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POTENTIOMETRIC RESPONSE OF Ag/AgCl SENSOR IN PORTLAND AND SLAG CEMENT PASTES

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Abstract

Determination of the free chloride content in a concrete structure is important for evaluation of the risk of corrosion of reinforcing steel. The Ag/AgCl sensor is sensitive to chloride ions and exhibits an open circuit potential (OCP) that depends on the chloride ions activity in the environment. The interference of hydroxide and sulfide ions in the pore solution of cementitious materials with the sensor affects the stability of the sensor's OCP.

In this paper, the sensor's OCP (i.e. sensor reading) in Portland and slag cement pastes is monitored over 300 days of immersion in solutions with different chloride concentration. The results show the applicability of the chloride sensor for continuous and non-destructive determination of the free chloride content in Portland cement paste. The significantly different OCP of the sensor in slag cement paste was attributed to the interference of sulfide ions and formation of Ag_2S on the sensor's surface. Hence, the content of free chloride ions in slag cement paste could not be determined from the sensor's OCP. The acid-soluble chloride and water-soluble chloride in the cement pastes were also determined after 300 days of immersion of specimens in the solutions. In case of Portland cement paste, the measured acid and water-soluble chlorides were compared to the sensor reading. The acid and water-soluble chlorides were higher than sensor reading. The release of physically and chemically bound chlorides into the acid and water solvents were the main cause for this trend. The results show the importance of cement type and chloride binding ability of hydration products for the sensor's response and the acid and water-soluble chloride contents.

1. Introduction

The OCP response of a Ag/AgCl electrode as a chloride sensor follows the Nernst equation for a Ag/AgCl interface [1-3] and reflects the chloride ions activity in an environment. The interference of hydroxide and sulfide ions with the sensor can deviate the sensor's response from the expected value [1-6]. Although the stability of the embedded chloride sensor in cementitious materials has been studied, the extent of interference of hydroxide ions is still under debate [7, 8]. The slag-containing cementitious materials are known for a high amount of water-soluble sulfates and sulfide ions [9]. The interference of sulfide ions with the sensor was also identified [2, 10], while no experimental evidence in cementitious materials to confirm the interference from sulfide ions has been found.

In this paper, the OCP response of the chloride sensor in cement pastes made of Portland and slag cement is monitored during immersion of specimens in solutions with different chloride concentration. After 300 days, the destructive leaching methods (acid-soluble and water-soluble chlorides [11]) were used to determine the chloride content in the specimens. The observed difference between the acid-soluble chloride, the water-soluble chloride and the free chloride content inferred from the sensor's response is discussed with respect to the chloride binding ability of cement hydration products.

2. Materials and procedures

2.1. Specimen preparation and exposure condition

The specimens were cement paste cylinders with cast-in Ag/AgCl sensors. The chloride sensor's response was assessed in cement pastes (w/c=0.4) made of ordinary Portland cement (CEM I 52.5 N) and blast-furnace slag cement, i.e. CEM III/A 52.5 N with 35-64% of slag [12]. The cement producer was ENCI cement, The Netherlands. The sensors were prepared by one-hour anodization of Ag wire in 0.1 M HCl solution [13]. The sensors were cast-in the cylinders in such a manner, that only 1 cm length of sensors was exposed to the environment, leaving an active surface of 0.32 cm^2 for the sensors.

After curing in a sealed condition for 28 days, the specimens were immersed in a simulated pore solution (0.1 M KOH + Sat. Ca(OH)$_2$), pH=13, with different chloride concentrations (10 mM, 100 mM, 500 mM and 1000 mM). A control case, based on chloride-free solution, was also tested. To keep the concentration of chloride ions as constant as possible, the volume ratio of solution to paste was maintained at 40 [14], and the containers were closed to prevent evaporation. Two replicates per specimen type were immersed in the solutions. The specimens were retained in the solutions for 300 days to reach a state of equilibrium between the chloride ions in the solution and that in the specimens.

2.2. Test methods

2.2.1. Electrochemical measurements

The cylindrical specimens were immersed in simulated pore solution with different chloride concentrations. The OCP of the sensors versus saturated calomel electrode (SCE) was monitored during 300 days using PGSTAT 302N potentiostat.

