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Polarization Behaviour of Silver in Model Solutions

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***Abstract*—When studying chloride-induced corrosion in reinforced concrete structures, essential information of interest is the concentration of chloride ions in the system. The absence of a reliable method for monitoring the free chloride ions justifies the attempts towards establishing a feasible practice in the application of the already known Ag/AgCl electrode, as a chloride sensor. To identify the governing mechanism and cognition of causes for instability of the chloride sensors in highly alkaline medium (as concrete), it is necessary to study the polarization behaviour of silver in different aqueous solutions resembling the concrete environment. Following expectations and well-known fundamental background, the results from this work confirm that in the presence of chloride ions, silver chloride is the predominant reaction product, forming on the silver surface. Whereas, in the absence of chloride ions and/or presence of interfering ions, such as hydroxide ions, the oxidation process of AgCl formation is significantly dependent on the chloride concentration in the medium. Therefore, the formation of a stable AgCl layer on a Ag substrate (as would be required for sensors application for example) is a function of the presence and amount of interfering ions, together with the chloride concentration in the medium.**

***Index Terms*—Ag/AgCl electrode, chloride sensor, concrete, potentiodynamic polarization, alkaline solution**

I. INTRODUCTION

The wide use of Ag in the form of Ag/AgCl electrodes in industrial technologies, medical instruments and as a reference electrode in electrochemistry led to numerous investigations of its behaviour in different mediums [1]-[5].

Within the last 30 years, attention has been drawn to the application of silver, coated with silver chloride, as a chloride sensor in reinforced concrete structures. The main purpose of this application is to measure the concentration of chloride ions nondestructively [6]-[8]. The presence of various ions, such as OH^-, SO_4^{2-}, Cl^- etc. can affect the functionality of the chloride sensors in the medium. This prompted further studies on the different oxidation states of Ag in highly alkaline solutions, resembling the concrete environment. To assess the silver behaviour in reinforced concrete structures, it is wise to investigate the performance of silver in aqueous model solutions using electrochemical techniques such as e.g. potentiodynamic polarization (PDP).

Literature studies provide a suitable foundation for understanding the possible oxi/redox reactions on the surface of silver in highly alkaline solutions. Despite the considerable knowledge, available and reported in the current state-of-the-art, there is still a debate and a disagreement over the mechanisms by which AgCl films nucleate, grow on a silver substrate and may exist together with other silver compounds [5]-[10].

For example, electrochemical evidence shows that not always simple reaction sequences are sufficient to explain all fluctuations in anodic currents and current maxima, observed during an electrochemical test such as potentiodynamic polarization [11], [12]. This is despite the fact that kinetic response can be hypothesized by employing electrochemical thermodynamics e.g. through considering Pourbaix diagrams for Ag in relevant medium. Hypothesizing or modelling an electrochemical performance based on thermodynamic principles, can later-on be validated through kinetics i.e. through electrochemical methods. If results would be coupled to the surface analysis at certain stages during electrochemical testing, a complete overview of the AgCl layer formation and growth could be at hand, as reported in [5].

The synergy of these methods and related considerations has been already, partly, approached in our work [13], [14], correlating potentiometric response of Ag/AgCl surfaces in simulated pore water, X-ray analysis and microscopic investigation. This work adds-up to the already reported results, by considering various aspects of the purely electrochemical response of Ag only in various model solutions.

II. EXPERIMENTAL MATERIALS & METHODS

Silver wires of 99.5% purity with 1 mm diameter supplied by Salomon's Metalen B.V. Netherlands, were used in this study.

Different solutions were prepared from crystalline NaCl (Sigma-Aldrich Corporation) and demineralized water. Cement extract solution (CE) was prepared by mixing CEM I 42.5N and water with the ratio of 1:1. The suspension was rotated for 24 hours, before filtration and obtaining the extract solution (pH~13). Although the CE

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medium was supposed to be chlorides-free, chemical analysis of the solution showed chloride content of about 10 mM in the solution. This is because of chlorides present at levels of < 0.03 % in the original cement (ENCI, NL specifications) and the chloride ions in the mixing water.

A saturated calomel electrode (SCE) and Pt mesh as a cage were used for reference and counter electrodes, respectively. The test cell setup followed a 3-electrode configuration.

The test specimens were 1 mm-diameter silver wires of 1 cm length. The silver wires were cleaned for 2 hours in concentrated ammonia, then immersed in demi water overnight prior to the polarization tests. To monitor the formation and growth process of silver compounds on the Ag substrate, the Ag wire specimens were polarized from −200 mV to more than +1500 mV versus open circuit potential (OCP) of Ag in the relevant solution at a scan rate of 0.5 mV/s.

