SELF-HEALING CONCRETE IN AGGRESSIVE ENVIRONMENTS

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SUMMARY: Although certain crack widths are allowed in reinforced concrete structures, without having immediate effects on the structural stability, they may impair the durability and service life of the structure in the long term. Cracks wider than 10 µm will result, for instance, in a faster penetration of chlorides into the crack and from there onwards into the concrete matrix. Fortunately, the autogenous healing ability of concrete may close cracks of up to 100 µm completely. The further hydration of binder particles, will be supplemented by the deposition of calcium carbonate crystals in case of wet/dry cycles. In case of marine infrastructures in tidal zones, the presence of magnesium sulfates may enhance the crack sealing by means of brucite precipitation. These processes will result in reduced chloride penetration rates. If the cracks are larger than 100 µm or the conditions are not favourable for autogenous healing, autonomous healing mechanisms can be incorporated. In this case, healing is obtained through encapsulated polymeric healing agents, superabsorbent polymers, microbial agents, expansive additives, etc. With encapsulated polyurethane based healing agents, a reduction of the chloride concentration by 75% or more was obtained in a zone with a 300 µm wide crack after chloride diffusion tests, relative to the case in which cracks were not healed. As a result, the service life of reinforced concrete elements in marine environments could be increased with a factor of about 10. Neutron radiography images obtained during a capillary sorption test indicated that release of encapsulated polyurethane in wet conditions was favourable for the polyurethane reaction. As an alternative to the autonomous healing with encapsulated polyurethane, also the incorporation of encapsulated water repellent agents and corrosion inhibitors, has proven to effectively delay reinforcement corrosion during electrochemical measurement campaigns. Accelerated corrosion tests on cracked, manually treated mortar samples, allowed to rapidly screen different agents for their efficiency.

SAMOZACJELJUJUĆI BETON U AGRESIVNIM OKOLIŠIMA

SAŽETAK: Iako je u armiranobetonskim konstrukcijama dopuštena određena širina pukotina koja nema neposredne učinke na konstrukcijsku stabilnost, one mogu dugoročno utjecati na trajnost i uporabni vijek konstrukcije. Pukotine šire od 10 µm prouzročit će, primjerice, brži prodor klorida u pukotinu a onda dalje u betonsku matricu. Na sreću, sposobnost autogenog zacjeljivanja betona može pukotine do 100 µm u cijelosti zatvoriti. Daljnja hidratacija čestica veziva dopunit će se odlaganjem kristala kalcijeva karbonata pri ciklusima mokro/suho. Kod morske infrastrukture u zoni plime prisutnost magnezijeva sulfata može poboljšati brtvljenje pukotina taloženjem brucita. Ti procesi dovest će do smanjenja brzine prodora klorida. Ako su pukotine veće od 100 µm ili uvjeti nisu povoljni za autogeno zacjeljenje moguće je ugraditi mehanizme autonomnog zacjeljenja. Tada do zacjeljenja dolazi s pomoću ugrađenih polimernih tvari za zacjeljenje, superapsorbirajućih polimera, mikrobnih sredstava, ekspanzivnih dodataka itd. S ugrađenim sredstvima za zacjeljenje na osnovi poliuretana dobiveno je smanjenje koncentracije klorida za 75 % ili više u području s pukotinama širim od 300 µm nakon ispitivanja difuzije klorida, u usporedbi sa slučajem u kojem pukotine nisu zacijeljene. Posljedica toga je da se u morskom okolišu uporabni vijek armiranobetonskih elemenata može produljiti s faktorom oko 10. Slike neutronske radiografije dobivene tijekom ispitivanja kapilarnog upijanja pokazuju da je otpuštanje ugrađenog poliuretana u vlažnim uvjetima bilo povoljno za reakciju poliuretana. Druga mogućnost umjesto autonomnog cijeljenja s ugrađenim poliuretanom jest ugradnja vodoodbojnih sredstava i inhibitora korozije koji dokazano učinkovito odlažu koroziju armature tijekom izvođenja elektrokemijskih mjerenja. Ubrzana ispitivanja korozije na raspucalim ručno obrađenim uzorcima morta omogućuju brzo ocjenjivanje učinkovitosti različitih tvari.

