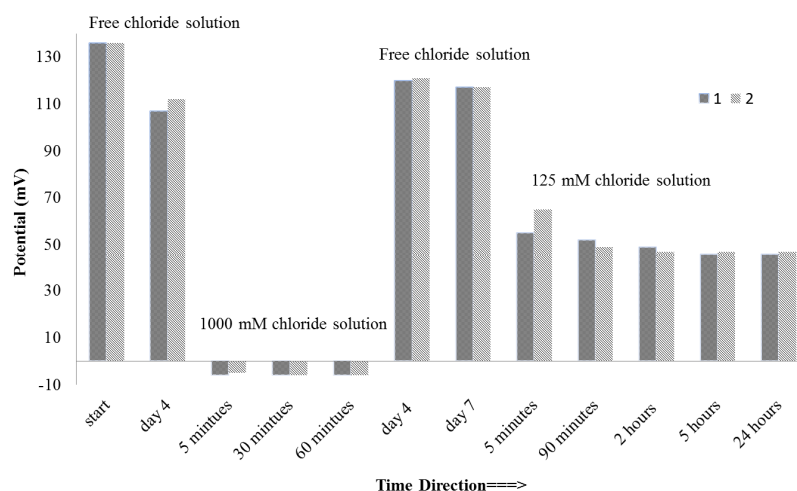


Figure 3 Stability of the electrodes in simulated pore solutions: Cl-free and Cl-containing (1000 mM ,125 mM)

After potential stabilization, the sensors were re-immersed in SPS free of chloride ions (days 4 and 7 in Fig.3). The potential of the sensors shifted back anodically to ~ 120 mV (in contrast to

the previously observed 110 mV before immersion in SPS with 1000 mM chloride concentration). In other words, the sensors were partially recovered after immersion in the SPS with chloride ions. This change in the potential can be attributed to the formation of silver chloride (instead of silver oxide) on the surface of the sensors in the SPS with chloride, a predominant reaction when chloride ions are present. Between 4 and 7 days treatment in this “second” chloride-free treatment, the OCP shifted again toward the characteristic values for a Ag/Ag₂O interface of ~ 110 mV (117 mV were observed, denoted to mixed potential from AgCl contribution at the stage of 7 days).

Finally, the sensors were exposed to SPS with 125 mM chloride ion concentration. In this solution, the OCP of the sensors was established at the level of 46 mV after 24 hours of immersion (Fig. 3), 46 mV corresponding to the relevant chloride concentration in this case. It can be concluded that the “stabilization” time (or AgCl layer recovery) of the treated sensors differs depending on the chloride concentration in the solution. At higher chloride concentration, the sensors stabilize faster. This result is in line with the previous study [8] where it was shown that the intact sensors stabilize faster at higher chloride concentration.

3.3. EIS response of Ag/AgCl in SPS solutions

The EIS response of the sensors in the previously discussed conditions and environment was recorded at open circuit potential, AC voltage of 10 mV amplitude (rms) in the frequency range of 1 kHz to 10 mHz. The initial response of the Ag/AgCl sensors in Cl-free environment (day 1, Fig.4) presents two clearly distinct time constants, with possible contribution of an additional chemical /electrochemical process in the low frequency domain.

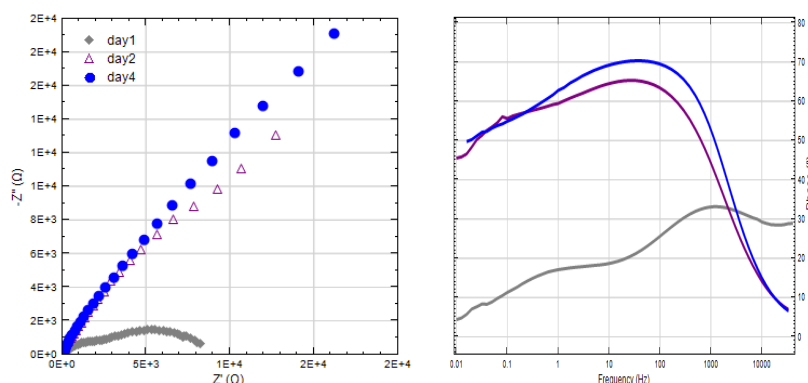


Figure 4 EIS response of Ag/AgCl sensors in Cl-free SPS solutions after 1,2 and 4 days of immersion

