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Potentiometric response of chloride sensors in cementitious materials of varying chemical composition and water-to-cement ratio

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Abstract

Free chloride ions are the main cause of steel corrosion in reinforced concrete structures. Ag/AgCl electrodes, as chloride sensors, are predominantly sensitive to chloride ions and respond electrochemically to the chloride ion activity in the environment. This is reflected by changes of the open circuit potential (OCP) of the sensors. To investigate the effect of the cement-based matrix on OCP readings, this paper presents the electrochemical responses of chloride sensors, embedded in cement paste specimens of hydrated pure cement phases of different water-to-binder ratios. The specimens were immersed in alkaline solutions with various chloride concentrations. The results show dependency of the OCP of the sensor on the surrounding hydrated cement-based matrix. This effect was more pronounced when the specimens were immersed in solutions of lower chloride concentration. In contrast, these effects were negligible at high (> 500 mM) chloride concentrations.

1 Introduction

For the past decades, in order to prevent and/or control premature concrete deterioration, attempts have been made to develop a continuous chloride monitoring system which would provide reliable results and will replace the destructive methods for chloride analysis. A new sensor technology would be superior not only in terms of efficiency and effectiveness, but also more accurate compared to the traditional ways of powder drilling and wet chemical analysis for chloride content of cement-based materials [1]. The traditional silver/silver chloride (Ag/AgCl) electrode, as chloride sensor, is sensitive to chloride ions. According to the Nernst equation, this electrode exhibits a certain electrochemical potential that depends on the chloride ion activity in the environment. By measuring the potential of the Ag/AgCl electrode, the Cl-ion activity can be determined, which can then be converted to chloride concentration, using mean activity coefficient [2, 3, 4].

Therefore, Ag/AgCl sensors can determine the chloride content non-destructively and continuously. The small dimensions of such sensors provide highly localized measurements, e.g. accurately at the depth of the reinforcement, rather than average values over a comparatively large concrete volume under investigation, which is the case when using other techniques [2, 3, 4]. Although the concept and performance of Ag/AgCl electrodes are fundamentally well known due to wide use in electrochemistry, the estimation of the chloride content in cement-based materials with respect to the OCP of embedded Ag/AgCl electrodes is still a challenge for researchers [3, 4].

It is known that 1mV deviation in the OCP of the sensor will result in an error of approximately 4% in terms of chloride concentration, which can be considered as

negligible [5, 6]. However, a measurement error of a few millivolts adversely affects the accuracy of the test method. Sources of errors can be attributed to factors such as the sensor properties e.g. AgCl layer morphology, and the properties of the environment around the Ag/AgCl electrode e.g. pH, interfering ions, etc. Moreover, the geometrical position of the Ag/AgCl sensor with respect to the reference electrode may introduce diffusion limitations, a comprehensive discussion on which is reported by Angst et al. [3, 5, 6]. With this respect, an additional and one of the most important challenges for the application of chloride sensors in alkaline environment, as concrete, is the contribution of the properties of the cementitious material to the potentiometric response i.e. the OCP reading of the sensor.

It is well known that chloride ions, present in the pore system of cementitious materials, can be either physically adsorbed and/or chemically bound by the constituents of the cement hydration products [7, 8]. In other words, the chloride ion activity which the sensor actually “reads” may be affected by the presence of hydration products and fine pores (gel pores) in the interfacial transition zone (ITZ) between the sensor and cement paste. With respect to chloride binding, it is well known that the hydration product of aluminate phases e.g. $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ (C_3A), dominate the chemical binding of chloride ions and the hydration product of silicate cement phases e.g. $3\text{CaO}\cdot\text{SiO}_2$ (C_3S), control the physical binding. The contribution of these binding mechanisms to the response of the sensor is an aspect that has been scarcely discussed

Factors and properties that matter are: water to cement ratio (W/C), cement constituents with ability to bind chloride physically and/or chemically, porosity and pore size distribution at the sensor and cement paste interface [6]. With regard to the pore size distribution, the ITZ porosity is often higher than that in the bulk matrix of cement paste [9, 10]. In the ITZ, the capillary porosity is generally higher with better interconnectivity and therefore, the hydration products are more porous [11].