1. INTRODUCTION

Cracks in concrete need to be repaired as soon as possible to avoid concrete deterioration and reinforcement corrosion. Maintenance and repair works impose high direct and indirect costs to society and some structures are even not accessible for inspection and repair. In marine structures, crack formation will accelerate the penetration of chlorides, which will induce rebar corrosion. Fortunately, small cracks in concrete have the ability to heal autogenously. For this process, the presence of water is crucial to stimulate hydration of unhydrated binder particles and carbon dioxide presence will enhance calcium carbonate precipitation. However, the influence of the seawater on this healing process is yet uncertain [1].

In addition, to increase the self-healing capacity of concrete elements, different methods have been explored to obtain autonomous crack healing [2]. In this case, healing is obtained through encapsulated agents, superabsorbent polymers, microbial agents, expansive additives, etc. One promising approach is the embedment of brittle capsules filled with polymeric healing agents inside the concrete. Crack formation leads to capsule breakage and release of the polymeric healing agent, which fills up the crack and forms a barrier which prevents fluid ingress through the cracks. An option further explored currently is the use of encapsulated corrosion inhibitors. Generally, corrosion inhibitors are applied by adding them to the fresh concrete mix or by applying them on the hardened concrete to impregnate the matrix from the surface. Adding the inhibitor into the concrete with the mixing water is a user friendly technique, but concrete properties such as setting time or compressive strength may be affected unfavourably. For application on the concrete surface, the penetrability is mostly an issue leading to an insufficient molar concentration ratio between inhibitor and chlorides [3]. The aim of the current study was to combine the advantages of both water repellent agents (WRA) and corrosion inhibitors (CI). The WRA and/or CI are contained inside capsules which are located close to the reinforcement bar, to provide a high concentration of the inhibitor at the location of the steel reinforcement without influencing the properties of the concrete. At the moment of crack formation, the capsules break and release their content in the vicinity of the rebar leading to a reduced corrosion risk for the steel reinforcement [4].

2. MATERIALS AND METHODS

To investigate the influence of marine environments on autogenous crack healing in cementitious materials, ordinary Portland cement mortar samples and blast-furnace slag mortar samples containing 100 µm and 300 µm wide cracks were permanently immersed in chloride solutions as well as in combined chloride and sulphate solutions, as explained more in depth in [1]. Another part of the samples were exposed to wet-dry cycles in the same solutions. Autogenous crack healing was evaluated by means of microscopic measurements over time. The resistance against chloride penetration was measured and evaluated by means of colorimetric measurements and chloride profiles.

Secondly, accelerated chloride diffusion tests on (un)cracked and self-healing concrete with encapsulated polyurethane based healing agents were performed, as explained in [5]. Concrete samples with self-healing properties contained cylindrical borosilicate glass capsules (length: 35 mm, internal diameter: 3.00 ± 0.05 mm, wall thickness: 0.175 ± 0.030 mm) filled with a one component polyurethane based healing agent. Artificial cracks of 300 µm width were created. Chloride profiles were obtained after 49 and 133 days exposure. The self-healing efficiency at multiple depths i below the exposed surface (SHE_i) was defined as the difference between the chloride concentration in cracked concrete and the concentration in healed concrete, divided by the difference in concentration between cracked and uncracked concrete [5].

Furthermore, the effectiveness of an encapsulated low viscosity (150-250 mPas at 25 °C) polyurethane based healing agent has been investigated by means of capillary water absorption tests on mortar while monitoring the time-dependent water ingress with neutron radiography (facility NEUTRA of the Paul Scherrer Institute in Switzerland), as explained in [6]. Standardized cracks were created in prisms with dimensions of 40 × 40 × 160 mm^3 by positioning 300 µm thick metal plates in the molds up to a depth of 20 mm. For the samples without self-healing properties, the metal plates were removed from the mortar at the moment of demolding. For samples with self-healing properties, the metal plates were removed after the curing period of 28 days. For some additional samples, cracks were only created (and triggering of the self-healing process occurred) just before exposure to the water absorption test.

