

Self-protection concrete measures as prevention measure from chloride transport and corrosion of reinforcement

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Abstract. Incorporation of additives into a reinforced concrete matrix to delay or even completely avoid the initiation of corrosion during the service-life of the construction is a widely pursued topic. One of the new promising technologies achieving increased interest is to incorporate corrosion inhibitors encapsulated in layered double hydroxide (LDH). LDH structures follow a controlled release of the inhibitor while chloride is efficiently trapped at the same time. Another type of nanostructure additive offering self-protection ability in concrete is polyhedral oligomeric silsesquioxanes (POSS) developed to exhibit water-repellent functionalities protecting the reinforcement from corrosive attack. In the present laboratory work, the enhanced performance of concrete infrastructures in a marine environment was studied using a SCC design. The addition of LDH (0.5, 1 and 2 % by mass of binder (bmb)) and POSS (2 and 4 % additive level) was explored. Migration and diffusion Cl transport tests have been performed towards corrosion protection of reinforcing bars. The results showed that Cl transport decreases with the concrete maturity, and this is even more effective for concretes with LDH and POSS. This delay effect is more pronounced in the unidirectional diffusional Cl transport. LDH is significantly retarding the initiation of rebar corrosion.

1 Introduction

The growing demand in the construction industry to build structures with long service-life, necessarily of at least 50 years, leads to evaluating the incorporation of corrosion protection methods in current engineering projects. Reinforcement corrosion is the main cause of degradation and decreased in service-life of concrete structures with chloride induced corrosion as the most common cause. The development of advanced materials that incorporate new functionalities or new designs and concrete technologies are feasible pathways with the aim of improved the protection of reinforcement against corrosion and extended service-life of concrete structures.

Two tendencies are followed to extend the service-life, the action on the concrete or on the reinforcement, that is to affect the transport of Cl and to improve the resistance to corrosion of the reinforcement and to delay or inhibit corrosion initiation.

1.1 Encapsulated inhibitors

The encapsulation of corrosion inhibitors is achieving increased interest in the last two decades as a new promising technology to incorporate corrosion inhibitors into concrete. Several encapsulation

methodologies are being developed although the inhibition effectiveness is still at the lab level.

Layered double hydroxide (LDH) is one of the technologies referred in the literature to corrosion inhibition. LDH have a layered structure, composed by two external layers that exhibit a positive charge and one inner that contains water molecules and anions, [1-3]. LDH are based on Hydrotalcites layer minerals which are structurally derived from the brucite mineral- $Mg(OH)_2$.

The anionic exchange capability of LDH is the most vital property concerning its application in concrete. Mg-Al hydrotalcites have a large surface area, great ability to anion exchange, entrap chloride ions, and if loaded with an anion having inhibitor capability can prevent corrosion of reinforcement [4, 5]. In the case of LDH loaded with an anion inhibitor, the inhibition response mechanism is based on ion exchange between free chloride ions and the intercalated inhibitive anions in the hydrotalcite matrix and simultaneous release of the inhibitor [6]. In alkaline simulated pore solutions, Cl capture and inhibitor release and inhibition efficiency is shown [3, 7, 8]. The corrosion inhibition efficiency associated with the inhibitor released from the LDH has also been demonstrated in mortar like in [7, 9] with a larger time to corrosion onset due to Cl transport decrease. However, insufficient relevant studies are carried out in concrete formulations.

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1.2 Water-repellent self-protection additives

As a new innovative materials technology, specific derivatives of organically modified polyhedral oligomeric silsesquioxanes (POSS) have recently been investigated as water-repellent additives to give effective self-protection to modified bulk concrete.

POSS derivatives are particulate hybrid organic inorganic materials composed of a spherical robust silicon-oxygen framework with a diameter of about 1.5 nm that can be functionalized with a variety of organic substituents following a cost-efficient two-step synthesis route [10]. These hybrid materials appear as a new generation of core-shell carriers due to several advantages such as well-defined structures and ability to introduce multifunctionality. Specific functionalisation in POSS derivatives is aiming at introducing water-repellent properties and is reinforcing the concrete matrix without inducing mechanical stress to the bulk material but acting like pore blockers and pore liners under severe conditions.