Within immersion (day 2 and day 4, Fig.4), the magnitude of impedance and phase angle significantly increase, denoted to transformation of the AgCl layer into hydroxide/oxide layer in this environment. The charge transfer resistance at the Ag/AgCl interface is reduced and becomes dominated by diffusion limitation (blocking pores and voids) and/or mass transport phenomena within the formation of the already relevant Ag/Ag₂O interface. Upon subsequent immersion of the sensors in Cl-containing environment, the EIS response immediately reflects the recovery of the Ag/AgCl interface – initial and subsequent drop in impedance and phase angle values are observed for the 125 mM and 1M chloride concentration (Fig.5, left). For comparative purposes and in order to clarify the contribution of previously or subsequently formed and/or modified AgCl/Ag₂O layers, the EIS response of a Ag wire in 1M NaCl solution is presented in Fig.5 (right) as an overlay to the response of a Ag/AgCl sensor in SPS+1MNaCl.

Fig. 6 presents the preliminary equivalent circuits, employed for fitting the EIS response, including an overlay of response (symbols) and fit (line) for the Ag/AgCl sensor after four days of immersion; Table 1 presents the preliminary fit parameters. As can be observed, the chosen

electrical circuits give a globally good fit result, however, adjustments are necessary in order to account for the exact surface phenomena.

Although further investigation is needed in order to clarify the observed layers' transformation through correlation of surface layer properties (via microscopy and X-ray analysis) and EIS response, based on the recorded behaviour at this stage, hypothetic behaviour is summarised in what follows. Within immersion of the sensors in chloride-free alkaline environment, the Ag/AgCl interface gradually transforms to Ag/Ag₂O interface, reflected by the characteristic OCP changes (Figs. 2 and 3) and alterations in charge transfer/polarization resistance (Table 1).

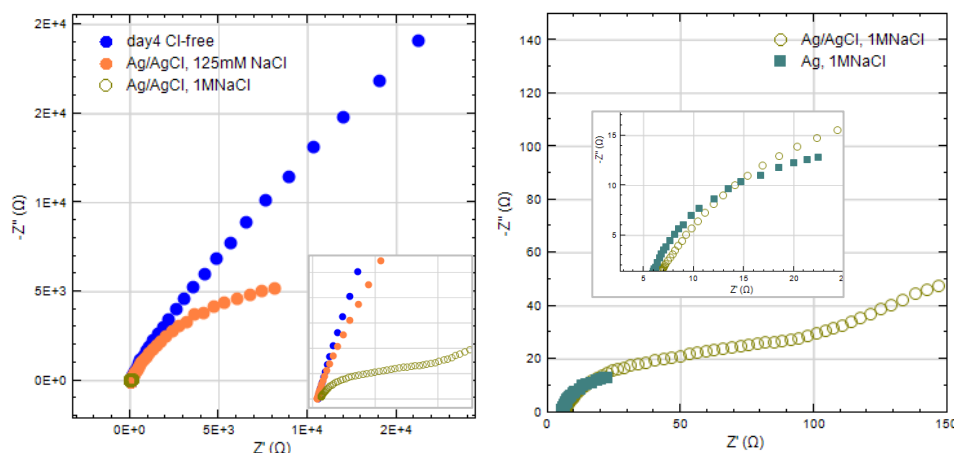


Figure 5 EIS response of Ag/AgCl sensors in Cl-free SPS solutions (day 4) and in chloride-containing solutions (left) ; overlay of Ag rod and Ag/AgCl sensor response in 1MNaCl

