Repair of concrete in environments with chlorides or subjected to freeze-thaw scaling

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Abstract. Crack formation further decreases the durability of structures when chloride ions associated with freezing temperatures are present. Therefore, preventing the entry of aggressiveness is imperative to guarantee the service life. Repair actions might recover the liquid-tightness when cracks occur. A water repellent agent (WRA) and a sodium silicate (SS) solution were applied to self-repair cracks in the current research. The repair occurred by manual injection of cracks to obtain a proof-of-concept for the possible self-healing efficiency. Two extreme conditions have been assessed after the healing period, the first referring to continuous immersion in a chloride solution, and the second applying freeze-thaw conditions with de-icing salts. Chloride ingress was evaluated through the colour change boundary test. In addition, optical microscopy analysis was used to measure the crack width and to observe differences before and after exposure. SS prevented the chloride ingress through the crack in both conditions. However, the method used to verify chloride ingress did not give consistent results for the WRA due to its hydrophobicity. Microscopic analysis showed that both agents could avoid chloride ingress in the cracks. For the samples exposed to freeze-thaw cycles, only chloride ingress measurement could indicate the healing performance as the scaling destroyed the surface.

Keywords: Concrete, Repair, Chlorides, Freeze-thaw, Water repellent agent, Sodium Silicate.

1 Introduction

Seawater or de-icing salts are an aggressive environment for concrete structures. Damage associated with extreme temperatures can increase degradation, since ice formation in the pores creates internal tension generating more cracks. Moreover, the presence of chlorides within reinforced concrete causes corrosion and results in spalling and delamination. The moisture content is an essential factor contributing to chloride penetration and can increases aggressiveness [1]. The transport mechanism switches in saturated conditions. Three different ways of transport can occur, such as sorption, diffusion and penetration. Diffusion occurs in a completely saturated condition, e.g. structures submerged in seawater or covered by a salt solution layer, for instance, pavements covered by ice when de-icing salts contribute to thawing.

Preventing chloride ingress allows to increase the service life of the concrete and reduces the cost of maintenance. Hence, efforts in finding solutions to guarantee the durability of concrete structures exposed to chlorides are widespread in the literature [2][3]. Many alternatives are available, from surface treatments to self-healing technologies. In practice, surface treatments based on hydrophobic features or silica-based compounds are used to block the aggressiveness of the environment. However, cracks generally occur, allowing the ingress of aggressive substances via destroyed surface protection, necessitating new actions.

Self-healing technologies are the solution to guarantee protection when damage occurs. In addition, it can help to ensure repair by quick response, not depending on maintenance activities. Self-healing agents such as hydrophobic or silica-based materials can be introduced in cementitious materials using macrocapsules [4] or microcapsules [5][6]. Nevertheless, most research has focused on analysing these hydrophobic products as surface protection, not as a potential self-healing material [7]. The literature reports several materials to prevent water or chloride ingress, such as water repellents with silane/siloxane/acrylate bases, sodium acetate, sodium silicate, and fluoropolymers. However, their efficiency as a self-healing mechanism for cracked concrete to prevent chloride ingress and water ingress at ambient and freezing temperatures is unknown [4][5][6][8].

Water repellent agent (WRA) has the aim to protect surfaces by hydrophobic impregnation. Three different active components can promote the hydrophobic ability, such as silane-based [2][4][7][9][8][10], silane-siloxane based [4][8], and siloxane-acrylate-based [4][8]. Van Tittelboom et al. [4] have described the advantages of using a water repellent as healing agent applied in macrocapsules is that they remain functional after reloading. Besides, permanent sealing of the cracks avoids ingress of water and aggressive agents [4][8]. However, the WRA cannot block carbon dioxide penetration [4]. Al-Kheetan et al. [2] present that the moisture content during the application has an important role in preventing water and chloride ingress. The water repellent penetrates through the capillary pores. Therefore, impregnation of specimens in dry condition increases the benefits of the product due to higher penetration. Water repellents as a surface treatment also showed higher resistance and less mass loss under freezing conditions [11].

Sodium silicate (SS) has been studied as cargo in a microencapsulation system to promote the self-healing ability in cementitious matrices [6]. The advantage is the suitable interaction with cement-based materials due to its composition based on silica. Furthermore, sodium silicate reacts with calcium hydroxide (CH) in the presence of water to form a calcium silicate hydrate (C-S-H) rich in silica that is the main product of cement hydration [5][6][10]. Sodium silicate reduces the water uptake due to healing the cracks [5][6]. In contrast with WRA, the SS needs water to trigger the reaction. Since the cracks are physically closed, a higher strength is expected, together with a significant potential to block chloride ingress even when considering freezing temperatures.