It is shown [11] that non-reactive hydrophobic hybrid POSS derivatives modified with water-repellent functionalities can be mixed as admixtures in concrete formulations to give high resistance to chloride transport inducing a reduction of chloride ingress in concrete compositions designed to withstand harsh marine exposure conditions [12]. Furthermore, water-repellent POSS derivatives have been positively evaluated to improve durability of concrete specimen when exposed to specific accelerated test conditions related to leaching and freezing/thaw cycles as well as to ice abrasion [13,14].

The service life of the energy infrastructures located in severe environment as in marine exposure can be significantly reduced. One of the most expected damages under this severe operating condition for reinforced concrete is corrosion of reinforcement due to Cl penetration. The incorporation of two functional additives, an encapsulated inhibitor (LDH) and a water repellent additive (POSS) is studied to improve the concrete performance by reduction of Cl transport and retardation of corrosion onset. This challenging task has been addressed in the LORCENIS EU project [15].

2 Experimental method

2.1 Concrete composition

Self-compacting basic concrete (SCC) was developed based on the following requirements: workability requirements (SF2), minimum strength class C50/60 reduced number of binder/components (2), reduced amount of superplasticizer, good open-time/workability and good durability properties (frost, Cl ingress). The concrete composition is shown in Table 1. To this SCC concrete mix the LDH and POSS additives were added.

LDH was added at 0.5, 1 and 2 % by mass of binder (bmb) dosage while POSS was used at 2 and 4% additive level. The dosages selected of LDH and POSS were based on maintaining the flowability of the concrete developed [15]. Accordingly, in all mixes the

self-compactness was maintained and flowability was even increased with the addition of LDH and POSS. The SP dosage was maintained with the addition of LDH or POSS.

Table 1. Concrete composition.

Concrete components	Dosage
CEM I 52.5 R (kg/m ³)	350
Fly Ash (kg/m ³)	140
Sand 0/4 (kg/m ³)	1090
Gravel 4/16 (kg/m ³)	575
w/b	0.35
Superplasticizer (SP) (% weight of cement)	1
Admixture for increasing freeze-thaw resistance (kg/m ³)	2
LDH (%)	0.5/1/2
POSS (%)	2/4

2.2 Chloride transport tests

Accelerated tests by migration following NT Build 492 [16] and unidirectional diffusion using EN 12390-11 [17] were performed for the chloride transport characterisation.

In migration Cl transport tests, the testing samples were cylinders of 10 cm of diameter and 5 cm of height, cores obtained from cylinders of Ø 10 x 20 cm, discarding 1 cm of up and bottom parts. Three specimens were tested for each SCC mix design (REF, LDH and POSS) and different curing periods (56 days and 12 months). For these tests, the concrete sample was first preconditioned in saturated Ca(OH)₂ solution under vacuum. The electrodes were stainless steel meshes. At the end of the test, the specimens were cut and the fracture surfaces sprayed with AgNO₃ for determination of the Cl penetration depth. Finally, the non-stationary chloride migration coefficient ($D_{app\ mig}$) was calculated.

For Cl diffusion 10x10x10 cm concrete specimens were used. 1 cm from the upper surface was cut to allow the exposure of the bulk concrete without skin interference. The samples were saturated in distilled water under vacuum. A ponding with 3% NaCl solution was placed on the concrete surface. Two samples were tested for each type of concrete. After 12 months of exposure the chloride profile was obtained through grinding and homogenization of each millimetres layer until 10 cm depth and then further every 2 mm. The total Cl (acid attack) and the free Cl⁻ (water soluble) were analysed by a titration method using 0.1 M silver nitrate and an automatic titrator. The results expressed as percentage by mass of sample (% bms). Finally the non-stationary chloride diffusion coefficient (D_{app}) was obtained.

