

Potentiometric response of Ag/AgCl sensor in Portland and slag cement pastes

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

Publication date

2018

Document Version

Accepted author manuscript

Published in

Proceeding of the Workshop on Concrete Modelling and Material Behaviour in honor of Professor Klaas van Breugel

Citation (APA)

Pargar, F., Koleva, D., & van Breugel, K. (2018). Potentiometric response of Ag/AgCl sensor in Portland and slag cement pastes. In G. Ye (Ed.), *Proceeding of the Workshop on Concrete Modelling and Material Behaviour in honor of Professor Klaas van Breugel: Special "Klaas van Breugel" Sessions during the Rilemweek 2018* (Vol. PRO 126, pp. 214-221). Rilem.

Important note

To cite this publication, please use the final published version (if applicable).
Please check the document version above.

Copyright

Other than for strictly personal use, it is not permitted to download, forward or distribute the text or part of it, without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license such as Creative Commons.

Takedown policy

Please contact us and provide details if you believe this document breaches copyrights.
We will remove access to the work immediately and investigate your claim.

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

Farhad Pargar*, Dessi Koleva*, Klaas van Breugel*

* Delft University of Technology, Faculty of Civil Engineering and Geosciences, Department Materials & Environment, Stevinweg 1, 2628 CN Delft, The Netherlands

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 Ag₂S 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. $\text{Ca}(\text{OH})_2$), $\text{pH}=13$, 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 $\sim 140 \text{ mV}$ 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 ($\text{AgCl}/\text{Ag}_2\text{O}/\text{AgO}$) [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 $\text{AgCl}/\text{Ag}_2\text{O}/\text{Ag}_2\text{S}$ 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 $\text{Ag}/\text{Ag}_2\text{S}$ electrode (-935 mV vs. SCE) [19] and the potential for Ag_2S formation in an alkaline solution (ca. -790 mV) [20, 21].

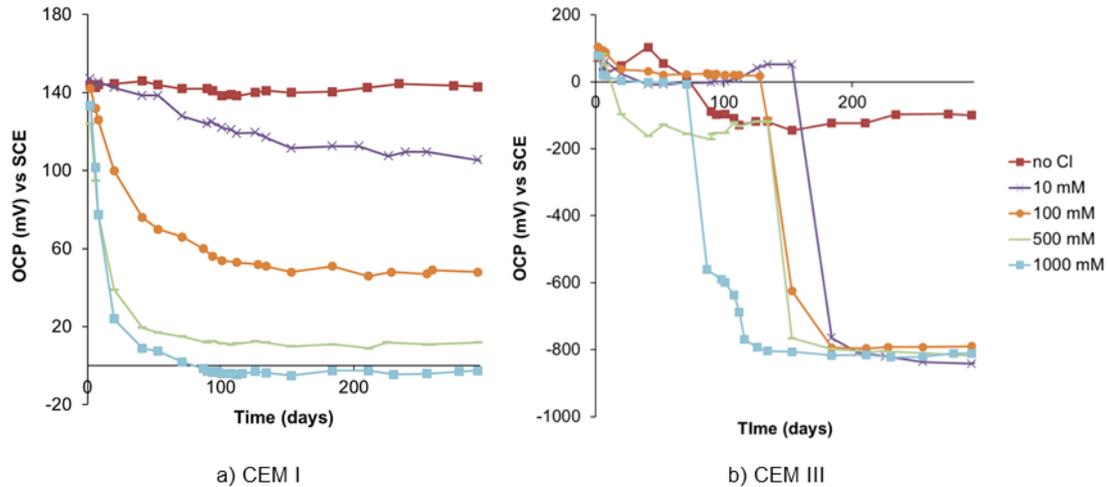


Figure 1: The OCP response of chloride sensor in (a) CEM I specimens and (b) CEM III specimens over time.

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 concentration. 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 $\text{AgCl}/\text{Ag}_2\text{O}$ 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 ($K_{\text{sp}}\text{Ag}_2\text{S}=1.6\times 10^{-49}$ at 25°C) in comparison to AgCl ($K_{\text{sp}}\text{AgCl}=1.8\times 10^{-10}$ at 25°C) and Ag_2O ($K_{\text{sp}}\text{Ag}_2\text{O}=2\times 10^{-8}$) 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.