The significance of this study starts from the lack of knowledge related to the performance of a potential autonomous healing agent. Repairs consume time and are expensive, even more, if they are delayed, and damage increases with time. In this way, self-repair provided by encapsulated materials can promote the recovery in time, decreasing extra costs and improving the performance. An autonomous healing agent can be a great solution as cargo in encapsulation technologies. However, first, the possible products need to be tested under extreme conditions to prove the efficiency before investing time and budget in developing a methodology to encapsulate them.

This research presents the assessment of the efficacy of two protective materials (SS and WRA) that can be used for self-repair. The potential of those materials is investigated by manual injection in cracked concretes and by evaluating the resistance against chloride ingress and freeze-thaw scaling. It aims to assess the performance of a water repellent agent with solvent-based silane and a sodium silicate solution. Their details are in Section 2.3. Two severe exposure classes were assumed following the European standard [1]. The class XS2 corresponds with permanent submersion in a chloride environment. The class XF4 relates to conditions of high water saturation with the presence of de-icing salts under freezing and thawing cycles.

The main objective is to verify the product's performance to prevent chloride ingress considering a suitable self-repair in cracked concretes under those environmental conditions. After their efficiency is proven, further studies evaluating encapsulation systems for concrete exposed to extreme conditions will be conducted.

2 Materials and methods

2.1 Specimens preparation and concrete composition

The geometry of the cast cylindrical specimens was 100 mm in diameter and 50 mm in height. After casting, the specimens were stored in an air-conditioned room (at 20±2°C and at least 95% relative humidity) for 24 hours. Subsequently, samples were demoulded and placed in the same air-conditioned room until the cracks were created at 56 days. Three series of samples were considered: (1) cracked, (2) cracked and repaired with WRA, and (3) cracked and repaired with SS. The samples were subjected to two different environment conditions (described in detail in Section 2.4): three samples were cast for each series for chloride immersion and four samples for freeze-thaw conditions.

For the concrete composition, some thresholds were considered, such as a water/cement ratio (w/c) of 0.45, a minimum strength class C35/45, and minimum cement content of 340 kg/m^3. Those limitations are related to the requirements of the exposure class, XS2 and XF4, in EN 206 [1]. Table 1 gives the concrete composition.

Table 1. Concrete composition.

Materials	Quantity (kg/m^3)
CEM I 52.5 N	341
Limestone filler	182

Sand 0-4 mm	672
Gravel 2-8 mm	766
Water	153
Superplasticizer (Glenium 27 BASF)	8.98

Table 2 shows the fresh and hardened concrete properties. Compressive strength and air voids analysis were done 28 days after casting. The compressive strength was tested on three cubes of 150 mm, according to NBN EN 12390-3. The mean compressive strength was equal to 80.3 MPa. The air void analysis is an automated test for analysing the spacing factor of hardened concrete. Four slices of 100x100x20mm were extracted from two cubes of 100 mm. The study requires polishing the concrete surface and executing a contrast enhancement of the surface, as described in ASTM C 457 [12]. The spacing of the air voids is considered a good indicator for freeze-thaw durability. It is the distance from any point in the paste to the wall of the nearest air void. Pigeon et al. [13] indicated a critical spacing factor for different types of concrete, i.e., if the value is larger than the critical value, the deterioration of the concrete under freeze-thaw will be higher. For a high-performance concrete, the critical spacing factor is 600 µm. A regular concrete with a w/c ratio of 0.5 has a critical value of 500 µm, and a silica fume concrete has 250 µm as critical spacing factor [13]. The measured spacing factor will be compared with the limit of 600 µm considering the compressive strength result in this study. The results presented in Table 2 show that the protection offered by these air voids against the harmful effects of freezing and thawing cycles is probably not sufficient. In this way, extra protection could help to improve this resistance, and the repairs can promote it around the crack wall compared to concrete without any treatment.

Table 2. Concrete features in the fresh and hardened stage.

Concrete features				
Fresh properties	Density (kg/m^3)	2344	(NBN EN 12350-6:2019)	
	Air content (%)	3.2	(NBN EN 12350-7:2019)	
	Slump flow (cm)	53	(NBN EN 12350-8:2019)	
		µ	**σ**	**CoV (%)**
Hardened properties	Compressive strength (MPa)	80.3	0.9	1.1
	Spacing factor	639	57.4	9.0

2.2 Crack creation

The Brazilian splitting test was executed to crack the cylindrical specimens. First, the samples were opened entirely into halves. Next, a silicon sheet with a thickness of 100 µm was placed on the edges of the crack to obtain a specific crack width. Finally, two steel clamps tied the halves together with the silicone sheets in between to guarantee the crack width [14][15].