2.2.2. Chemical analysis

The acid-soluble chloride and water-soluble chloride in the bulk matrix of cement pastes were determined after 300-day immersion of the specimens in solutions with different chloride concentration (as specified in Section 2.1). The acid-soluble and water-soluble chlorides were extracted from the dried paste samples following the standard procedures [15-18]. The extracted solutions were analyzed for chloride content with Spectroquant ® NOVA 60 photometer and a chloride test set-up (Chloride Cell Test – NO. 114730). The photometer and the chloride test set-up are commercially available from Merck company.

3. Results and discussion

3.1. OCP measurement of chloride sensor

The OCP response of the chloride sensor in cement paste specimens made of CEM I 52.5 N and CEM III/A 52.5N was recorded periodically over 300 days (Fig. 1). Since the sensor's OCP for two replicates per specimen type followed a similar trend, only the average OCP value is presented in the figure. During the immersion period, the chloride ions penetrated gradually from the external solution towards the sensor's surface. The sensor's OCP in Portland cement paste (CEM I specimens, Fig. 1a) shifted from ~140 mV toward a stable cathodic potential value, depending on the chloride concentration in the solution. The relatively stable sensor's OCP in the

case of chloride-free solution (no Cl in Fig. 1a) is an indication for the formation of a certain product layer on the sensor's surface ($AgCl/Ag_2O/AgO$) [2, 5]. Therefore, the sensor's response in CEM I specimens reflects the chloride ions activity in the cement paste (Fig. 1a). The sensor's OCP in slag cement pastes (CEM III specimens, Fig. 1b) follows a different trend which is not in accordance to Nernst equation for a Ag/AgCl interface. During the hydration of slag cement, Ag_2S forms on the sensor's surface due to the chemical reaction of sulfide ions (S^{2-}) with the AgCl layer. The rate of Ag_2S formation makes the sensor's OCP deviating from the expected response (compare Fig. 1a with Fig. 1b).

The initially anodic OCP response of the sensor in CEM III specimens (0-120 mV, Fig. 1b) was attributed to the mixed potential of a $AgCl/Ag_2O/Ag_2S$ interface [2]. During immersion in the alkaline solution, the sensor's OCP shifted towards -200 mV in the control case (no Cl, Fig. 1b) and -800 mV in chloride-containing solutions. The negative sensor's OCP was the consequence of the higher amount of Ag_2S on the sensor's surface. The presence of Ag_2S on the sensor's surface shifts the sensor's OCP towards the standard potential of a Ag/Ag_2S electrode (-935 mV vs. SCE) [19] and the potential for Ag_2S formation in an alkaline solution (ca. -790 mV) [20, 21].
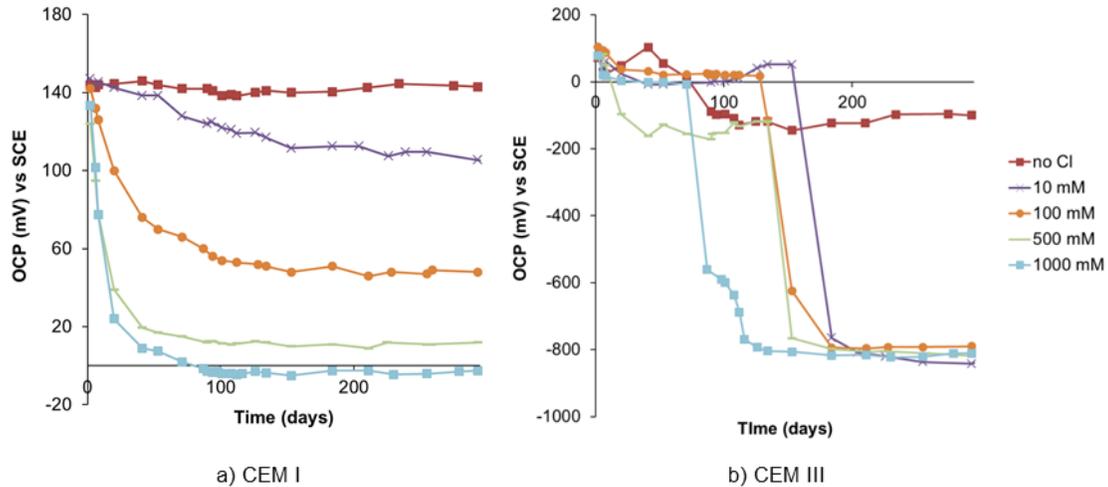
a) CEM I   b) CEM III

Figure 1: The OCP response of chloride sensor in (a) CEM I specimens and (b) CEM III specimens over time.