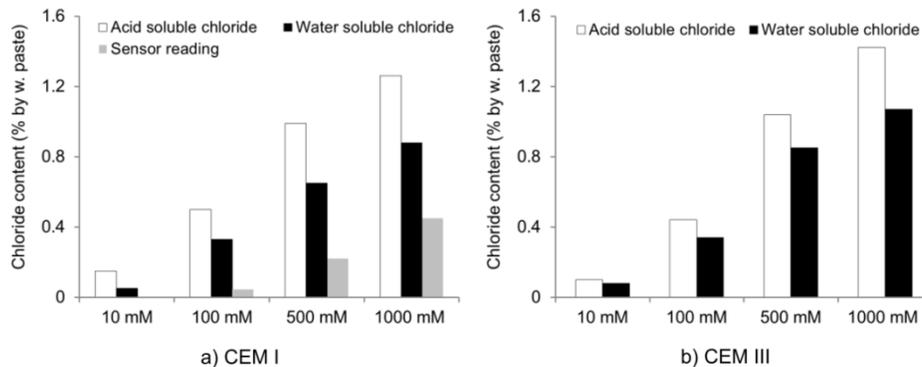


Figure 2: The measured chloride content by different methods in (a) CEM I specimen and (b) CEM III specimen after 300 days of immersion in solutions with different chloride concentration.

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 Ag₂S 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 Ag₂S 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 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

- [1] Duffo, G. S., Farina, S. B. and Giordano, C. M. (2009). Characterization of solid embeddable reference electrodes for corrosion monitoring in reinforced concrete structures, *Electrochimica Acta*, Vol. 54(3), p. 2010–2020.
- [2] Femenias, Y. S. Angst, U., Caruso, F. and Elsener, B. (2015). Ag/AgCl ion-selective electrodes in neutral and alkaline environments containing interfering ions, *Materials and Structures*, p. 1-15.
- [3] de Vera, G., Climent, M. A., Anton, C., Hidalgo, A. and Andrade, C. (2010). Determination of the selectivity coefficient of a chloride ion selective electrode in alkaline media simulating the cement paste pore solution, *Journal of Electroanalytical Chemistry*, Vol. 639(1), p. 43-49.
- [4] Elsener, B., Zimmermann, L. and Bohni, H. (2003). Non-destructive determination of the free chloride content in cement-based materials, *Materials and Corrosion*, Vol. 54 (6), p. 440–446.
- [5] Pargar, F., Koleva, D. A. and van Breugel, K. (2017). Determination of Chloride Content in Cementitious Materials: From Fundamental Aspects to Application of Ag/AgCl Chloride Sensors, *Sensors*, Vol. 17(11), 2482.
- [6] Abbas, Y., Pargar, F., Koleva, D. A., van Breugel, K., Olthuis, W., & van den Berg, A. (2018). Non-destructive measurement of chloride ions concentration in concrete—A comparative analysis of limitations and prospects. *Construction and Building Materials*, 174, 376-387.
- [7] Karthick, S., Kwon, S. J., Lee, H. S., Muralidharan, S., Saraswathy, V. and Natarajan, R. (2017). Fabrication and evaluation of a highly durable and reliable chloride monitoring sensor for civil infrastructure, *RSC Advances*, Vol. 7(50), p. 31252-31263.
- [8] Jin, M. Xu, J., Jiang, L., Xu, Y. and Chu, H. (2015). Investigation on the performance characteristics of chloride selective electrode in concrete, *Ionics*, Vol. 21(10), p. 2981–2992.
- [9] Vollpracht, A., Lothenbach, B., Snellings, R. and Haufe, J. (2016). The pore solution of blended cements: a review, *Materials and Structures*, Vol. 49(8), p. 3341-3367.
- [10] Graedel, T. E. (1992). Corrosion mechanisms for silver exposed to the atmosphere, *Journal of the Electrochemical Society*, Vol. 139(7), p. 1963-1970.
- [11] Arya, C., Buenfeld, N. R. and Newman, J. B. (1987). Assessment of simple methods of determining the free chloride ion content of cement paste, *Cement and Concrete Research*, Vol. 17(6), p. 907-918.
- [12] NEN-EN 197-1 (2011). Cement - Part 1: Composition, specifications and conformity criteria for common cements, European Committee for Standardization.
- [13] Pargar, F., Kolev, H., Koleva, D. A., & van Breugel, K. (2018). Microstructure, surface chemistry and electrochemical response of Ag|AgCl sensors in alkaline media. *Journal of Materials Science*, 53(10), 7527-7550.
- [14] Qiang, Y., Caijun, S., De Schutter, G., Dehua, D. and Fuqiang, H. (2011). Chloride ion concentration on the surface of cement-based materials in chloride solutions, *Journal of the Chinese ceramic society*, Vol. 39(3), p. 544-549.
- [15] RILEM TC 178-TMC. (2002). Analysis of total chloride in concrete, *Material and Structures*, 35, p. 583-585.
- [16] RILEM TC 178-TMC. (2002). Analysis of water-soluble chloride content in concrete,