2.3 Corrosion tests

As no standard exists for this type of test, the corrosion initiation has been determined following the protocol proposed within RILEM TC-235-CTC and described in

[18]. Ten reinforced concrete samples were tested for each concrete type, reference and functionalized with 1 and 2 % LDH. Samples were obtained from 15x15x15 cm casted concrete cubes having a steel rebar embedded in the centre. The rebar was pre-oxidized before embedding in concrete following the procedure described in [18]. The samples were kept in a chamber at 95±5%RH and 20°C until testing. The samples were cut from one surface at a covering depth of approx. 1.5 cm from the rebar. The rest of the surfaces were coated with epoxy resin to allow only one face for Cl penetration. The final reinforced concrete samples were preconditioned through a pre-drying period in a chamber at 30 % RH and 20 °C, for 3 months, and finally 1 week at 50 °C. After preconditioning, the samples were submerged in 3.0 % NaCl solution.

The detection of corrosion onset was continuously recorded through electrochemical techniques: corrosion potential (E_{corr}), using an Ag/AgCl reference electrode and corrosion rate (i_{corr}) measurements, the results from this method not shown in the present paper. The onset of stable corrosion was defined when the potential has dropped from its initial passive level by at least 150 mV or the E_{corr} remains more negative than -231mV Ag/ClAg during of at least 15 days [18, 19]. Once corrosion initiation was confirmed sampling of concrete at the rebar level was taken and Cl content assessed.

3 Results and discussion

3.1 Chloride transport reduced by LDH

The chloride transport in REF concrete when using the migration transport, shows some dispersion mainly at low hydration ages but similar trend with evolution of maturity (hydration). A clear decrease of non-stationary Cl migration coefficient, $D_{app\ mig}$ from NTB-492, is observed due to the retarded hydration of the fly ash that is effective at a later stage, as this can be appreciated in Figure 1. According to [20], the classification of concretes for potential durability with respect to reinforcement corrosion and associated with durability indicators for non-stationary migration coefficient, $D_{app\ mig} \times 10^{-12} \text{ m}^2/\text{s}$, at 3 months age: > 50 very low, 10-50 low, 5-10 medium, 1-5 high and <1 very high. The REF concrete can be classified to show high durability.

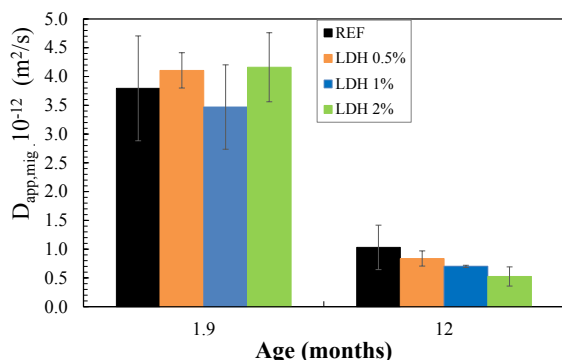


Fig. 1. $D_{app\ mig}$ from NT Build 492 in concretes containing LDH.

The addition of the functional additive LDH in different quantities, see figure 1, also give low $D_{app\ mig}$ that decreases with the maturity of the concrete. At early ages of hydration (1.9 months) the addition of different dosages of LDH seems not to have clear impact on the diffusion coefficient. At 12 months of hydration the addition of LDH shows a positive impact with $D_{app\ mig}$ being lower than that for the reference. The increasing content of LDH also shows beneficial effect in reducing the Cl transport at 1 year exposure.

The unidirectional diffusion coefficient of chlorides, D_{app} , is analysed after 12 months of exposure with 1 and 2 % LDH. The 0.5 % LDH was not tested in chloride diffusion test. The chloride profiles at 12M of the reference concrete are displayed in Figure 2, with the comparison of the total and free chloride profiles of the reference concrete and of the LDH 1 and 2 %. The decrease of the chloride transport with the addition of LDH is very pronounced. Higher Cl penetration are detected with the reference concrete up to 15 mm depth, while it is lower than 10 mm with the LDH. Also the ingress of Cl is reduced by LDH. Increasing dosage of LDH gives improving efficiency. The decrease in Cl in the concrete bulk is also identified by analysing the free Cl content. The amount of free Cl is always lower in presence of LDH, and this effect is more evident with higher LDH dosages. Besides, lower amounts of free Cl are measured with LDH, probably as a consequence of the inhibitor's ability to capture Cl as proposed in [3, 6].