Finally, to test the efficiency of (combinations of) WRA and CI, accelerated corrosion tests were performed on standard mortar prisms (sand:cement:water = 3:1:0.5; 40 x 40 x 160 mm^3). One smooth reinforcement bar with a diameter of 8 mm was placed centrally along the length of the molds (Figure 1). Artificial cracks were introduced by placing brass plates of 300 µm thickness in the mold up to the mid-level of the reinforcement bars. These plates had a width of around 40 mm and had a half sphere drilled out at the bottom with the same radius as the reinforcement bar for positioning onto the rebar (Figure 1.A). Samples were demoulded after 24 hours and the brass plates were removed at the same time. Finally, samples with a targeted thickness of 12 mm were sawn from the prismatic mortar specimens after the trowelled surface was smoothened (Figure 1.B). For the accelerated corrosion test, the edges of the samples were covered 10 mm high on the sides with aluminum butyl tape to ensure that only the cracked surface was exposed to the chloride solution. Furthermore, an electrical connection was made with the reinforcement bar by means of a copper wire. An overview of the different test series with their corresponding code is given in Table 1. The cracks were repaired by injecting the WRA and/or CI, which were not admixed (Table 1), into the crack by means of a syringe with a needle. For every specimen, a volume of 0.43 ml was injected.

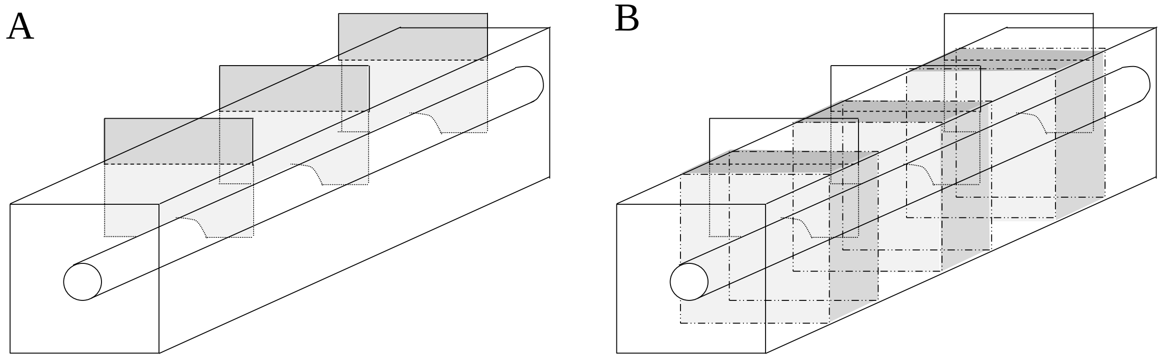

Figure 1. Preparation of the reinforced mortar samples used for the accelerated corrosion test.

Table 1. Test series used for the accelerated corrosion test (mortar)

Code	State	Injected products	Admixed products
UN	Uncracked	-	-
CR	Cracked	-	-
B	Cracked	CI / WRA, silanes (MasterProtect 8000 CI)	-
S	Cracked	CI, amino alcohols (Ferrogard 903 Plus)	-
SF	Cracked	WRA, silanes (Sikagard 705 L)	CI, amino alcohols (Ferrogard 901 S)
N	Cracked	CI, sodium nitrite	-

To evaluate the performance of the different WRA and CI in a short time-span, an accelerated corrosion test was performed. The mortar prisms were positioned inside a plastic box on two line supports with the crack facing downward and a stainless steel mesh in between the supports as shown in Figure 2. The mesh and the bottom of the specimen were submerged into a 165 g/l NaCl solution. The copper wire of the specimen and the stainless steel mesh were respectively connected to the positive and the negative terminal of a power supply. An electric potential of 12 V was imposed between the rebar and the mesh The imposed voltage on the reinforcement steel increased the velocity of chloride ion movement in the sample, hence accelerating the corrosion process together with the higher concentration of NaCl solution. During the test, every 1.5 hours the current was monitored and a visual observation of all specimens was performed.

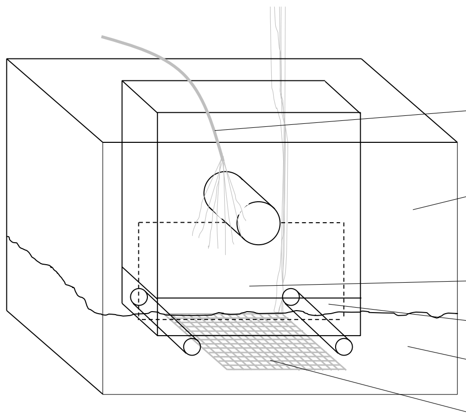

Figure 2. Test setup used for the accelerated corrosion test.

