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Pargar, Farhad; Koleva, Dessi; Koenders, Eddie; van Breugel, Klaas

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Non-destructive evaluation of chloride-induced corrosion in reinforced concrete: electrochemical impedance spectroscopy sheds new light on generally applied sensors performance*

F. Pargar, D.A. Koleva, E.A.B. Koenders and K. van Breugel, TUDelft, *The Netherlands*

Abstract— Service life of reinforced concrete structures exposed to chloride enriched environment is well known to be mainly determined by steel passivity breakdown in the event of chloride-induced corrosion initiation and propagation. Since Cl⁻ induced (localized) corrosion is caused by the free (water-soluble) chloride, present in the pore network of a reinforced concrete structure, quantifying the level of free chloride locally, e.g. via embedded Ag/AgCl electrodes (chloride sensors), is a generally accepted and applicable approach to monitor the time to corrosion initiation. The measurement is essentially a potential (voltage) reading over time and as such logically depends, among other factors, on the electrical and microstructural properties of the surrounding medium. Therefore, an accurate determination of the time to corrosion initiation significantly depends on the properties of relevant interfaces, such as the steel/cement paste interface and/or the Ag|AgCl|cement paste interface.

In this paper, steel rods were coupled with Ag/AgCl sensors and embedded in cement paste cylinders. The specimens were immersed in simulated pore solution, containing 855 mM chloride concentration. Electrochemical impedance spectroscopy (EIS) was employed for quali-/quantification of the corrosion process on the steel surface (medium to low frequency response), while simultaneously providing information for the electrical properties of the bulk cement-based matrix through the high frequency response. The open circuit potential (OCP) values of both sensors and steel rods were recorded for more than 30 days. The results show a good agreement between sensor readings and steel electrochemical response i.e. time to corrosion initiation was recorded via steel OCP readings, whereas the relevant chloride content was estimated via the sensors' OCP readings.

I. INTRODUCTION

For several decades, attempts have been made to achieve clearer understanding of the circumstances that give rise to the passive film breakdown of steel in concrete, with particular interest directed towards situations where chloride ions are the primary cause of corrosion. It has also been proved to be very difficult to account adequately for the widely observed variability in critical (threshold) chloride levels corresponding to corrosion initiation and propagation under different circumstances. Several variables appear to affect the risk that a given level of chloride will result in steel depassivation and it has been far from easy to reach consensus as to how best to incorporate these into robust service life models for structures exposed to chloride ingress. This is important in practice because the predicted times to initiate corrosion of steel bars at a given cover depth are often sensitive to modest changes in the assumed value of the chloride threshold [1].

To this end, a more detailed knowledge of the concentration of the free chloride ions is valuable when studying chloride-induced corrosion in reinforced concrete. Determination of the free chloride content in concrete is generally performed via several known techniques, e.g. pore water extraction or leaching techniques require destructive sampling and can thus not be used for continuous monitoring of the free chloride content. In addition, these methods give average values of the sample volume under investigation, which leads to erroneous results in the case of concentration gradients [2].

Considering the drawbacks of destructive techniques, attempts have been made to measure the free chloride concentration in the pore solution by means of embedded ion selective electrodes [3]. A non-destructive and continuous way to measure the free chloride concentration in-situ would thus be highly desirable both for on-site monitoring and research purposes in several fields related to monitoring steel corrosion in concrete. Silver/silver chloride electrodes are sensitive mainly to chloride ions and according to Nernst equation exhibit a certain electrochemical potential that depends on the chloride ions activity in the medium. Due to the small dimensions of such chloride sensors they allow highly localized measurements, e.g. accurate measurements at the steel reinforcement depth can be performed, rather than obtaining average values over the comparatively large concrete volume under investigation [1].

The corrosion state of steel re-bars in reinforced concrete, and thus estimation of corrosion initiation and further propagation, is generally determined via electrochemical techniques (applicable for both lab and field conditions). The more commonly used methods are recording the open circuit potential (OCP) readings for the embedded steel (half-cell potentials) and linear polarization resistance (LPR) measurements [4]. The OCP readings are just an indication of passive state, corrosion initiation and/or transition to active corrosion. The probability of corrosion initiation is greater than 90% when the recorded OCP values are more negative than -270 mV relative to the saturated calomel electrode (SCE). A shift to more "active" state i.e. cathodic potential is associated with the so-called "threshold chloride content" [5]. Potential (OCP) readings, however, are not sufficient to determine the state of steel corrosion, since they are affected by a number of factors, which include polarization by limited oxygen diffusion, concrete porosity and the presence of highly resistive product layers. Therefore, it is generally accepted that OCP records must be complemented by other methods, because although reliable relationships between potential

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F. Pargar is with the Materials & Environment, Department, Delft University of Technology, The Netherlands (: +31 (0)15 27 84742; fax: +31 (0)15 27 86383; e-mail: F.Pargar@tudelft.nl).