Additionally, W/C ratio is one of the important parameters, controlling not only the ITZ porosity, thickness but also the amount of bound chloride in the hydrated cement matrix and in the vicinity of the sensor. It is mostly reported that the binding of chloride ions in cement paste increases with W/C ratio [12]. The hydration degree of cement paste with higher W/C is higher compared to cement paste with lower W/C. This can result in more chloride binding sites for cement paste with higher W/C in comparison to cement paste with lower W/C [12]. Moreover, reducing the W/C results in an ITZ with characteristics that are not that different from those of the bulk paste [13] i.e. are similar. As reported by Cwirzen and Penttala [14], on W/C=0.30, a barely detectable transition zone (<5 μm wide) between aggregates and cement paste was recorded. However, at higher W/C (0.42), 30–40 μm transition zone was found with higher capillary porosity, increased content of calcium hydroxide and ettringite, elongated C-S-H particles and fewer unhydrated cement particles compared to these in the bulk cement paste [14, 15, 16].

It can be expected that the influence of the cementitious material on the potential response of the sensor is a function of the ITZ properties. It has been hypothesized that the effect is prevailing in those locations at the sensor/cement paste interface, where gel pores dominate. In contrast, when larger pores are present, the relative importance of the electrical double layer at the interface between hydration products and aqueous phase decreases and the activity of chloride ions in the solution inside the pores of

cement paste (pore solution) would be more like the corresponding value at external storage solution (bulk solution) [3, 6].

In this work, the influence of different W/C ratios and mix designs on the potentiometric response of chloride sensors are evaluated. The paper does not comment on possible side effects and/or other known sources of errors, e.g. sensor morphology, diffusion potentials and interfering ions. Ag/AgCl sensors were embedded in cement paste cylinders made from C₃S in the presence and absence of C₃A. The cement paste cylinders were maintained in simulated pore solution with different chloride concentrations. The OCP of the sensors were recorded periodically over 300 days. The response of the sensors was evaluated with regard to the W/C ratio, the mix design and the corresponding chloride concentration in the external solution.

2 Experiments

2.1 Specimens preparation

Ag/AgCl sensors were prepared by one hour anodization of a 1 mm thick silver wire in hydrochloric acid at current density of 0.5 mA/cm². The sensors were embedded in cement paste cylinders, 1 cm diameter, in which only 1 cm length of the sensor was exposed to the environment and the remaining parts were isolated by epoxy. The cement paste cylinders were made from pure cement compounds: (C₃A, and C₃S) to correlate the electrochemical response of the sensor to the expected microstructure of hydrated cementitious materials e.g. different hydrated cement phases, particular features of the pore system and therefore, different chloride content in the interfacial transition zone between the sensor and cement paste. The mix designs used in the paste production are summarized in Table 1.

Table 1. Mix design of the cementitious materials used in this study

Pure phases (%)	W/C=0.35		W/C=0.4		W/C=0.5	
	C3S	C3S+C3A	C3S	C3S+C3A	C3S	C3S+C3A
C ₃ S	100	87	100	87	100	87
C ₃ A	-	10	-	10	-	10
Gypsum	-	3	-	3	-	3

2.2 Test methods and procedures

After curing in sealed condition, the specimens were immersed in simulated pore solution (0.1 M KOH + Sat. Ca(OH)₂), pH=13, with different chloride concentrations (10mM, 100 mM, 500 mM and 1000 mM); a control, chloride-free case was also tested. To maintain the chloride ion concentration relatively constant, the volume ratio of solution to cement paste was maintained at 40 and the containers were closed to prevent evaporation. The OCP of the sensors versus saturated calomel electrode (SCE) was monitored over 300 days.

3 Results and discussion

Within the process of chloride penetration into the cement-based specimens, the open circuit potential (OCP) of the embedded sensors gradually shifts to more cathodic values (Figure 1). This is as expected and fundamentally determined by the Nernst equation i.e. the OCP readings for the sensors reflect the changes in chloride ion concentration/activity in the surrounding pore solution.

The potential response of the sensors over time is divided into four regions; A, B, C and D (Figure 1a). In region A (up to day 50), the OCP of all sensors (except those in Cl-free medium) sharply shift towards cathodic values, followed by stabilisation in region B (50 to about 150 days). The stabilisation in region B is not relevant for the specimens in 10 mM chloride concentration at w/c ratio < 0.5 - Figure 1a) to d). Obviously, at lower W/C ratio i.e. lower porosity, reduced volume of available pore solution, lower matrix diffusivity, combined with the lower chloride content, the OCP stabilisation tends to take longer time. The value around which stabilisation occurs, as in region B for most of the investigated cases, is determined by the chloride ion activity at the sensor surface. A stable value was accepted to be achieved when the difference with subsequent measurements was ~1 mV (a potential difference, generally considered as negligible [5, 6]). In the run of the test, in region C and D, the sensors' potentials gradually and fully stabilise, which for the Cl-free cases and those at low Cl content is achieved at more cathodic values within region D. In contrast, for the specimens at higher chloride concentrations (> 100 mM), the sensor's potentials maintain stable cathodic values as already established within region B. The main features within the potentiometric response of the sensors with varying W/C ratio and mix design are discussed in what follows.