3. RESULTS

As explained more in detail in [1], autogenous crack healing occurs quite fast by means of calcium carbonate precipitation and ongoing hydration when mortar is cyclically exposed to wet/dry conditions. In case of continuous immersion, autogenous crack healing occurs much slower and mainly by means of ongoing hydration. The composition of the environmental solution, with or without chlorides, has no significant influence on the healing mechanism. However, the presence of magnesium sulphate results in the formation of a brucite layer, sealing the cracks (Figure 3). Crack widths lower than 105 µm are able to heal autogenously. Crack widths larger than 105 µm will also heal but not completely. As a result, crack healing in these larger cracks will not much improve the resistance against the penetration of aggressive substance such as chlorides.

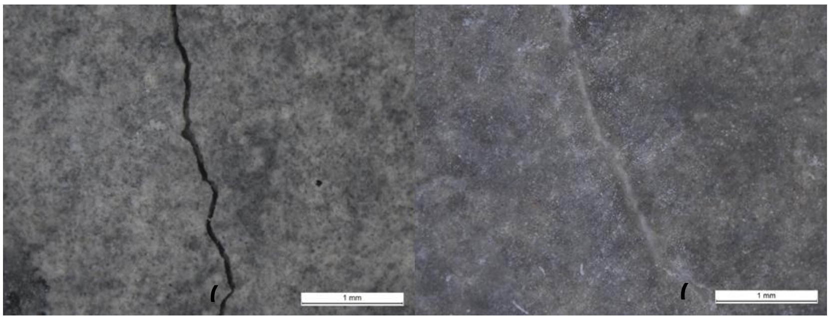

Figure 3: Crack with initial width of ~ 100 µm in OPC mortar before (left) and after (right) 196 days immersion in 165 g/l NaCl + 42.5 g/l $MgSO_4$ [1]

It appears that 10 µm is the critical crack width for chloride penetration, and at lower crack widths the mortar behaves as being uncracked (Figure 4).

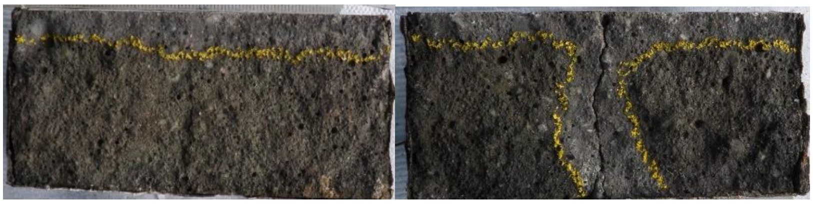

Figure 2: Chloride penetration in autogenously healed mortar with a remaining crack width < 10 µm (left) and > 10 µm (right) [adapted from 1]

In case of autonomous crack healing of artificial cracks (width 300 µm) with encapsulated polyurethane, the experimentally obtained chloride profiles at the two exposure periods of 49 and 133 days were positioned in between the profiles of the uncracked and the cracked specimens, except for the outer layer (0-4 mm) [5]. From a depth of 6 mm onwards, the SHE was always above 75%. It was shown that this reduction of chloride concentration in the zone around the crack will increase the service life of the structural element with a factor of about 10.

In the previous experiments, the healing agents were allowed to harden 24 h before bringing them in contact with water. However, in real structures, contact with water may occur immediately after crack formation. This effect was investigated in [6] by taking neutron radiography images of specimens where exposure to water started immediately after formation of the standardized crack through removal of the thin metal plates which triggered the release of the healing agent. In contrast with the specimens where the polyurethane in cracks had already hardened (Figure 5, left), these specimens (Figure 5, right) show an enhanced healing efficiency. It appears that the immediate contact of the moisture-curing polyurethane with water creates the optimal conditions for its reaction.