D.A. Koleva, is with the Materials & Environment, Department, Delft University of Technology, The Netherlands (e-mail: D.A.Koleva@tudelft.nl).

E.A.B. Koenders is with the Materials & Environment, Department, Delft University of Technology, The Netherlands (e-mail: E.A.B.Koenders@tudelft.nl).

K.vanBreugel is with the Materials & Environment, Department, Delft University of Technology, The Netherlands (e-mail: K.vanBreugel@tudelft.nl).

and corrosion rate can be found in the laboratory for well-established conditions, these can in no way be generalized, since wide variations in the corrosion rate are possibly in very narrow range of potentials [6].

For field applications, portable devices (e.g. GECORR or CorroMap) are able to record OCP values, concrete resistivity and to approximate corrosion current densities via galvanostatic or potentiostatic tests. For lab conditions, more sophisticated methods can be additionally employed and records coupled to the aforementioned tests, resulting in a thorough evaluation of the reinforced concrete system. Electrochemical Impedance Spectroscopy (EIS) for example is a very useful non-destructive technique, providing information not only for the corrosion state of the steel reinforcement, but simultaneously determining bulk matrix properties. In other words the electrochemical behavior of the steel reinforcement can be studied in detail and evaluated in relation to the development of pore network capacitance and resistance or alterations in global electrical resistivity of the bulk matrix and properties of interfaces. Additionally, properties of interfaces (e.g. cement paste/aggregates interface, steel/cement paste interface, or sensors/cement paste interface) and relevant phenomena are logically determining ion and water transport, including chloride ions transport and subsequent corrosion initiation in reinforced concrete. Considering embedded chloride sensors (as the hereby studied Ag/AgCl electrodes), EIS is a useful technique for determination of the electrochemical state of the sensors and the electrical properties of the sensors/cement paste interface. This would account for the alterations of the AgCl layer in the highly alkaline environment of cement paste, possible transformation of the AgCl to Ag₂O and microstructural changes upon chloride ions penetration and “detection”. In other words, EIS can simultaneously detect the electrochemical state of both sensors and steel, as well as the bulk matrix properties within cement hydration and conditioning when both sensors and steel are embedded in the cement-based specimens.

In this paper, steel rods were coupled with Ag/AgCl sensors and embedded in cement paste cylinders. The specimens were immersed in simulated pore solution, containing 855 mM chloride concentration. The open circuit potential values of both sensors and steel rods were recorded for more than 30 days. Electrochemical impedance spectroscopy was employed for qualification of the electrochemical state of both chloride sensors and steel rods, while simultaneously providing information for alterations of electrical properties of the surrounding bulk matrix. The EIS response for the embedded steel rods only is reported. The OCP records for both sensors and steel are presented and discussed.

II. EXPERIMENTS

Silver wires (99,99% purity), 1 mm in diameter and 2.5 cm in length, were used for preparing the Ag/AgCl sensors according the following procedure: (1) - the Ag wires were cleaned for 2 hours in concentrated NH₄OH and immersed in distilled water overnight; (2) - an exposed length of 1.5 cm was anodized in 0.1M HCl for 1 hour at a current density of 0.5 mA/cm²; (3) - the anodized silver wire was soldered to a copper wire and the 0.5 cm of soldered zone and non-anodized part were protected with an epoxy resin; the exposed length of the sensors was 1 cm.

Steel wires of 1 mm diameter and 15 cm in length were acetone-cleaned; the wires were epoxy-insulated except an exposed length of 1 cm. The sensors and steel wires were embedded in 1 cm in diameter cement paste cylinders. Cement paste with water to cement ratio (w/c) of 0.4 (CEM I 42.5 N) was used in this study. After curing in a sealed condition for 30 days, the specimens were immersed in simulated pore solution (SPS) (0.63M KOH + 0.05 M NaOH + Sat. Ca(OH)₂) with 855 mM chloride concentration and the pH of 13.6. The OCP values versus a saturated calomel reference electrode (SCE) were continuously recorded for both embedded steel and Ag/AgCl sensors; EIS was employed at certain time intervals, using 10 mV AC perturbation (rms) in the frequency range of 50 kHz to 10 mHz using potentiostat PGSTAT 302N (Metrohm), combined with GPES/FRA software. For the EIS tests a 3-electrode cell arrangement was used, MMO Ti cylinder positioned around the cement paste cylinder served as a counter electrode, the steel rod (or Ag/AgCl sensor respectively) served as working electrode and an external SCE electrode (immersed in the solution) served as a reference electrode.