The crack width of the realistic cracks was measured at maximum six selected zones and at least four along the crack length at the top side of the specimens, i.e., the surface in contact with salt solutions, with five measurements performed in each zone. Crack widths were measured at the same places immediately after crack creation, after curing of the repair agents, and after exposure to the harsh condition. Table 3 describes the data collected for each series immediately after crack creation. The measurements were executed with a stereomicroscope, Leica S8 APO, with DFC 295 camera.

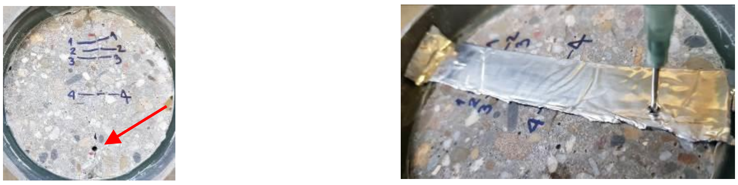
Table 3. Data related to the crack width for each series immediately after crack creation.

	Reference (REF)	Sodium silicate (SS)	Water repellent (WRA)
Minimum (μm)	124	102	105
Maximum (μm)	160	149	170
μ (μm)	143	119	135
σ (μm)	16	14	26
CoV (%)	11%	11%	19%

2.3 Repair products

Two commercial products generally used as a protective surface treatment were employed. First, the products were injected into the crack by means of a syringe. The syringe is placed in a hole with a diameter of 3 mm and a depth of 30 mm made in one side of the sample, indicated by the red arrow in **Fig. 1**a. Next**,** an aluminium butyl tape was applied over the crack to protect the area near the crack mouth (**Fout! Verwijzingsbron niet gevonden.**b). Finally, the product was injected until the release of the agent was noticed on the other side of the crack on the same surface. This procedure guarantees an appropriate and complete distribution of the product inside the crack. The syringe was kept in place for around one minute to assure proper absorption by the matrix. It is important to mention that the specimens already had the sides and bottom sealed by a waterproofing resin beforehand.

Two different procedures were selected considering different saturation and curing time before exposure to the harsh conditions to guarantee an adequate performance of the repair products used. The WRA has better efficacy when applied in dry conditions. Hence, the specimens were maintained in the oven for three days at 40°C to guarantee lower moisture content, increasing the product's penetration in the concrete matrix. For the curing period, no water is required. Thus, after being injected with WRA, the specimens were stored in an air-conditioned room (at 20±2 °C and 60% relative humidity) for two days. Subsequently, they were placed in the exposure conditions. In contrast, sodium silicate performs better in wet environments. In this case, the injection was made in the surface dry condition, i.e., the specimens were stored in an air-conditioned room (at 20±2 °C and 60% relative humidity) for one day before the injection. The curing time was 14 days, and the specimens were placed with the crack facing downwards in contact with water (water level 5 mm above the bottom of the specimens) until they were subjected to the exposure condition.



(a) (b)

Fig. 1. Repair execution: (a) hole made at the edge of the crack indicated by the red arrow, and (b) syringe placed in the hole while the crack is covered by aluminium butyl tape.

Water repellent agent. A commercially available agent named Sikagard®-705L produced by the company Sika was applied. It is a one-component, solvent-free agent with low viscosity (1.9 mPa.s at 25°C) based on silane technology, and a hydrophobic coating is formed by covalent bonds. The density at 20°C is 0.88 g/cm^3, and it has the appearance of a water-like liquid.
Sodium silicate. A commercial product was used, with a density of 1.35 g/cm^3, viscosity of 130 mPa.s at 20°C, and pH between 11 to 11.5. The appearance is a colourless liquid product.

2.4 Exposure conditions

Two chloride environments were considered as exposure conditions. They are described in detail in the following sections. In both environments, there is the penetration of chlorides by diffusion as the samples were maintained saturated during the complete experiment.

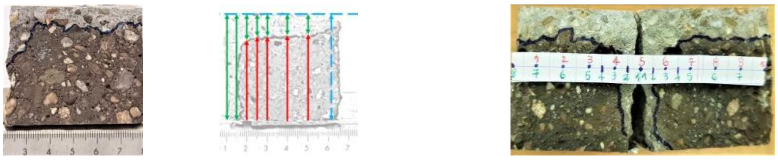
Chloride immersion. The chloride attack was carried out by immersion in a 33 g NaCl /liter solution at 20°C for 30 days. The specimens were waterproofed with an epoxy resin at the bottom, and on the sides, only the top surface had contact with the salt solution. The samples were placed with the top facing upwards. The salt solution was 10 mm above the surface.
Freeze-thaw with de-icing salts. The experiment is based on the standard CEN/TS 12390–9 [16]. The chamber is automatically programmed to perform one cycle per day, changing the temperature from -20°C to 20°C. The specimens were covered by a 3 mm layer of 3% NaCl salt solution. In total, 56 cycles were conducted.