For the samples cast with C3S only at the lowest W/C ratio of 0.35, the control cases and those conditioned in environment with lowest chloride content (10 mM) present the largest variation of OCP records for replicate specimens. This was observed from stage A to stage D – Fig.1a). However, such a variation between replicates was not recorded for specimens, conditioned in solutions with higher chloride content i.e. >100 mM chloride concentrations (Figure 1a). In contrast, the OCP values between replicates for all specimens at the same W/C ratio of 0.35 but of different mix design i.e. C3S+C3A mix – Fig.1b), were reproducible. In this case almost identical OCP values for replicates conditioned in the same external solution were observed, irrespective of chloride concentration.

The higher potential difference between the replicates in the case of mix C3S at W/C 0.35 (Fig.1a) might be attributed to different ITZ properties (porosity, pore size, calcium hydroxide and C-S-H distribution, etc.), compared to the mix design of C3S+C3A at the same W/C ratio (Fig.1b). Next to that, similar values between replicates were recorded for almost all other cases (Fig.1 b to e). Obviously, in this case, W/C ratio is not the only controlling parameter, but rather cement hydration and local chemistry of the pore solution play a role, in addition to the well-known factor of varying matrix heterogeneity with varying mix design. These aspects are certainly dominant in chloride-free and low chloride concentration environment, since discrepancies between replicates were not observed at chloride levels > 100 mM.

The mix design, namely the C₃A content, has an even more pronounced effect on the sensors' OCP readings when the W/C ratio increased to 0.5 (Fig.1f), relevant for

chloride-free environment only. A trend for the combined effect of C3A and W/C ratio, however, cannot be found, considering the well reproducible response of replicate sensors in C3S+C3A at W/C ratio of 0.4 (Fig.1d). Therefore, the observed differences between replicate specimens in chloride-free environment at different W/C ratio and mix design (compare Fig.1a,b,d,f) can be partly attributed to phenomena, related to the absence of chloride ions in the external solution [2, 17] and the high pH of the pore solution, as follows.

In the absence of chloride ions in the external solution and hence Cl-free pore solution, the AgCl layer is not stable and dissolves, releasing Ag^+ and Cl^- . In an environment of high pH (as the pore solution), the silver ions will react with unlimited source of hydroxide ions, which will gradually transform the Ag/AgCl sensor to a silver/silver oxide sensor and will result in OCP shift towards 100 mV or more cathodic values [17]. Additionally, it is known that the silver oxide composition and the hydroxide ions activity in the environment further influence the potential of the already formed silver/silver oxide sensor [18]. For example, AgO is a semiconductor with a high conductivity but Ag₂O has a low conductivity (10^{-8} ohm.cm). AgO is insoluble in water, while Ag₂O dissolves to the extent of 0.01 g/l [18]. Therefore, it is expected that in the absence of Cl ions, alterations within the complex silver oxide layer can gradually block the pores and impede the faradaic reaction on the sensors' surface. This process is likely to favour the shift of the sensor's potential to more cathodic values (60-100mV), as actually recorded - Figure 1f - for chloride-free cases.

This trend was not observed in C3S specimens with the same W/C ratio of 0.5, although a similar to C3S+C3A pore size distributions at the sensor/cement paste interface was expected (Figure 1e). In other words, for C₃A-free mixes, the cathodic shift of OCP values for sensors in Cl-free medium was not observed. Additionally, the recorded values for replicates were almost identical. Here again, the C₃A content seems to play a dominant role for the response of the sensors in Cl-free medium. The responsible mechanism, in addition to the previously discussed AgCl layer dissolution and transformation to AgO, is most likely denoted to the different chloride binding capacity of C3S and C3S+C3A specimens. For C3S specimens, only physical Cl binding would be relevant, whereas for C3S+C3A specimens, both physical and chemical Cl binding will be at hand. As previously discussed, within the AgCl layer dissolution, both silver and chloride ions are available in the pore solution. In the studied systems (cement paste of high pH and Cl-free), the silver ions behave as above discussed. The chloride ions, on the other hand, will be transported through the pore network within the bulk cement-paste material. The consequence will be reduction of chloride ions content at the interface of the sensor.