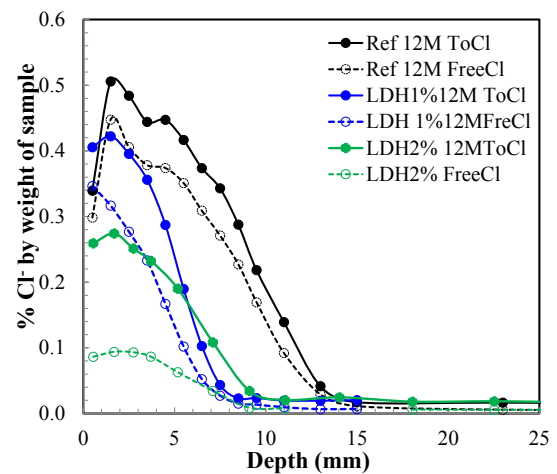


Fig. 2. Cl profile with LDH at 12 months.

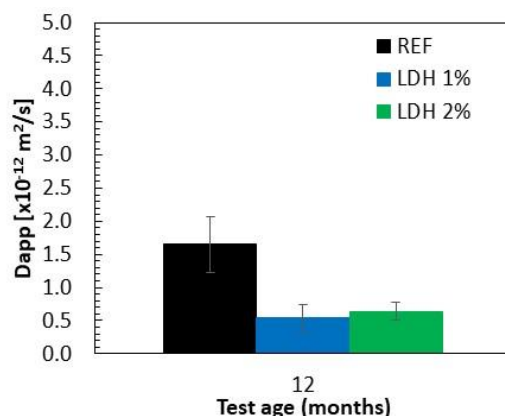


Fig. 3. D_{app} from unidirectional Cl diffusion coefficient with LDH.

The most important aspect to note from these results is that the diffusion coefficient of the SCC mix design is significantly reduced when using LDH, as shown in figure 3, by about 50 % during the recording period indicating that service life will be extended.

3.2 Chloride transport reduced by POSS

The addition of the functional additive POSS in different dosages (Figure 4) also provides low transport of Cl as concluded from migration tests, $D_{app\ mig}$. The chloride transport decreases with maturity of the concrete. At early ages of hydration (1.9 months), the addition of different quantities of POSS seems to have no impact on the chloride transport compared to the reference concrete. However, after 12 months of exposure the impact of 2 and 4 % POSS increases with a strong decrease of $D_{app\ mig}$ so that the durability classification changes from high, as found for REF concrete to very high in presence of POSS, according to the criteria suggested in [20].

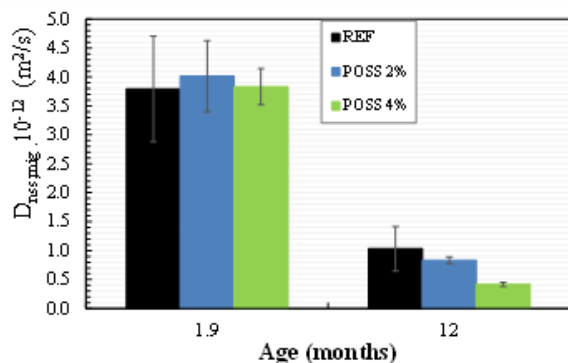


Fig. 4. $D_{app\ mig}$ from NT Build 492 in concretes containing POSS.

The penetration after 12 months in the unidirectional diffusion test also shows a protective effect for concrete due to the addition of POSS, as shown in Figure 5. Lower Cl penetration depths are realized, with 15 mm for REF concrete in comparison to about 10 mm SCC with POSS.