2.5 Method to assess the repair efficiency

Chloride ingress. The chloride penetration was measured perpendicular to the crack after splitting the specimens, after 30 days in chloride immersion and after 56 days in freeze-thaw cycles. Once the surface was dry, a 0.1 mol/L silver nitrate solution was sprayed on the fractured cylinder halves to visualise the chloride ingress. The chloride-contaminated zone appeared lighter. A marker was used to trace the penetration front.

The location of the colour change boundary was measured from the top for chloride immersion condition as the surface remained intact during the exposure (Fig. 2a).

In contrast, the chloride ingress was calculated from the bottom to the top for the specimens subjected to freeze-thaw cycles since each sample's height was reduced due to the surface deterioration by freezing. Fig. 2b illustrates the measurements using different colour arrows with a picture on a greyscale image. The red arrow represents the measurement for freeze-thaw specimens, the blue arrow the height of the specimen, and the green the measurement of the chloride immersion specimens. The first 20 mm from the crack surface measurements were taken each 5 mm, and then each 10 mm (Fig. 2c). The measurements were made using a digital calliper gauge.



(a) (b) (c)

Fig. 2. Chloride ingress in cracked specimens: (a) example of a sample after chloride immersion, (b) example of a sample after exposure to freeze-thaw cycles on a greyscale image with a focus for the arrows that indicate the measurement method, and (c) example of both sides of the sample with the detail of the measurements.

3 Results and discussions

3.1 Chloride ingress

Fig. 3 presents the chloride ingress after 30 days of submersion in the chloride solution for each test series. Three samples were done for each series, resulting in six analysed surfaces for each series. The markers represent the mean value and the error bar the standard deviation. The Y-axis represents the crack wall, i.e., if the chloride ingress reaches 50 mm, it means that chlorides cross the specimens completely. Along the X-axis is the half diameter of the specimen equivalent to 50mm. The sodium silicate was efficient to prevent the chloride ingress through the crack according to the colour boundary difference.

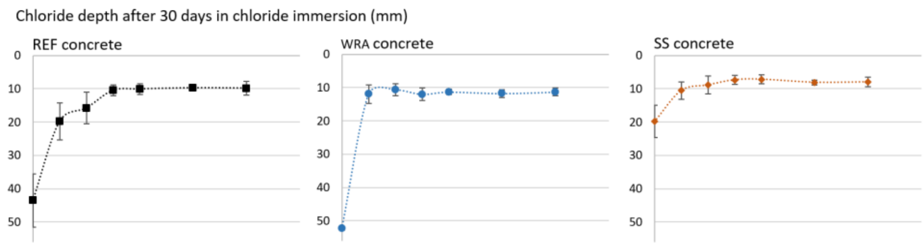


Fig. 3. Chloride ingress after 30 days in chloride immersion (33 g NaCl / l) for each series.

The water repellent agent demonstrated a possible inconsistent result when spraying silver nitrate due to its hydrophobic characteristic. Hydrophobic material increases the contact angle of the surface, repelling any liquid. Therefore, the silver nitrate was repelled in the areas where the water repellent was impregnated. Hence, it did not show a colour difference in those areas preventing a proper verification. In this way, further analysis to measure chloride ingress quantitatively by extracting powder in different layers needs to be performed to confirm the obtained results.

Fig. 4 shows the results obtained for chloride ingress after 56 cycles of freezing and thawing with de-icing salts for each test series. The graphs follow the same parameters as described in Fig. 3. Again, sodium silicate was able to prevent the chloride ingress, even after freezing and thawing cycles. In this way, it can be supposed that the formed healing products are able to survive the freezing temperatures. However, the water repellent agent, like described previously, did not allow the penetration of the silver nitrate due to its hydrophobicity to verify the colour change boundary in the treated area. Hence, it is possible that the presented results do not give a reliable estimation of the chloride penetration. Therefore, additional chemical analysis can be used to prove the efficiency of WRA to prevent chloride ingress.