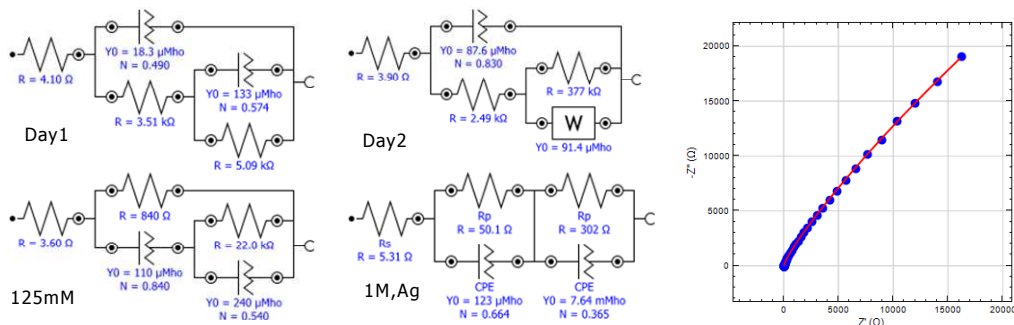


Figure 6 Equivalent electrical circuits (left) and overlay of EIS response and fit (right)

Table 1 – EIS fit parameters – preliminary results

	R_s	R_1	Q_1	n	R_2	Q_2	n	W	χ^2
	Ω	$k\Omega$	$Y_o (\mu Mho)$		$k\Omega$	$Y_o (\mu Mho)$		$Y_o (\mu Mho)$	
Day1	4.1	3.5	18.3	0.5	5	133	0.6		0.03
Day2	4.1	1.4	180	0.8	107			134	0.002
Day4	3.9	2.5	88	0.8	377			92	0.001
125mM	3.6	0.8	110	0.8	22	240	0.5		0.04
1M	4.3	0.05	123	0.6	0.3	7640	0.4		0.04
1M Ag	5.3	0.03	121	0.8	0.09	3100	0.6		0.05

The response for the Ag/AgCl sensors in chloride-free environment is initially modelled by resistors and pseudo-capacitances only, whereas for later immersion stages, a W impedance is introduced in order to account for diffusion/mass transport phenomena. Upon changing the environment to Cl-containing such, the electrochemical reaction of AgCl layer formation is the dominating one (Ag/AgCl in 125mM, Fig.5) i.e. W impedance is not observed, accompanied by drop in charge transfer/layer resistance and increase of pseudo capacitance values (Fig.5,6,

Table 1). Comparing the response of the Ag/AgCl sensors in SPS + 1M NaCl in the high frequency domain to the one of Ag in 1M NaCl (Fig.6), both with established OCP at -6 mV, the following is relevant: clearly the contribution of previously formed AgCl, subsequent transformation of AgCl to Ag₂O and finally recovering of AgCl upon re-immersion in chloride-containing environment is reflected by more than 1 time constant in the response for Ag/AgCl sensors in the low frequency domain. However, the preliminary simulation/fit procedure, reveal similar capacitance and resistance values for the electrochemical reaction (at Ag/AgCl interface) and variation in these for the chemical phenomena (at AgCl/solution interface), which is consistent with the initiation of AgCl layer formation for the case of Ag rod only and transformation at interfaces for the case of Ag/AgCl sensors. The next step of this investigation, involving microscopic surface analysis and final EIS fit and simulation is expected to justify and visualise the observed phenomena on the Ag/AgCl sensors' interface upon immersing in altered environment and thus justify the limitations of sensors' stability with respect morphology and transformations in the AgCl layer.

4 Conclusion

The following conclusions can be drawn from the present preliminary investigation:

- In alkaline chloride-free solution, the potential of the silver/silver chloride sensors changes over time, denoted to the formation of silver oxide;
- The more rapid change in sensors' potential in SPS with 1000 mM chloride can be attributed to the enhanced formation of silver chloride (instead of silver oxide) on the surface of the sensors when chloride ions are present. In contrast, within lower chloride concentrations (as the 125 mM solution), longer stabilisation time is required (i.e. the reaction of AgCl formation is impeded compared to 1000 mM)
- The impedance measurements show a pronounced difference in electrochemical response for the differently conditioned sensors, which is also with respect to the relevant environment. For chloride-free solutions, the magnitude of impedance increases with time of conditioning, denoted to the plausible formation of Ag₂O within the AgCl layer, blocking pores and exerting microstructural changes in the AgCl layer itself. Additionally, in Cl-free environment, the Faradaic reaction associated with AgCl layer formation is not taking place – all these result in increased impedance values with time of conditioning.
- In chloride-containing solutions, the EIS response shows significantly lower magnitude of impedance which corresponds well to the chloride concentration i.e. the lowest $|Z|$ was recorded for the 1000 mM solution.

5 References

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