The electrochemical tests were performed using PGSTAT 302N potentiostat (Metrohm Autolab B.V., Netherlands) at room temperature.

The potentiodynamic response of silver was recorded in the following model solutions:

- 0.1 M HCl (pH=1.4),
- 0.1 M NaCl (pH~6), 1 M NaCl (pH~6),
- CE (pH~13), CE with 1 M NaCl (pH~13),

as well as in simulated pore solution (SPS), essentially representing 0.05 M NaOH+0.63 M KOH+Sat. $Ca(OH)_2$ (pH=13.6).

The solution of 0.1 M HCl is a medium, typically used for anodization and chloride sensor preparation. Whereas, SPS is the highly alkaline solution, free of chloride ions, being of interest in view of potential transformation of silver chlorides into silver oxides. The potentiodynamic polarization of Ag in various solutions was employed as a screening technique for deriving information on AgCl formation and/or transformation.

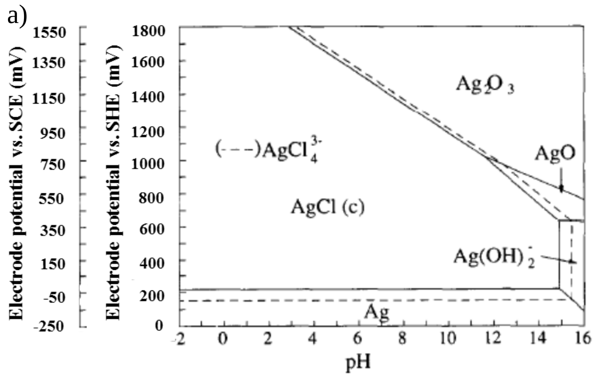
III. RESULTS AND DISCUSSION

Table I summarizes reported information on the specific features, observed during Ag polarization tests in various environmental conditions, e.g. the electrode potentials at which maximal anodic currents (anodic peaks) were recorded in a specific solution and linked to specific compounds. As can be observed, a certain potential range was denoted to the formation or existence of a certain oxides, hydroxide or salt of silver. The potential ranges vary for identical compound and similar or identical environment. The reported values, of course, need to be considered also in view of the relevant, as reported, test conditions. These aspects, in fact, justify the observed variation in Table I.

In highly alkaline medium, free of chloride ions, formation of different forms of silver oxide is as expected. Whereas, silver chloride is the predominant reaction product of silver in chloride-containing medium. Silver chloride formation can either overweight or counteract silver oxide formation in chloride-containing alkaline medium. The relevant interactions strongly depend on the chloride concentration in the environment.

TABLE I: SUMMARY OF THE OBSERVED PEAKS ON THE SILVER SURFACE DURING POLARIZATION TESTS

Surface product	Peak (mV vs SCE)	Test Solution	Reference
$AgOH–Ag(OH)_2^-$ monolayer	+172	0.1 M NaOH	[11]
Ag_2O multilayer	+245		
AgO	+339		
$Ag_2O_3(s)$	+663		
AgOH	+146	1 M NaOH	[12]
Ag_2O	+226		
AgO	+556		
Ag_2O_3	+606		
oxygen evolution	>+656		
$AgOH–Ag(OH)_2^-$ monolayer	+67	1 M NaOH	[15]
Ag_2O multilayer	+184		
AgO	339		
$Ag(OH)_4^-(aq)$	+602		
$Ag_2O_3(s)$	+688		
$AgOH–Ag(OH)_2^-$ monolayer	+143	4 M NaOH	[16]
Ag_2O multilayer	+225		
AgO	+605		
$Ag(OH)_4^-(aq)$ and $Ag_2O_3(s)$	+695		
AgCl	+180	0.15 M NaCl	[5]
AgCl	+79	0.1 M KCl + 1 M KOH	[17]
Ag_2O	+136		
thick layer of Ag_2O	+201		
AgCl	+73	0.1 M NaCl	[18]