The higher chloride binding capacity of C3S+C3A pastes accelerates the depletion of chloride ions, which in turn results in the faster dissolution of the original AgCl layer into the surrounding pore solution. Additionally, higher W/C favours higher diffusivity and in the presence of C₃A increases the available chloride binding sites [8].

Therefore, in the specimens of mix design C3S+C3A at W/C=0.5, the enhanced chemical chloride binding, the lack of alternative source of chloride ions and the highly alkaline environment (pH=13), determine that the silver chloride layer is more distinctly transformed into silver oxide, reflected by the significantly different OCP records from all control cases (Fig.1f).

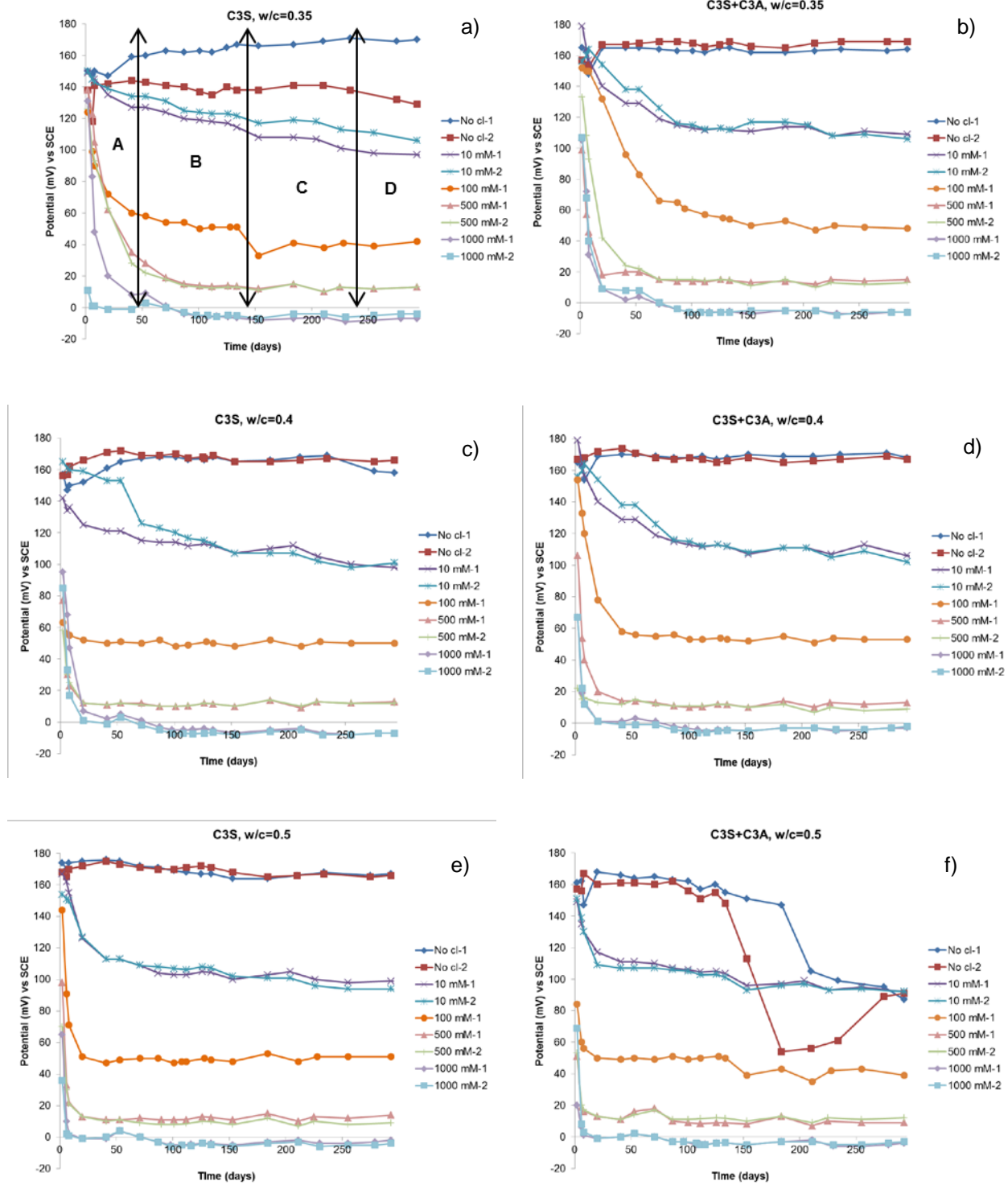


Figure 1: the potential readings of chloride sensors over time

As theoretically expected, various W/C ratios and mix designs affect the chloride binding and pore size distribution in cement paste within the process of cement hydration in the run of the experiment. To account for these effects, Fig.2 shows the sensor's potentials after 140 days (stage B) of immersion, when the equilibrium between the external medium and the internal pore solutions is rather established [19] and most of the sensors demonstrate a stable potential.

As seen in Fig.2, in the absence of chloride ions in the external solution and hence Cl-free pore solution, most of the sensors demonstrate potential higher than 150 mV, except for the replicates of C3S;W/C=0.35 as discussed before. In 10 mM chloride concentration, the sensors, embedded in specimens of W/C 0.35 present more anodic potentials for both mix designs of C3S (left) and C3S+C3A (right) compared to W/C 0.5. This is most likely the result of increased portion of finer pores (gel pores) at the sensor/cement paste interface in W/C=0.35, which means reduced chloride content at the sensor surface [6, 14, 16]. This influence becomes less evident at higher chloride concentration (> 100 mM). The larger effects at low chloride concentration