III. RESULTS AND DISCUSSION

A. Open circuit potentials for steel rods and sensors

The OCP for both sensors and steel rods were monitored over time, Fig.1. Within chloride penetration, the potential of the sensors gradually shifts to more cathodic values (Fig.1b), which is as expected and fundamentally determined by the Nernst equation i.e. the potential readings for the sensors reflect the changes in chloride ions concentration/activity in the surrounding pore water. Since both sensors and steel rods were embedded together in one and the same cement-based sample, it is expected that the potential readings for the steel (Fig.1a) would also reflect chloride arrival at the steel surface in terms of corrosion initiation. The OCP for steel will shift cathodically upon steel de-passivation. In other words, a correlation between OCP readings for steel on one hand and for the sensors on the other hand will reflect simultaneously the chloride content and corrosion initiation in each cement-based sample. Some fluctuations and exceptions were observed for the steel rods within treatment, denoted to oxygen availability at the steel/cement paste interface. Cathodic values for the OCP of steel can be denoted not only to chloride arrival at the steel surface, but can also reflect oxygen deficiency in the hereby employed (submerged) conditions. Further, fluctuation in OCP values for steel from active (cathodic) to more anodic potentials are well in line with the fundamental behavior of steel in such environment i.e. in Cl-containing alkaline medium, active behavior is normally accompanied by attempts for re-passivation. Further, although close behavior was observed for all replicates (two

equally prepared and conditioned specimens hereby discussed – specimens 1 and 2), entirely identical response can not be expected, considering the extreme heterogeneity of the system under study. Despite the above observations, a generally good correlation of results was observed in terms of chloride arrival at steel/sensor interfaces: in the beginning of the test, when no chloride penetrated yet the cement paste, anodic values for the sensors' OCPs were recorded (135 mV), which is well in line with the potential values for steel, relevant to passive state (> -276 mV). At the time of corrosion initiation, the OCP values for steel shift to potentials more cathodic than -276 mV, while the OCP values for the sensors shift to more cathodic values as well: in specimen 1 - 17 mV and in specimen 2 - 15 mV were recorded, corresponding to chloride levels of about 500 mM.