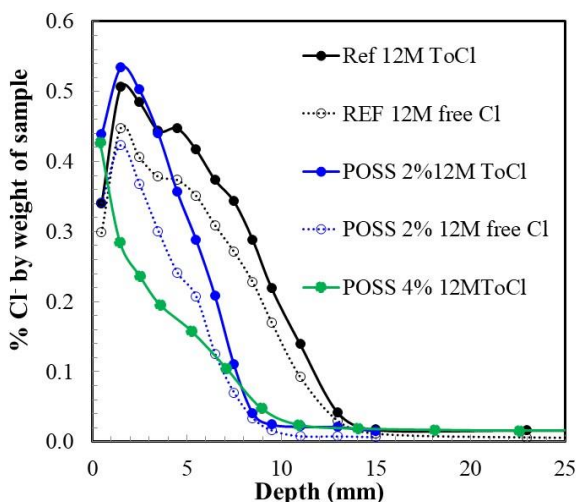


Fig. 5. Cl profile with POSS at 12 months.

The profile for free chlorides was evaluated in REF and 2%POSS. The comparison of the total and free chloride profiles of the concretes marked with REF and POSS shows that the ratio of free and total chlorides does not significantly change for POSS compared to the same ratio in REF. This change was more dominant for the addition of LDH.

The D_{app} values at 12M for REF concrete and POSS with 2 and 4 % are given in Figure 6.

The results show that there is a significant decrease in D_{app} with POSS additions. These results confirm also findings from previous migration tests according to [20] where concretes functionalized with POSS are classified as very high resistant to chloride ingress.

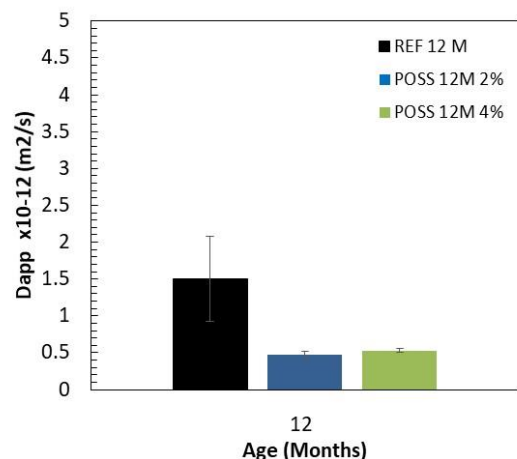


Fig. 6. Nat Cl diffusion coefficient with POSS.

The Cl transport is also significantly diminished with the POSS additive, as observed for LDH, confirming that both additives will contribute to extend the initiation period according to Tuuti model [21] and prolong the service life. The expected effect with POSS was to reduce the transport due to the hydrophobic character of the additive that would prevent the concrete bulk from the penetration of water. Long-term studies will inform more effectively on the duration of the improvement.

3.3 Corrosion inhibition

The detection of corrosion onset was performed in REF concrete compared with dosages of 1 and 2 % LDH. The test is completed when evidence of corrosion initiation is detected. In the present paper only E_{corr} results for REF and 1 % LDH are presented. To identify the onset of corrosion from E_{corr} data, it has been considered that at least a decrease of 150 mV compared to the initial E_{corr} , in passive state, needs to be recorded to move to the active corrosion state, and its permanence in time, as suggested in [18]. Thereby, E_{corr} is continuously recorded.

After 1 year of exposure only samples from the REF concrete have shown indication of corrosion risk, as shown in Figure 7, that have trespassed the region of 50 % risk of corrosion, marked with dash lines in the E_{corr} figure.

Corrosion potential measurements during 1 year of exposure to chloride solution show more anodic values

for concretes with LDH additions than for REF samples with results shown in Figure 8.

Another aspect to highlight from these results is the high dispersion in E_{corr} with that reference concrete samples, varying from medium risk (50 %) to high risk (> 90 %) of corrosion and recovery. Two reasons could be attributed to this observation, as consequence of the peroxidation of the bar that could facilitate the nucleation corrosion initiation sites, followed by a re-passivation process until reaching a new stage with more negative potentials indicating the increasing risk of corrosion initiation.