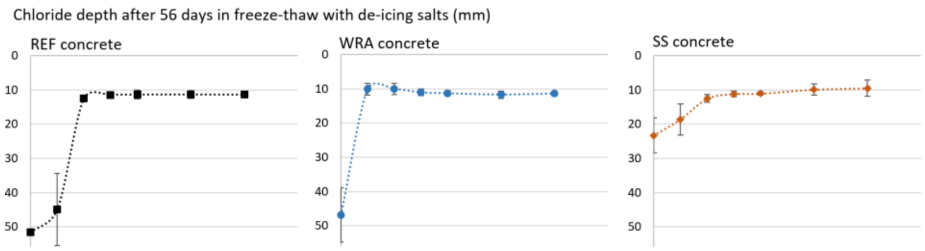


Fig. 4. Chloride ingress after 56 cycles of freezing and thawing with de-icing salts for each series.

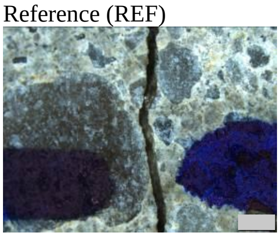
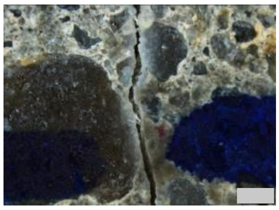
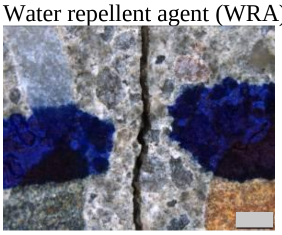
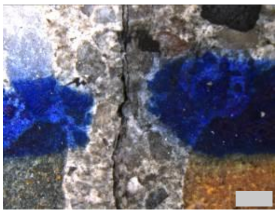
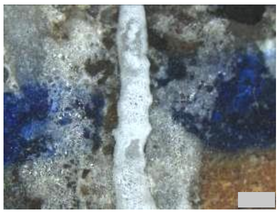
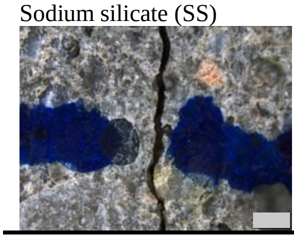
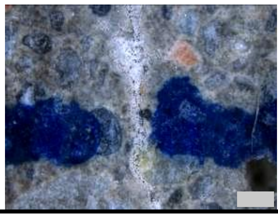
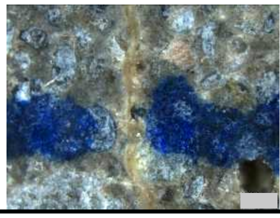
3.2 Crack closure

However, in freeze-thaw cycles, only the chloride ingress method allows evaluating the performance. The scaling destroyed the surface, and microscopic images could not be taken after exposure.

Table 4 shows one example for each series of images collected at the crack creation day, before exposure to chloride immersion, i.e., after injection and curing, and after exposure to chloride immersion for each series. The water repellent agent appears colourless after injection only with a smooth brightness due to its coating ability. However, after chloride immersion, the crack was closed entirely, probably combining autogenous healing products with the water repellent or it could be related to the WRA itself. Further analysis needs to be done to understand better the healing effects formed.

Sodium silicate demonstrates healing capacity after injection and curing. Studies with similar sodium silicate solution used as cargo in microcapsules showed by elemental analysis that the formed products are mainly ettringite and calcium-silicate-hydrate (C-S-H) [6]. After chloride immersion, the healing effects became more visually consistent, also changing the colour. However, in freeze-thaw cycles, only the chloride ingress method allows evaluating the performance. The scaling destroyed the surface, and microscopic images could not be taken after exposure.

Table 4. Microscopic images for concretes subjected to chloride immersion condition, (a) after crack creation, (b) before exposure, and (c) after exposure. The scale bar represents 500 µm.

(a) Crack creation day	(b) Before exposure	(c) After exposure
Reference (REF)		
		
Water repellent agent (WRA)		
		
Sodium silicate (SS)		
		

4 Conclusion

The sodium silicate prevented the chloride ingress through the crack during chloride immersion and freeze-thaw cycles with de-icing salts. Likewise, the healing products formed by sodium silicate could survive the extreme conditions assessed. However, the method used to verify chloride ingress by spraying silver nitrate does not give consistent results for the water repellent agent due to its hydrophobicity. Therefore, further chemical analysis to confirm the chloride content must be done to verify the results obtained and prove the ability of WRA to prevent chloride ingress. In contrast, the microscopic analysis showed that both WRA and SS were able to close the cracks under chloride immersion condition.

Overall, both products used for repair showed good efficiency and reduced chloride ingress compared to the reference concrete. Their ability enables them to be used in encapsulation systems and produce self-healing concrete for application in extreme conditions.

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