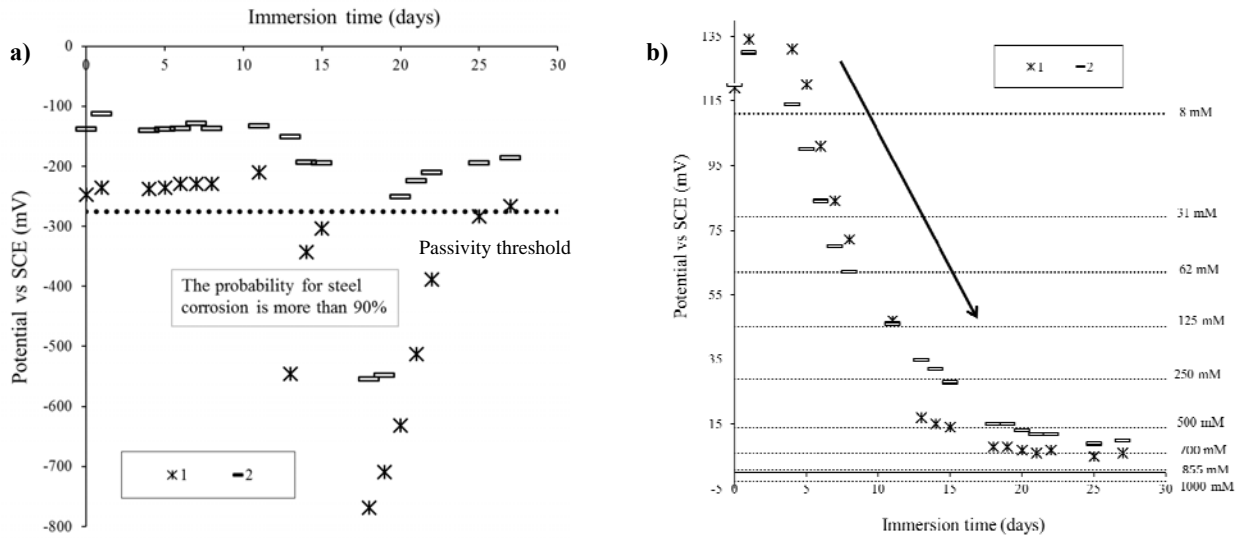


Figure 1. The OCP readings of steel rods(a) and chloride sensors (b) over time

While the OCP values for the sensors remain similar or change to more cathodic values within the progress of chloride penetration, the OCP values for steel shift to more anodic values towards the end of the experiment, indicating attempts for re-passivation. Additionally, limited oxygen levels and chloride binding determine the alterations of active/passive behavior for the steel rods within conditioning. Therefore, OCP is not sufficient for in depth investigation of the systems under study, but can be used as an indication only for corrosion initiation at the steel reinforcement. Quantitative methods, determining corrosion currents or polarization resistance (R_p) values, are necessary to claim corrosion state of the steel reinforcement. EIS was employed in this study in order to provide information not only for corrosion state of the steel rods (electrochemical response), but also information for alterations in the surrounding bulk matrix. The EIS response in the high frequency domain (50 kHz to 1 kHz in this study) is attributed to properties of the bulk matrix in terms of connected and disconnected pore network and contribution of solid phases [8]. The medium to low frequency response (1 kHz to 10 mHz) is denoted to charge transfer resistance (and polarization resistance respectively) of the steel rods and transformations (mass transport or redox processes) in the product layer on the steel surface. The response is further evaluated qualitatively and quantitatively. Qualitative evaluation is simply comparing the magnitude of real impedance and phase angle with time of conditioning (the higher the magnitude of $|Z|$ - the more corrosion resistant behavior). For example, Fig.2 further below (section 2) shows a close to capacitive behavior i.e. passive state of the steel rods in both specimens 1 and 2 between 1 and 11 days. Decline of the EIS response i.e. distorted or semi-circles, inclination towards the real axis – e.g. Figs.3 and 4 is denoted to chloride arrival at the steel surface and corrosion initiation. Possible “reverse” in EIS response towards increase in magnitude of $|Z|$ and inclination to the imaginary axis (Fig.4) is denoted to attempts for re-passivation of the steel reinforcement or diffusion/kinetic limitations within product layers formation and re-distribution which gives rise to global polarization resistance values for the steel – e.g. latest recorded intervals in Fig.4. The quantitative evaluation of the EIS response and thus deriving charge transfer resistance or global polarization resistance (i.e. corrosion resistance) for the embedded steel is performed via attribution of an equivalent electrical circuit to the observed features in the EIS response and fitting the latter (an example in Fig.5), in order to derive the corresponding resistive and capacitive contributions. EIS tests for steel in cement-based materials, test set-ups and data interpretations are given in more details in [8, 9].

B. Electrochemical impedance spectroscopy – response for steel rods

Figures 2 to 4 present the EIS response for the steel rods as a complex plane Nyquist and a Bode (phase only) plot in the two replicate specimens 1 and 2 as an overlay of chosen time intervals (OCP values as previously depicted in Fig.1a). The responses for both specimens present a transition from passive (1 to 11 days) - to active (15 to 18 days, Fig.3) - to re-passivation behavior (20 days onwards, Fig.4). Although identically prepared, specimens 1 and 2 exhibit a slight deviation in time of

corrosion initiation, which is in line with the recorded OCP values (Fig.1a). Next to that, the bulk matrix properties of specimen 1 differ from those of specimen 2, which is also the primary reason for the delay in the time to corrosion initiation for specimen 2. Some major features of the EIS response and main considerations are discussed in what follows (Note: all EIS plots and the best fit parameters in Table 1 are presented as non-normalized values since the surface of steel rods and sensors was equal, as well as geometry of the cement-based specimens i.e. a direct comparison of response and values is possible and accurate).

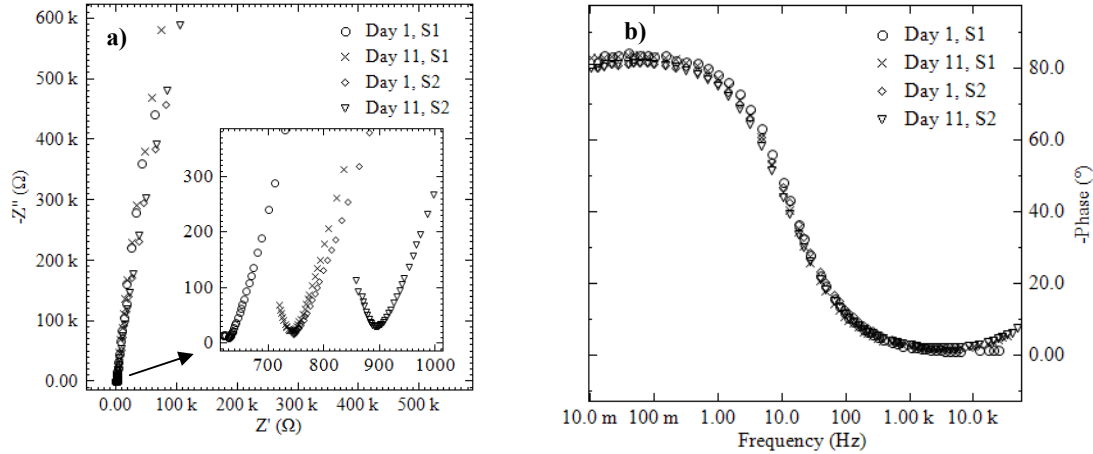


Figure 2. Nyquist plot (a) and Bode (phase only) plot (b) for specimen 1 (S1) and specimen 2 (S2) after 1 day and 11 days immersion in SPS solution

Fig. 2 presents the response of specimens 1 and 2 for 1 and 11 days of conditioning, depicting a close to capacitive behavior in the low frequency domain i.e. passive state for the steel rods. The high frequency domain (inlet in Fig.2) reflects the alterations in bulk matrix properties – increase in resistance from approx. 600 Ohm to > 750 Ohm for specimen 1 and from 750 Ohm to ~ 900 ohm for specimen 2, denoted to densification of the bulk cement-based matrix within the process of cement hydration.