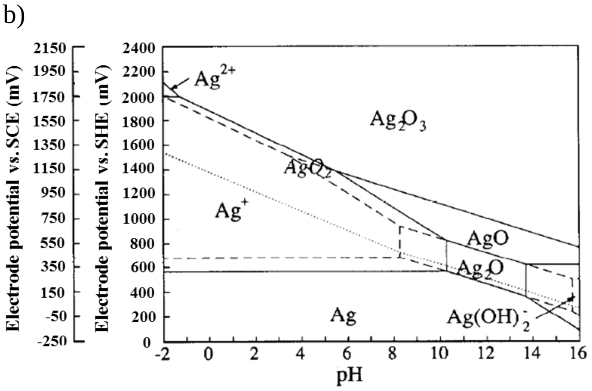


Figure 1. a) Pourbaix diagram for a silver-chloride-water system at 25 ° C for $a_{Ag} = 10^{-4.2}$ (~7 ppm): solid line, $a_{cl}^{-} = 1$, dashed line, $a_{cl}^{-} = 2$. b) Pourbaix diagram for a Ag-water system at 25 ℃; —— $a_{Ag}=10^{-4}$, - - - $a_{Ag}=10^{-2}$, .….$a_{Ag} = 10^{-2}$ with Ag_2O present [19].

Hence, the given information in Table I was used for discussion on the obtained results and for comparative purposes. The outcomes in this work are also discussed in view of thermodynamically plausible reactions and performance in certain environmental conditions, by considering the Pourbaix diagram for the Ag-H_2O-Cl and Ag-H_2O systems at 25°C (Fig. 1).

Pourbaix (potential - pH) diagrams map out thermodynamic stability of metal species and compounds at various combinations of equilibrium potential and pH in aqueous medium under standard conditions.

The Nernst equation is used for constructing these diagrams, hence, they can only provide thermodynamic information and an indication for what would be a chemical process, or an electrochemical reaction, respectively in a certain medium. Kinetic information cannot be obtained by these diagrams, however, they will answer the questions "if" and "why" a kinetically-controlled process would occur.

To this end, the Pourbaix diagrams for Ag were looked-up for discussion on the results in this work, considering the diagrams for Ag in water, both in the presence and absence of chloride ions.

The Pourbaix diagram for the Ag-H_2O-Cl system (Fig. 1a) shows a large area of predominance for AgCl(c), crystalline AgCl, when chloride ions activity is one (solid equilibrium line).

The increase in the activity of chloride ions to two (the dashed line), is predicted to cause dissolution of solid silver chloride as tetrachloroargentate (I), $AgCl_4^{3-}$ ions [19]. At high potential and high pH values, the existence of silver oxide compounds is thermodynamically possible, which is reflected in the Pourbaix diagram by reducing the area relevant to the silver chloride compound (Fig. 1a). Therefore, the alkalinity of the solution significantly affects the AgCl stability in the medium.

Fig. 1b shows the Pourbaix diagram for the Ag-H_2O system. In acidic/ neural environment, Ag °is stable under weakly oxidizing conditions, while its stability domain reduces with increasing the pH and potential. In alkaline solution, silver undergoes oxidation reactions that introduce Ag_2O and other silver oxides, depending on both potential of Ag and pH of the solution.

Accordingly, electrochemical evidences (Table I) show that thermodynamic data (Fig. 1) cannot always explain the observed features of the Ag response in electrochemical tests.

In the following, the PDP response of Ag in 0.1 M NaCl, 0.1 M HCl and 1 M NaCl solutions is presented. The PDP curves in both NaCl and HCl solutions show a similar trend (Fig. 2), and account for the formation of AgCl as the main reaction product.

With PDP polarization, AgCl formation was reported to be responsible for the observed features in the relevant response e.g. AgCl nucleation at ca. 50 to 100 mV after corrosion potential (E_{corr}), followed by a sharp increase in the anodic current and establishment of a diffusion current at potentials more noble than E_{corr} The limitations were denoted to the existence of an already developed AgCl layer, as reported previously by Ha and Prayer [5]. The these authors linked the electrochemical states with surface morphology in order to elucidate the hypothesized processes during polarization. They terminated the anodic polarization at different overpotentials to monitor the surface morphology of the AgCl layer with scanning electron microscope (SEM). Although different conditions applied in ref. [5], the PDP response presented similar features to the observed in Fig.2. Therefore, the PDP response in this study will be linked to potential morphological transitions and product layer formation, as previously observed and reported in [5].