For the CEM III specimens, the sensor's OCP in the chloride-containing mediums is more negative than the sensor's OCP in the control case (chloride-free). The concentration of silver ions on the silver substrate increases with increasing the chloride concentration in the medium. Hence, higher amount of Ag_2S can form on the sensor's surface. The increase in the content of Ag_2S on the sensor's surface shifts the sensor's OCP towards negative OCP values (e.g. -800 mV). By increasing the chloride concentration from 10 mM to 1000 mM, the OCP of the sensor shifts to negative potential values after a shorter time of measurement (Fig. 2b). This observation is mainly due to the high tortuosity and low connectivity of the pore network in slag cementitious material, which controls the rate of chloride penetration in CEM III specimens [Ortega et al., 2017]. The rate of chloride penetration is lower for 10 mM chloride concertation. Consequently, chloride ions need longer time to reach the sensor's surface and shift the sensor's OCP towards negative potential. Although the chloride content could not be inferred from the sensor's

response, the significant change in the sensor's OCP indicates the presence of free chloride ions at the sensor's surface.

The sensor's OCP in the initial period (10 days) of immersion in the solution is anodic (e.g. 50 to 120 mV) in comparison to the sensor's OCP in the later stage (e.g. -100 to -800 mV after 10 to 150 days). The anodic OCP response indicates the initially lower amount of Ag_2S on the sensor's surface. Therefore, the initial sensor's response is the potential from $AgCl/Ag_2O$ with a slight contribution from Ag_2S. In contrast, the negative OCP of the sensor in the later period of immersion is mainly the potential from Ag_2S with minor impact from $AgCl$ and Ag_2O.

Based on thermodynamic principles and Gibbs free energy (-110 KJ/mol for $AgCl$ and -41 KJ/mol for Ag_2S), the chloride sensor in a slag cement paste would recover after immersion in the chloride-containing solution due to the chemical reaction of Ag_2S to $AgCl$. However, the negative sensor's OCP in chloride-containing solution (e.g. -800 mV, Fig. 1b) did not indicate the sensor's recovery. The significantly lower solubility product of Ag_2S ($K_{sp}Ag_2S=1.6\times10^{-49}$ at 25°C) in comparison to $AgCl$ ($K_{sp}AgCl=1.8\times10^{-10}$ at 25°C) and Ag_2O ($K_{sp}Ag_2O=2\times10^{-8}$) is the main reason for the lack of the sensor's sensitivity to chloride ions [10, 22-25]. Moreover, Ag_2S, being the predominant reaction product of silver in CEM III specimens, results in the lack of possibility for the sensor to recover.