What should be noted is that the cement-based bulk matrix properties differ in specimens 1 and 2 from the beginning of the experiment, despite the identical specimen preparation and conditioning. This is as expected, since cement-based materials heterogeneity, non-uniformity of the pore network distribution and varying pore network connectivity and tortuosity normally account for differences in electrical properties of the matrix. The contribution of microstructural properties to the electrochemical response is in terms of varying bulk matrix diffusivity and permeability and consequently determines the ease of ions and water penetration to the steel surface. The result is more noble OCP values for the embedded steel in specimens 2 (higher electrical resistivity) and more cathodic OCP values for the steel rods in specimens 1 (less resistive) – Fig.1a. The influence of bulk matrix electrical properties on the response of the sensors at earlier stages (1 – 11 days) is less pronounced but becomes more obvious after 12 days of conditioning (Fig.1b) and will be discussed below with respect to chloride arrival at the relevant interfaces.

The passive state of the steel reinforcement is also reflected by a phase angle of approx. 85 degrees (Fig. 2b) and is as generally recorded for passive steel in cement-based materials [8]. The passive state reflected by EIS response (Fig.2) is supported by the OCP readings in that time frame – values more anodic than – 270 mV as depicted in Fig.1a). Meanwhile, the steel response is also well in line with the sensor response, for which the OCP change from 135 mV to 45 mV denotes for chloride concentration of max 125 mM in the surrounding cement matrix (Fig.1b).

Fig. 3 depicts the response for specimens 1 and 2 at 15 and 18 days of conditioning. At the stage of 15 days, the magnitude of impedance $|Z|$ and phase angle for specimen 1 sharply decrease, which is also reflected by the OCP readings in Fig.1- between - 350 and -750 mV. This is the point of corrosion initiation for specimens 1. Additionally, the bulk matrix resistance for specimen 1 decreases from approx. 750 Ohm at 11 days (Fig.2a) to approx. 400 Ohm at 15 days (Fig.3a). The decrease in bulk matrix electrical properties is attributed to both alteration in ionic strength of the pore water (linked to chloride ions penetration from the external medium) and micro-cracking, induced from corrosion initiation.

In contrast, although active behavior is relevant for the steel rod in specimen 2 as well (magnitude of $|Z|$ significantly reduced at 15 days, compared to 11 days - Fig.3a and Fig.2a; phase angle drop from 85 to 30 degrees), the high frequency response for specimen 2 shows similar features for 15 days as observed for 11 days (approx. 800 Ohm, inlets Figs.2a and 3a). This observation is in line with the recorded OCP values: the denser matrix (or lower pore network connectivity) in specimen 2 results in a delay of chloride ions penetration and explains the more noble OCP values for steel at 15 days and the more anodic (lower chloride concentration) OCP values for the sensors at this stage (Fig.1a,b). Further, a denser matrix is responsible for the following faster re-passivation of the steel rod in specimen 2, with an onset already at day 18 (Fig.3) with a rise of magnitude of $|Z|$ and phase shift towards 50 degrees

Whereas more cathodic OCP values for the steel rods, as in specimen 1, can be due to oxygen deficiency at the steel surface, the inclination of $|Z|$ towards the real axis (Fig.3a) can be only attributed to chloride arrival at the steel surface and therefore corrosion initiation. The latter process is taking place, since the chloride sensor embedded in the vicinity of the steel rods reads at that time OCP value more cathodic than 25 mV, which corresponds to chloride in the cement matrix of approx. 500 mM.