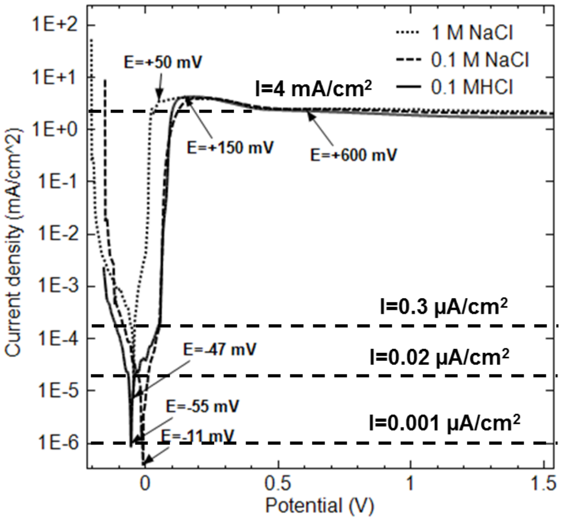


Figure 2. Potentiodynamic polarization curve of silver wire in 1M NaCl, 0.1 M NaCl and 0.1 M HCl solutions.

As seen in Fig. 2, the anodic behavior of silver was characterized by a low anodic current density (0.0001 µA/cm^2) at potentials near the corrosion potential, increasing to 0.3 µA/cm^2 at ca. +50 mV, followed by an abrupt increase towards 4 mA/cm^2 at overpotential of ca. +150 mV.

With continuing the polarization, an anodic current limitation can be observed as the potential is swept to more positive values. Increasing the potential to +600 mV is accompanied by decreasing the current density to lower values (2 mA/cm^2) compared to the recorded 4 mA/cm^2 at +150 mV. The limitation in current density can be interpreted as the coverage of the silver surface with AgCl layer. It was reported that the Ag surface after +150 mV is packed by AgCl particles [5].

The above considerations are also valid for Ag polarization in 1 M NaCl solution (Fig. 2). However, at higher chloride concentration (1 M), the increase of the current from 0.001 μA/cm^2 at E_{corr} (-47 mV) toward the diffusion limiting current (4 mA/cm^2 at +50 mV) occurred in a shorter range of potential (~100 mV), if compared with the corresponding value in 0.1 M NaCl. Consequently, by increasing the chloride content in the solution, the potential difference between E_{corr} and the potential relevant to the diffusion limiting current is significantly decreased. Thus, AgCl, as the predominant reaction product, exists in a wider range of potentials when the chloride content in the solution increases.

As previously discussed, alkalinity of the solution can introduce a limitation for the formation and/or stability of already formed AgCl. To study the possible interactions between silver, chloride and hydroxide ions, the PDP response of Ag in simulated pore solution (SPS), free of chloride ions, and cement extract solutions with 10 mM and 1 M chloride content was recorded and is shown in Fig. 3. The oxidation process at different overpotentials is attributed to a certain electrochemical reaction in the presence and absence of chloride ions in the medium.

The consecutive peaks relevant to passivation and dissolution of the product layer in SPS are replaced by a current "plateau" in the range of 170 mV to 1000 mV in CE solutions. In CE solutions, the presence of diffusion current with larger anodic polarization is similar to what was shown in neutral/acidic environment (Fig. 2) and can be interpreted as the subsequent influence of chloride ions in alkaline solution.

In contrast, and as previously discussed (Table I and Fig. 1b), silver oxide is the major silver compound that can form in highly alkaline solution free of chloride ions (SPS). During the anodic polarization of Ag in SPS and after corrosion potential (-167 mV), the maximum anodic current of 1 mA/cm^2 at potential of +220 mV can be observed. Increasing the potential towards +500 mV is accompanied by decreasing the current density. This trend followed by a sudden increase in the current density at +530 mV and subsequent attempt for re-passivation. Next is the increase in the current after +600 mV, when the silver is already in the transpassivity region, i.e. current due to dissolution of already available product layer on the silver substrate.

The above observation can be linked to the oxidation of Ag and formation of silver oxide compounds, in the following order: After corrosion potential, the active state of the silver is evident by the maximum current at +220 mV which is attributed to A_2O formation (Table I and Fig. 1b). According to Pourbaix diagram of silver ions in alkaline solution free of chloride ions (Fig. 1b), the Ag_2O can thermodynamically exist in the potential range of +100 mV to +350 mV.

The formation of Ag_2O at +220 mV is accompanied by decrease in the current density as the potential swept to +500 mV. This trend is followed by de-passivation at +530 mV and increase in the current due to AgO formation, as indicated in Table I and shown in Pourbaix diagram, Fig. 1b.

On the other hand, the presence of diffusion current (current plateau) at potential +170 mV in CE solution and +50 mV in CE with 1 M NaCl can be due to the AgCl formation in the product layer. As previously shown in Fig. 2, the formation of silver chloride is the main reason for the presence of stable current plateau in solutions containing chloride ions.