can be explained through the logarithmic correlation between the sensor potential and chloride concentration (Nernst equation) in which at chloride concentrations close to zero a minimum variation in the chloride content will strongly influence the sensor's potential [3, 4, 5, 6]. This can explain the more pronounced influence of ITZ on the potentiometric response of the sensors at 10 mM chloride concentration.

Additionally and in contrast to expected, at 1000 mM chloride concentration the sensor in cement paste with W/C=0.35 demonstrates more cathodic potential than the sensor in cement paste with W/C=0.5. Although this difference is not more than 2-3 mV and the exact phenomena behind this observation are still to be clarified, this behaviour can be partly attributed to the possible accumulation of chloride ions [20] at the sensor surface in such high chloride concentration, i.e. larger limitations to chloride ion transport at lower W/C ratio will be at hand.

Table 2 presents the range of sensor's potential in C3S and C3S+C3A specimens after 140 days (stage B) of immersion in medium of different chloride concentrations. To calculate the potential range, the difference between maximum and minimum recorded potentials is determined. As shown in Fig.2, the highest and lowest potentials are relevant to the sensors in W/C ratios of 0.5 or 0.35. Therefore, the potential range can simply imply the influence of W/C ratio on the potentiometric response of the sensor. Further, in order to compare the variability of the sensor's response in different chloride concentrations, the coefficient of variation (CV), ratio of standard deviation to mean value, for the chloride ion activities is calculated and presented in Table 2.

As mentioned before, 1mV deviation in the OCP of the sensor is approximately equal to 4% deviation in terms of chloride concentration [5, 6]. The range of sensor's potential at 10 mM chloride concentration is 3 to 4 times higher than the corresponding value at 100mM chloride concentration (Table 2).