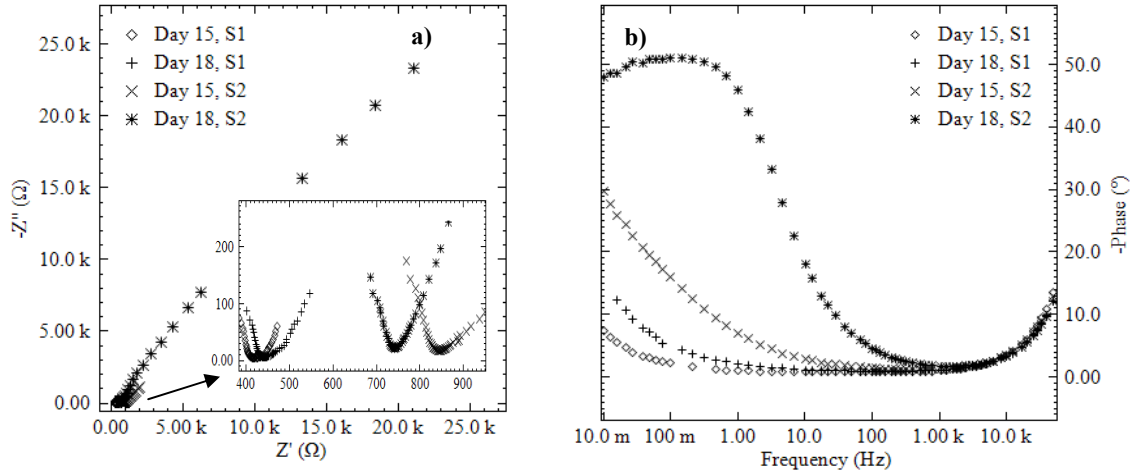


Figure 3. Nyquist plot (a) and Bode (phase only) plot (b) for S1 and S2 after 15 and 18 days immersion in SPS solution.

After 18 - 20 days of conditioning, the EIS response for specimens 1 and 2 shows an attempt for re-passivation – Fig.4, reflected by a shift back towards a more capacitive-like behavior in the low frequency domain, accompanied by increase in magnitude of $|Z|$ and phase angle of approx. 60 degrees at the stage of 25 days.

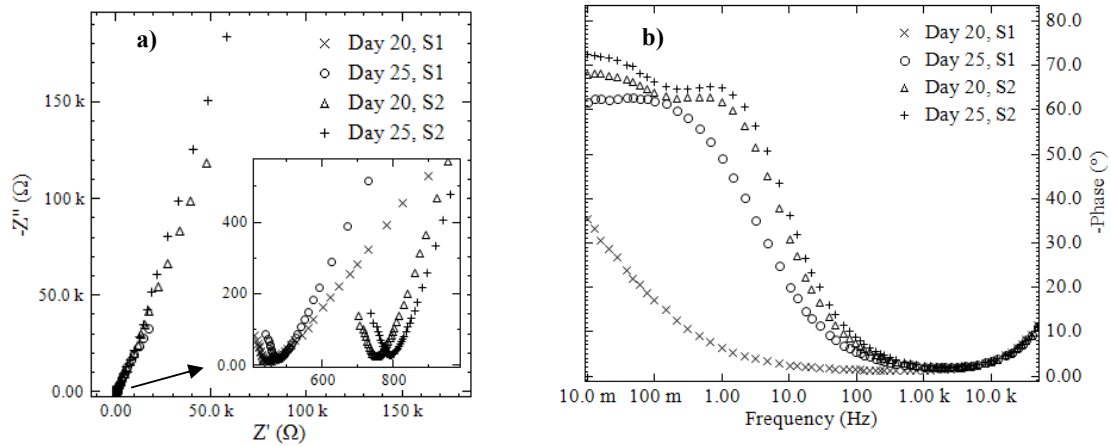


Figure 4. Nyquist plot (a) and Bode (phase only) plot (b) for S1 and S2 after 20 and 25 days immersion in SPS solution.

What can be noted is that a more pronounced effect of the formed on the steel surface product layer is related to specimen 2, with a clear contribution of a second time constant in the low frequency domain for the stage of 20 and 25 days (Fig.4b). Next to that, the high frequency response maintains similar features as for previous stages, the bulk matrix resistivity for specimen 2 remaining with higher electrical resistivity, compared to specimen 1. This is also reflected by the OCP readings for the sensor embedded in specimen 2, which shows more anodic values than the sensor in specimen 1 throughout the hereby investigated period. However, the OCP readings for both sensors give values more cathodic than 15 mV (to 8 mV), which would mean chloride concentration of more than 500 mM (to 700 mM) in the pore solution at the sensors and steel interfaces.

The as recorded EIS response for both specimens 1 and 2 were modeled with equivalent electrical circuits, consisting of a series of time constants – an example for the equivalent electrical circuit used to fit the response of specimen 2 at day 1 is given in Fig. 5, along with the corresponding response/fit plots.