In CE solution, the current plateau at potential +170 mV is close to the first current peak in SPS, free of chloride ions (+200 mV). The current relevant to the plateau in CE solution is 1 mA/cm^2 which is lower than 4 mA/cm^2, measured in CE solution with 1 M NaCl and also the neutral/acidic chloride solutions, as shown in Fig. 2. The lower current density of Ag in CE solution together with the fluctuation in the response after semi-plateau and the sudden increase in the current after 1000 mV (similar to SPS) can be interpreted as the significant contribution of silver oxide in the product layer of CE solution. Therefore, in the presence of low chloride concentration in the alkaline solution such as CE, the product layer is a complex of silver chloride/oxide with silver oxides as the predominant compound.

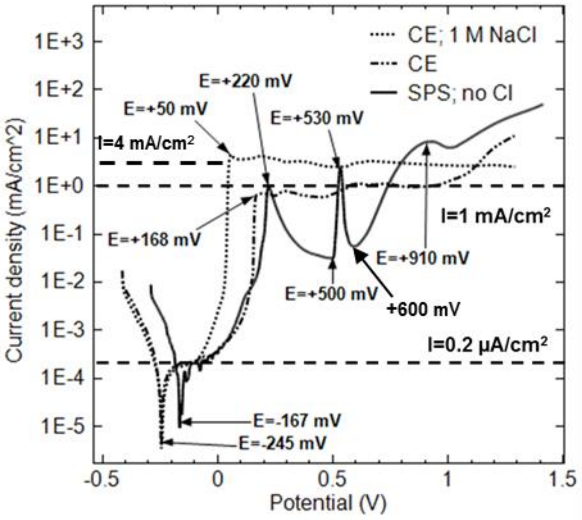


Figure 3. Potentiodynamic polarization curve of silver wire in simulated pore solution with pH 13.6, free of chloride ions.

On the other hand, the current plateau in CE solution with 1 M NaCl (Fig. 3) is in the same potential range (+50 mV) and current density (4 mA/cm^2) as observed in neutral/acidic solutions containing chloride ions (Fig. 2). Besides, the fluctuations in the anodic current is less, if compared with CE solution with 10 mM chloride content. All these observations indicate that the product layer of CE solution with 1 M NaCl is mainly consist of AgCl particles with negligible contribution from silver oxide compounds.

Therefore, the presence of chloride ions in alkaline solutions minimizes the interference from hydroxide ions by preferential reaction of Ag with chloride ions and AgCl formation.

The formation of different silver oxide compounds is reflected by several depassivation/repassivation process within the oxidation of Ag in highly alkaline solution, i.e. fluctuation in potentiodynamic response. While, the main reaction product in the presence of chloride ions is the silver chloride, which is evident from a unique increase in the current, and the active state of the silver afterwards.

IV. CONCLUSION

Studied in this paper is the mechanism and kinetics of the potentiodynamic formation of silver compounds on Ag in aqueous solutions resembling the concrete environment. This has been performed by investigating the potentiodynamic response of Ag in solutions that thermodynamically favors the formation of silver chloride and/or silver oxide, in the presence of different chloride concentration.

The potentiodynamic response of Ag in the environment is a function of chloride ions concentration as well as the presence of interfering ions such as hydroxide in the medium. By increasing the chloride concentration in the solution, the potential range relevant to the AgCl formation increases, extending the contribution of AgCl to the product layer and reducing the fluctuations in the response.

Consequently, the potentiometric determination of chloride ions in highly alkaline environment such as concrete can be limited by hydroxide ions interference. This is mainly due to the possible contribution of a complex silver oxide/chloride layer to the response of the sensor. The extent of influence depends on the chloride concentration in the medium.

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Farhad Pargar was born in Astaneh ashrafieh, Iran in 1981. He received bachelor degree in department of civil engineering, Guilan University, Rasht city, Iran (2003) and master degree in civil engineering departent, Tehran University, Tehran city, Iran (2006). He started the PhD program in civil engineering department in Delft university of Technology, Delft city, Netherlands (2011), which is still ongoing.

Over the last 10 years, he has worked intensively with different aspects of the durability of reinforced concrete structures and performed multidisciplinary research in the fields of materials science, corrosion and electrochemistry. Moreover, he had an intensive collaboration with industries, companies and universities. His PhD work has focused on development of continuous chloride monitoring system which would provide reliable results and replace the destructive methods for chloride analysis in cement based-materials.

Mr. Pargar is a staff member of RILEM, a member of Iranian Construction Engineering Organization, and former member of Iran Concrete Institute.