3.2. Determination of chloride content by leaching methods and sensor's response

Three methods were used for chloride determination in Portland (CEM I) and slag (CEM III) cement pastes after 300 days of immersion in simulated pore solution: (i) leaching in acid (acid-soluble chloride), (ii) leaching in water (water-soluble chloride) and (iii) potentiometry (chloride sensor's response). The acid-soluble chloride is the total (free+bound) chloride content in cementitious materials. The water-soluble chloride is the free chloride ions plus a part of physically and chemically bound chlorides [16, 26, 27]. The sensor can only detect the free chloride content. The acid and water-soluble chlorides together with sensor reading are presented in Fig. 2. The chloride content inferred from the sensor's response is shown for only CEM I specimens (sensor reading in Fig. 2a). The sensor reading in CEM III specimens did not reflect the amount of free chloride in the paste (Section 3.1). Hence, the sensor reading in CEM III specimens was not presented in Fig. 2b. Below, the acid and water-soluble chlorides in CEM I and CEM III specimens are discussed, followed by comparison of sensor reading and water-soluble chloride for only CEM I specimens.
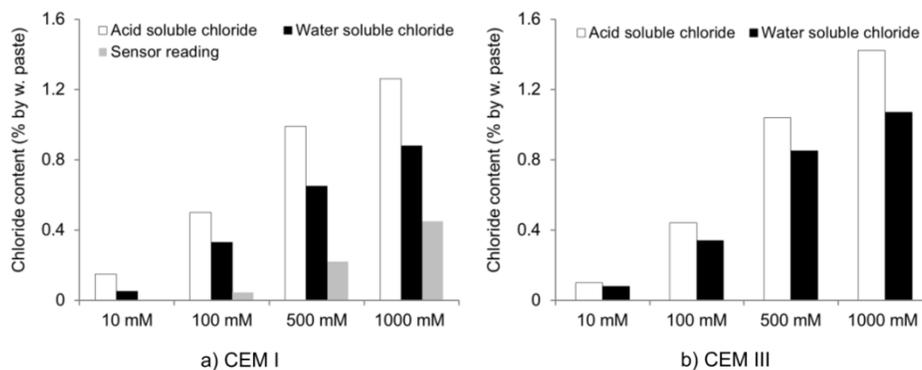
Figure 2: The measured chloride content by different methods in (a) CEM I specimen and (b) CEM III specimen after 300 days of immersion in solutions with different chloride concentration.

In Fig. 2.a, the amount of acid-soluble chloride in CEM I and CEM III specimens was higher than the amount of water-soluble chloride. This is because a part of bound chlorides (physically and chemically) is only soluble in water solvent during the water-soluble chloride determination [28-31].

The slag-containing cementitious materials are well-known for their ability to bind chloride ions chemically [32, 33]. Despite this general knowledge, the water-soluble chloride in CEM III specimens is high compared to that in CEM I specimens. This can be attributed to significant dissolution of chemically bound chlorides into the water solvent, as has been previously reported [34, 35]. Moreover, the physical chloride binding ability of CEM III specimens is low [36]. The slag hydration in CEM III specimens consumes calcium hydroxide. Hence, the concentration of calcium ions in the pore solution is reduced. The lower amount of calcium ions decreases the positive surface charge of hydration products (e.g. C-S-H), which can reduce the physical binding of chloride ions [37].

The acid and water-soluble chloride contents in CEM III specimens were similar to those in CEM I specimens (Figs. 2a, b). The slag cementitious materials are known for high tortuosity and low connectivity of the pore network [38]. This would result in a lower chloride penetration into the bulk matrix of CEM III specimens. Hence, the measured acid and water-soluble chlorides in CEM III specimens are lower than what can potentially be achieved.

The inferred free chloride content from the sensor's response in CEM I specimens was lower than the measured water-soluble chloride (Fig. 2a). The observed difference is due to the part of bound chloride released into the water solvent. Hence, the water-soluble chloride does not represent the free chloride content. Considering the presented results in this paper, the interpretation of the measured chloride by these approaches needs the knowledge of surrounding medium. In this regard, the influence of cement type and chloride binding ability of hydration products should be taken into account.

4. Conclusions

The sensor reading in cementitious materials was compared to the acid and water-soluble chlorides. The influence of the pore solution composition of a cement paste as well as chloride binding ability of hydration products on the chloride measurements was discussed. The OCP response of the chloride sensor in Portland cement paste was in accordance to the Nernst equation for a Ag/AgCl interface. The sensor's OCP in slag cement paste followed a different trend. The interference of sulfide ions with the AgCl layer of the sensor resulted in Ag_2S formation on the sensor's surface and a shift in the sensor's OCP towards significantly negative potential values (e.g. -800 mV). The formed Ag_2S did not transform back to AgCl. Hence, the free chloride content in CEM III specimens could not be determined by the sensor's response.

The sensor reading in CEM I specimens was significantly lower than the acid and water-soluble chloride contents. This is mainly due to the release of bound chlorides into the acid and acid and water solvents during acid and water-soluble chloride determination.

The results in this paper show the importance of cement type and chloride binding ability of hydration products for the sensor's response as well as the acid and water-soluble chloride contents. Despite the limitation of the chloride sensor for application in slag-containing cementitious materials, the potentiometry method is a promising approach for non-destructive and continuous determination of the free chloride content in the alkaline medium of cement-based systems.

5. References

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