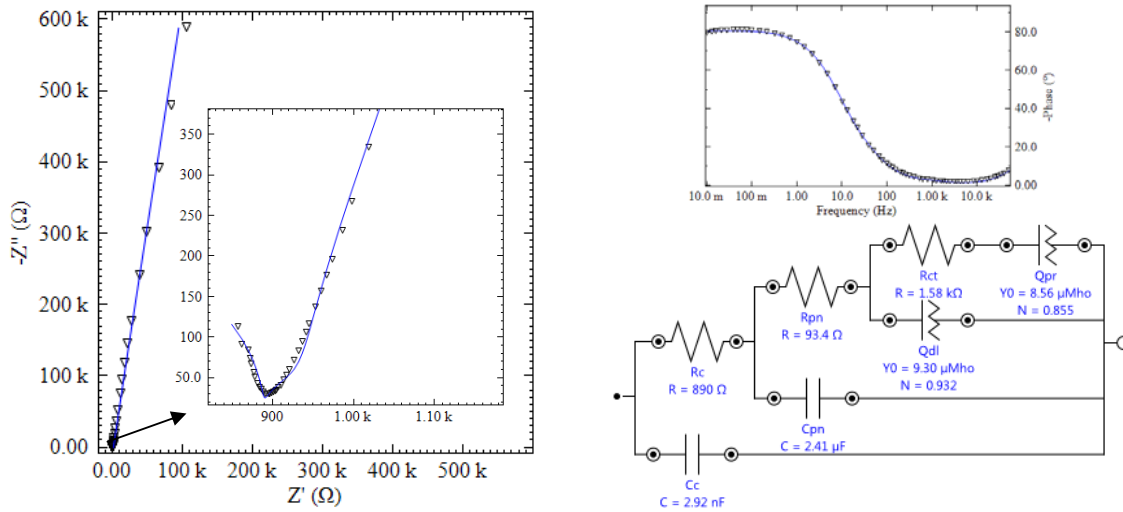


Figure 5. The equivalent electrical circuits for specimen 2 at day 11; Nyquist plot (left), Bode phase plot and fitting circuit (right)

Within EIS measurements, different equivalent circuit models may apply for one and the same system; similarly, increasing the complexity of a circuit would decrease the fit error by just mathematical considerations. For steel in concrete, which is a system of high complexity and heterogeneity, different circuits with equally good fit results can be used [9, 10]. However, the most reliable one would be the circuit with clearly defined physical meaning, attributed to the various parameters.

The circuits used in this study present a nested arrangement of time constants for all time intervals, related to bulk matrix properties, steel electrochemical response and contribution of product layer on the steel surface as follows: electrolyte resistance ($R_{el} \sim 8$ ohm) in series with: first and second time constant ($R_c C_c$ and $R_{pn} C_{pn}$) denoted to the contribution of the solid bulk matrix and connected pore network, followed by a third and fourth time constants ($R_{ct} C_{dl}$ and $R_{ox} Q_{ox}$), denoted to charge transfer resistance/double layer capacitance on the steel surface and mass/redox transformation within the product/oxide layer on the steel surface.

As seen from Table 1, the bulk matrix resistance (R_c) increases with time of conditioning (1 to 15 days) denoted to cement hydration. The corresponding capacitance in the range of 2 to 9 nF is representative for the solid phase of a cement-based material. The pore network resistance (R_{pn}) decreases between 1 and 15 days, with a pronounced drop at day 15, which is due to chloride penetration into the cement matrix. Further, increase in pore network resistance is observed, in line with the prevailing effect of cement hydration and “closing” pore space (intensified in the presence of chlorides) over ionic strength contribution. Micro cracking due to corrosion initiation is not significant for specimen 2, since the overall bulk matrix resistance maintains similar values from day 1 to day 25 (also reflected in Figs. 2 to 4).

TABLE I. BEST FIT PARAMETERS (SPECIMEN 2)

Element	R_c (Ω)	C_c (nF)	R_{pn} (Ω)	C_{pn} (μF)	R_{ct} (Ω)	C_{dl} (μF)	Q_{dl}		Q_{pr}		R_{ox} (kΩ)	Q_{ox1}		Q_{ox2}		χ^2
							Y0 (μMho)	n	Y0 (μMho)	n		Y0 (μMho)	n	Y0 (μMho)	n	
Day 1	752	8.89	188	4.53	1930		7.99	0.94	8.56	0.84						0.003
Day 11	890	2.92	93	2.41	1583		9.3	0.93	8.56	0.85						0.003
Day 15	814	1.3	29	1.53	24	28.6			2380	0.48						0.002
Day 20	737	1.98	44	1.96	236	10.3					28	34.5	0.82	29.1	0.74	0.003
Day 25	776	1.92	48	1.59	261	7.77					46	25.4	0.82	19.4	0.81	0.002

The changes in charge transfer resistance and double layer capacitance (accounting for corrosion state of the steel rods) exhibit a trend as follows:

- 1) at day 11 - a drop of R_{ct} compared to day 1, supported by the drop in R_{pn} for day 11 (from 188 to 93) due to apparent chloride penetration, also evident by the sensor OCP readings (Fig.1b);
- 2) corrosion initiation and significant reduction of R_{ct} at day 15 (from the kOhm range to 24 Ohm only), accompanied by a well pronounced contribution of product layer formation (Q_{pr} , with a clear pseudo-capacitive behavior ($n = 0.5$ at this stage) i.e.