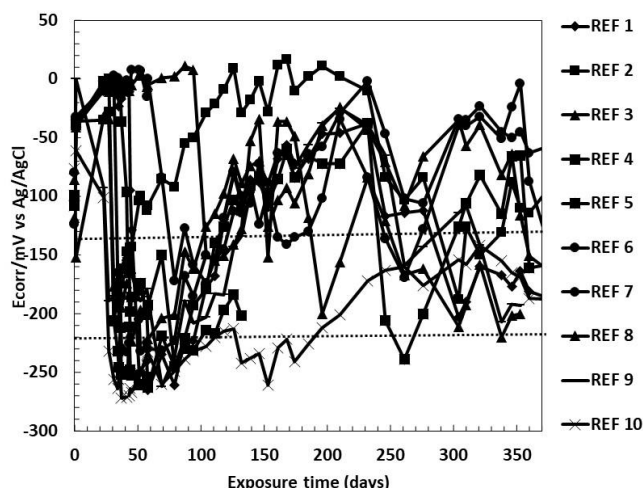


Fig. 7. E_{corr} evolution in NaCl solution in REF concrete.

However, this effect is not detected with the addition of LDH. The E_{corr} measurements in this case show only little deviation and are more anodic. This is probably due to the inhibitor released from the LDH that allows a dense passivation layer to be formed on the surface of the rebar even after peroxidation, and is stable during the 12 months of exposure. Longer exposure periods are ongoing to identify the ingress of Cl at level of the reinforcing bars after de-passivation. REF concrete samples have given threshold values from 0.2 to 0.4 % of total chlorides.

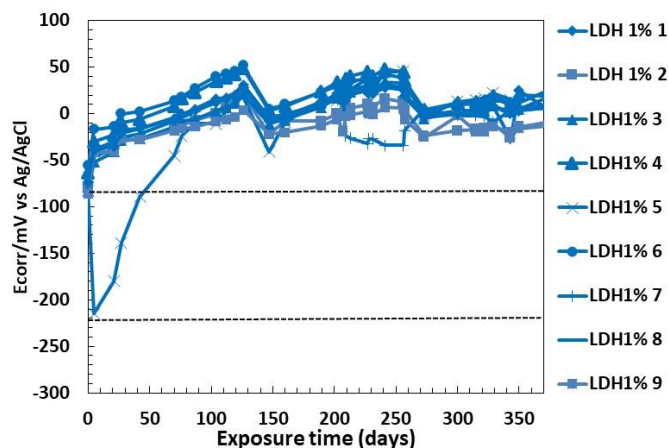


Fig. 8. E_{corr} evolution in NaCl solution in concrete with 1% LDH.

4 Conclusions

The severe exposure of assorted SCC samples to marine conditions have been simulated in the lab for durability focused in two main actions: the chloride transport and subsequent corrosion of reinforcement. The concrete performance has been analysed after incorporation of functional additives and compared to reference samples. The main experiences from the experiments in this scenario allow following conclusions:

- The reference concrete design shows high chloride transport and corrosion risk.
- The incorporation of LDH improves the resistance to chloride transport and slows down the chloride transport, demonstrated by diffusion and migration transport processes.
- The addition of POSS also shows a beneficial effect in delaying the chloride transport.
- Increasing additive dosage in the concrete bulk can impact the performance indicating the importance of an optimal dosage. The increase from 2 % to 4 % POSS dosage is beneficial for reducing the Cl transport while the increase from 0.5 to 2 % of LDH dosage reduces the Cl transport.
- Similar Cl transport values in migration (D_{mig} , after 1 year maturity) and diffusion (D_{app} , after 1 year exposure) tests were found with both POSS and LDH additive.
- The corrosion onset has a significant benefit with the incorporation of LDH, both for 1 % and 2 %. After 1 year exposure no corrosion risk was found with 1 % and 2 % LDH while in more than 50 % cases of corrosion onset were detected in the reference concrete.