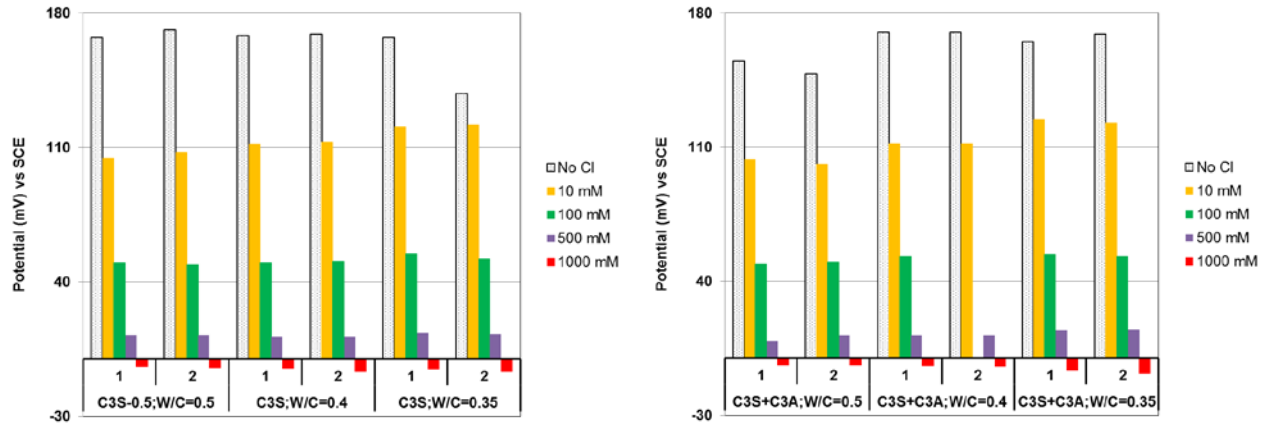


Figure 2: The potential readings of chloride sensors after 140 days (stage B) immersion in different chloride concentration; C3S specimens (left figure) and C3S+C3A specimens (right figure)

This range is 4 to 6 mV at 100 and 500 mM chloride concentrations corresponding to 16 to 24% difference in the measured chloride concentration.

Therefore, at 10 mM chloride concentration, up to 92% deviation between the measured chloride concentrations is determined in comparison to 16-24% at 100- 500 mM chloride concentrations. By increasing the chloride concentration to 1000 mM, the influence of W/C ratio on the sensor’s potential decreases to about 10%. This trend is in accordance with the continuous decrease of the CV with increasing the chloride concentration in the external solution, from 27-37% at 10 mM to 6-9% at 100-500 mM and lower than 4% at 1000 mM chloride concentration. These trends demonstrate the decline in the importance of the pore size distribution (W/C ratio) for the measured chloride ion activity at higher chloride concentration.

Moreover, the only evidence for the influence of C₃A addition on the potentiometric response of the sensor is at 10 mM chloride concentration when the potential range and CV of C3S+C3A mixture is higher than C3S mix (Table 2). This can be attributed partly to the more heterogeneous ITZ in C3S+C3A specimens, due to the presence of C₃A and gypsum phases and physically and chemically bound chlorides, in comparison to C3S specimens with only C₃S phase and the ability to bind chloride only physically.

Table 2. The range of sensor’s potential and coefficient of variation (CV) of chloride ion activities in different chloride concentrations

Chloride concentration in external solution (mM)	Potential difference of the sensors (mV)		CV (%)	
	C3S	C3S+C3A	C3S	C3S+C3A
10	17	23	27	37
100	6	5	8	8
500	4	5	6	9
1000	3	2	3	4

4 Discussion

In this study, the influence of chloride binding on the open circuit potential stability of the sensors was investigated with respect to: (i) the fineness of the pore structure as the result of cement paste with different W/C ratios (ii) cement hydration products with ability to bind chloride chemically and/or physically through the presence and absence of C_3A in the mix designs (iii) the chloride concentration in the pore solution and the possible effect of competing hydroxide ions in the absence of chloride ions. Following the derived results the main relevant outcomes are: the fineness of the pore structure significantly influences the stable potential of the sensor especially at low chloride concentration (10 mM chloride concentration). This behaviour is more evident at W/C 0.35 with larger proportion of finer pores at the ITZ between the sensor and the cement paste. Moreover, C_3A addition not only influences the potential response of the sensor at low chloride concentration (10 mM), but is also important for the long-term behaviour of the sensor, especially in the absence of chloride ions in the external environment and/or in the pore solution respectively.

Clearly, the above hypothesized phenomena should be justified by investigating the distribution of hydration products, particular features of the pore system and the chloride content at the interface between the sensor and the hydration products of cement paste.

5 Conclusion

1- The effect of mix design on the potentiometric response of the sensor can be mostly determined at low chloride concentration (10 mM). At high chloride concentration (>100 mM) the relative importance of mix design decreases implying the lower difference between the sensor's potential in various mix designs at higher chloride concentration.

2-It has been shown that, in chloride free solution, sensors embedded in cement paste with higher W/C ratio and potentially higher chloride binding capacity, are susceptible to loss of sensitivity more rapidly than those embedded in lower W/C ratio and/or lower rate of chloride absorption. In other words, C_3A addition accelerates the AgCl layer dissolution, minimises the faradaic reactions for AgCl formation and facilitates the reactions for silver oxide formation. This process gradually blocks the pores and shifts the sensor's potential towards more cathodic values.

3- Under the test condition of this study, the difference between the OCP of the sensors in different mix designs can be hypothetically attributed to the presence of fine pores (gel pores) and hydration products in the interfacial transition zone (ITZ) between the sensor and cement paste. This is an additional parameter, that should be considered with relevance to all other known sources within sensors' readings interpretation.

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