corrosion initiation is in line with the more cathodic OCP values for the sensors, Fig.1b, accounting for ~ 250 mM for specimen 2 and 500 mM for specimen 1;

3) the attempt for steel re-passivation (Fig.4) is reflected by increase in R_{ct} from day 20 onwards (Table 1), accompanied by a decrease in double-layer capacitance (C_{dl}) and already significant contribution of a mixed control of the redox process taking place in the formed product layer. The resistance of the product layer at this stage (R_{ox}) is in the range of kOhm with corresponding pseudo-capacitance values in the range of 30 μ Mho, consistent with limitations to further charge transfer on the steel surface. An additional pseudo-capacitance (Q_{ox2}) was added to the last time constant to account for increased product layer structural heterogeneity and diffusion (or mixed kinetic/diffusion) phenomena in the product layer. The fitting with the chosen equivalent circuits resulted in acceptable error in the range of 0.002 (Table 1).

IV. CONCLUSIONS

The following conclusion can be drawn from the present investigation:

- The simultaneously embedded in cement paste steel rods and chloride sensors provided useful information on chloride ingress (concentration respectively) and the time to corrosion initiation. The employed set-up and methodology appear to be very suitable and provide reliable and accurate results for the determination of chloride thresholds in reinforced cement-based materials. The results show that a cathodic shift of the OCP values for steel i.e. corrosion initiation, is well in line with the cathodic shift of the OCPs for the sensors (meaning increased Cl concentration).
- The steel rods exhibited re-passivation behavior after corrosion initiation, which is well in line with the fundamental mechanisms of chloride-induced corrosion in alkaline medium i.e. higher (than hereby studied) level of chloride content is necessary to maintain stable pit growth and enhanced corrosion rates.
- EIS proves to be a very useful technique for the investigated cases, since delays or limitations to electrochemical response are easily explained via microstructural effects, the latter derived from the high frequency response with EIS measurements. Further, a clear physical meaning (relevant phenomena respectively) can be attributed to both bulk cement based matrix and steel/sensor behavior in time of specimens conditioning.
- A good correlation of results for electrochemical behavior of steel rods and sensors was observed, in addition to the microstructural properties at the interfaces for the steel rods. It can be concluded that the sensors can detect the level of chloride at the steel reinforcement, which would cause the onset of corrosion initiation. However, further corrosion propagation and the rate of the process can not be assessed by the sensors, unless the equilibrium at the Ag/AgCl interface is diverted by increase in chloride concentration of the surrounding medium.

REFERENCES

- [1] C. L. Page, M. M. Page, "Durability of Concrete and Cement Composites", Woodhead Publishing, Cambridge, 2007.
- [2] U. Angst, C.K. Larsen, O. Vennesland and B. Elsener, "Monitoring the chloride concentration in the concrete pore solution by means of direct potentiometry", Proceeding International Conference on Concrete Solutions, Padua, Italy, 2009.
- [3] B. Elsener, L. Zimmermann and H. Bohni, "Non-destructive determination of the free chloride content in cement based materials", Materials and Corrosion, vol. 54, no. , pp. 440–446, 2003.
- [4] U. Angst, and O. Vennesland, "Detecting critical chloride content in concrete using embedded ion selective electrodes–effect of liquid junction and membrane potentials", Materials and Corrosion, Vol. 60, NO. 8, pp. 638–643, 2009.
- [5] S. Erdogdu, I.L. Kondratova, and T.W. Bremner, "Determination of chloride diffusion coefficient of concrete using open-circuit potential measurements", Cement and Concrete Research, Vol. 34, NO. 4, pp. 603–609, 2004.
- [6] H.W. Song, V. Saraswathy, "Corrosion Monitoring of Reinforced Concrete Structures-A Review" Int. J. Electrochem. Sci., Vol. 2, pp. 1- 28, 2007.
- [7] X. He and X. Shi, "Chloride Permeability and Microstructure of Portland Cement Mortars Incorporating Nanomaterials",
- [8] D.A. Koleva, "Pulse cathodic protection, an improved cost-effective alternative". PhD Thesis, Delft University Press, Delft, the Netherlands, 2007.
- [9] N. G. Thompson and K.M. Lawson, "An electrochemical method for detecting ongoing corrosion of steel in a concrete structure with CP applied," Strategic Highway Research Program, National Research Council, Washington, D.C. 1991.
- [10] F. Pargar, D.A. Koleva, E.A.B. Koenders, K. van Breugel, "The importance of chloride sensors stability in monitoring ageing phenomena in concrete structures: Ag/AgCl electrodes performance in simulated pore-water environment", Proceeding of 1st International conference on Ageing of Materials and Structures (AMS'14), pp. 542-547, 2014.