- Recommendation, Materials and Structures, Vol. 35, p. 586-588.
- [17] ASTM C1152. (2003). Standard Test Method for Acid-Soluble Chloride in Mortar and Concrete, American Society for Testing and Materials (ASTM) Philadelphia, PA.
- [18] ASTM C1218. (2008). Standard Test Method for Water-Soluble Chloride in Mortar and Concrete, American Society for Testing and Materials (ASTM) Philadelphia, PA.
- [19] Ives, D. J. and Janz, G. J. (1961). Reference electrodes, theory and practice (No. 541.3724). Academic Press.
- [20] Conyers, J. L. and White, H. S. (1999). Electrochemical growth of Ag₂S on Ag (111) electrodes. Coulometric and X-ray photoelectron spectroscopic analysis of the stepwise formation of the first and second monolayers of Ag₂S. The Journal of Physical Chemistry B, Vol. 103(11), p. 1960-1965.
- [21] Wan, Y., Wang, X., Wang, X., Li, Y., Sun, H. and Zhang, K. (2015). Determination and generation of the corrosion compounds on silver exposed to the atmospheres, International Journal of Electrochemical Science, Vol. 10, p. 2336-2354.
- [22] Raynauld, J. P. and Laviolette, J. R. (1987). The silver-silver chloride electrode: a possible generator of offset voltages and currents, Journal of neuroscience methods, Vol. 19(3), p. 249-255.
- [23] Payer, J. H., Ball, G., Rickett, B. I. and Kim, H. S. (1995). Role of transport properties in corrosion product growth, Materials Science and Engineering: A, Vol. 198(1-2), p. 91-102.
- [24] Levard, C., Hotze, E. M., Lowry, G. V. and Brown Jr, G. E. (2012). Environmental transformations of silver nanoparticles: impact on stability and toxicity, Environ. Sci. Technol, Vol. 46(13), p. 6900-6914.
- [25] Rajbhandari, A., Yadav, A. P., Manandhar, K. and Pradhananga, R. R. (2009). Characterization and applications of silver sulphide based membrane electrodes, Scientific World, Vol. 7(7), p. 19-23.
- [26] Chaussadent, T. and Arliguie, G. (1999). AFREM test procedures concerning chlorides in concrete: extraction and titration methods, Materials and Structures, Vol. 32, p. 230-234.
- [27] He, F., Shi, C., Chen, C. and An, X. (2015). Relationship between water-soluble and free chloride concentrations in cement-based materials, Materials Research Innovations, Vol. 19(sup8), S8-348.
- [28] He, F., Shi, C., Hu, X., Wang, R., Shi, Z., Li, Q. and An, X. (2016). Calculation of chloride ion concentration in expressed pore solution of cement-based materials exposed to a chloride salt solution, Cement and Concrete Research, Vol. 89, p. 168-176.
- [29] Yuan, Q., Deng, D., Shi, C. and De Schutter, G., Deng, D. and He, F. (2011). Chloride-ion concentration on the surface of cement-based materials in chloride solutions, Journal of the Chinese ceramic society, Vol. 39(3), p. 544-549.
- [30] Hu, X., Shi, C. and De Schutter, G. (2015). Influences of chloride immersion on zeta potential and chloride in concentration of cement-based materials, 14th International Congress on the Chemistry of Cement, p. 1-15.
- [31] Kopecko, K. and Balazs, G. L. (2017). Concrete with improved chloride binding and chloride resistivity by blended cement, Advances in Materials Science and Engineering, 2017-7940247.
- [32] Dhir, R. K., El-Mohr, M. A. K. and Dyer, T. D. (1996). Chloride binding in GGBS concrete, Cement and Concrete Research, Vol. 26(12), p. 1767-1773.
- [33] Luo, R., Cai, Y., Wang, C. and Huang, X. (2003). Study of chloride binding and diffusion in GGBS concrete, Cement and Concrete Research, Vol. 33(1), p. 1-7.

- [34] Yuan, Q. (2009). Fundamental studies on test methods for the transport of chloride ions in cementitious materials, Ph.D. thesis, Ghent University, Belgium.
- [35] Maes, M., Gruyaert, E. and De Belie, N. (2013). Resistance of concrete with blast-furnace slag against chlorides, investigated by comparing chloride profiles after migration and diffusion, *Materials and Structures*, Vol. 46(1-2), p. 89-103.
- [36] Florea, M. V. A. and Brouwers, H. J. H. (2014). Modelling of chloride binding related to hydration products in slag-blended cements, *Construction and Building Materials*, Vol. 64, p. 421-430.
- [37] Elakneswaran, Y., Nawa, T. and Kurumisawa, K. (2009a). Influence of surface charge on ingress of chloride ion in hardened paste, *Materials and Structures*, Vol. 42(1), p. 83-93.
- [38] Ortega, J. M., Sanchez, I., Cabeza, M. and Climent, M. A. (2017). Short-term behavior of slag concretes exposed to a real in situ mediterranean climate environment, *Materials*, Vol. 10(8), p. 915.