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References

1. A.M. Lauermannová, I. Paterová, J. Patera, K. Skrbek, O. Jankovský and V. Bartunek, *Appl. Sci.* **10**, 7989 (2020),doi:10.3390/app10227989
2. Z. M. Mir, A. Bastos, D. Höche and M. L. Zheludkevich, *Materials*, **13**, 1426 (2020) doi:10.3390/ma13061426
3. T. Yuming, Z. Xuhui, N. Le, Z. Yu. J. Wuhan Uni. Technol, *Mater. Sci. Ed.* **29**, 278–283 (2014)
4. D.G. Costa, A. B. Rocha, W.F. Souza, S. S.X. Chiaro, A.A. Leitão, *Applied Clay Science* **56**, 16–22 (2012)
5. J. Tedim, A. Kuznetsova, A.N. Salak, F. Montemor, D. Snihirova, M. Pilz, M.L. Zheludkevich, M.G.S. Ferreira, *Corrosion Science* **55**, 1–4 (2012)

6. H. Tatematsu, T. Sasaki, *Cement & Concrete Composites* **25**,123–129 (2003)
7. Y. Cao, S. Dong, D. Zheng, J. Wang, X. Zhang, R. Du, G. Song, C. Lin, *Corrosion Science* **126**, 166–179 (2017)
8. Y. Tian, C. Wen, G. Wang, P. Deng, W. Mo, J. Applied Electrochemistry **50**, 835–849 (2020)
9. Z. Yang, R. Polder, J.M.C. Mole, C. Andrade, *Cement & Concrete Research* **100** (2017) 186–202
10. F. Männle, F., C. Simon, C., J. Beylich, J., K. Redford, K., *Polybranched, organic/inorganic hybrid polymer and method for its manufacture*, US7960492 B2 (2011)
11. M. Pilz, E. Gallucci, *Modification of POSS derivatives for reinforcement of bulk concrete*, in Proceedings of the International LORCENIS conference on Durable Concrete for Infrastructure under Severe Conditions, 10-11 Sep 2019, Ghent, Belgium, ISBN: 978-9-463-88638-3, p 28-31 (2019)
12. M. Prieto, U. Mueller, F. Maia, M. Pilz, *Performance evaluation of functional admixtures in reinforced concrete under real marine service conditions*, in Proceedings of the XXIV NCF-Nordic Concrete Research Symposium, 17-19 Aug 2022, Stockholm, Sweden (2022)
13. M. Cruz Alonso, K. Villar Arribas, *Durability of concrete under combined action of leaching and freeze-thaw processes*, in Proceedings of the International LORCENIS conference on Durable Concrete for Infrastructure under Severe Conditions, 10-11 Sep 2019, Ghent, Belgium, ISBN: 978-9-463-88638-3, p 156-160 (2019)
14. A. Babaahmadi, U. Mueller, K.T. Fosså, G. Moen, *Ice abrasion resistance in high performance concrete engineered with new admixtures*, in Proceedings of the International LORCENIS conference on Durable Concrete for Infrastructure under Severe Conditions, 10-11 Sep 2019, Ghent, Belgium, ISBN: 978-9-463-88638-3, p 152-155 (2019)
15. LORCENIS: doi:[10.3030/685445](https://doi.org/10.3030/685445) (<https://cordis.europa.eu/project/id/685445>).
16. NT Build 492 Nordtest method. Concrete, mortar and cement-based repair materials: Chloride migration coefficient from non-steady-state migration experiments, (1999)
17. EN 12390-11. Testing hardened concrete - Part 11: Determination of the chloride resistance of concrete, unidirectional diffusion (2019)
18. T. Luping, J.M. Frederiksen, Ui M. Angst, R. Polder, M.C. Alonso, B.d Elsener, R.D. Hooton, J. Pacheco, *Experiences from RILEM TC 235-CTC in recommending a test method for chloride threshold values in concrete*. RILEM Technical Letters **3**: 25-3 (2018)
19. ASTM C876-15 Standard Test Method for Corrosion Potentials of Uncoated Reinforcing Steel in Concrete, (2022)
20. V. Baroghel-Bouny. *Durability indicators: Relevant tools for performance-based evaluation and multi-level prediction of RC durability*. Proceedings of International RILEM Workshop on Performance Based Evaluation and Indicators for Concrete Durability. p 3-30 (2006)
21. K. Tuuti, *Corrosion of Steel in Concrete*, PhD, Swedish Cement and Concrete Research Institute (CBI). 4-82, Stockholm (1982)