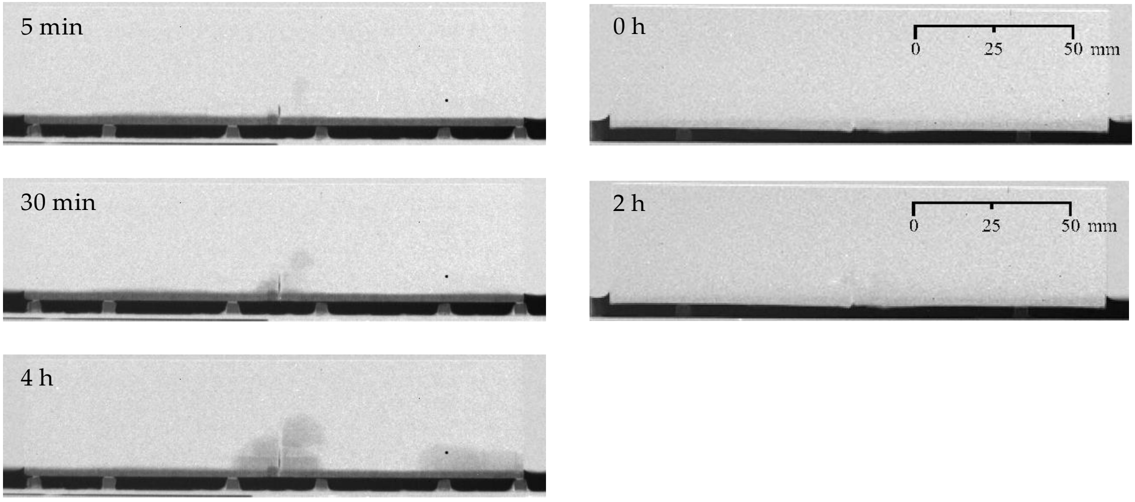

Figure 5. Water uptake in cracked mortar as a function of exposure time using neutron radiography: (left) crack healing before contact with water; (right) immediate contact with water after crack formation (adapted from [6])

Regarding the accelerated corrosion tests on mortars with WRA and/or CI, the current evolution was measured and the status of the rebar and surrounding mortar matrix was observed from the side of the samples. The current was recorded every 1.5 hours for a total of 31.5 hours. The mean current measured for all samples of each test series is plotted in Figure 6. Between 12 hours and 23 hours no current was measured due to the manual recording of these data points. If a current with a value of zero was recorded, it is assumed that no corrosion took place. Higher values indicated a higher probability of the corrosion reaction occurring. Comparing series UN and CR in Figure 6, shows that obviously higher current values were obtained for the latter. The evolution shows the increase to a peak, after which the current decreases again which can be explained by the hindering of transport of chlorides to the reinforcement due to the formed corrosion products which are acting as a barrier and due to the formation of horizontal cracks in the mortar matrix. The small peak noticed for the UN series around 7 hours was caused by one sample starting to show an unexpected behavior (see further), which later on stabilized again. The measured currents for the samples with admixed or injected WRA and/or CI are constrained by the cracked reference samples as an upper boundary, except for the second measuring period where series S resulted in the highest current with a peak around 25 hours. Samples treated with sodium nitrite (series N) showed a steady increase of the current at first after which a small decrease occurred, leading to a stable rate. For the SF series no current was measured during the entire test. Based on this accelerated corrosion test, one can conclude that the combination of Sikagard 705 L and Ferrogard 901 S (series SF) seems very promising to efficiently halt the corrosion initiation.

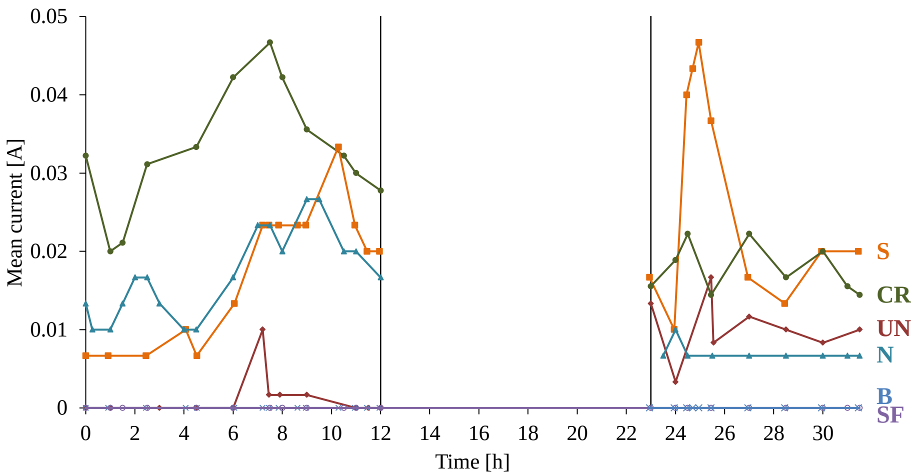

Figure 6. Evolution of the mean current over time for the different test series.

Together with the current recordings, pictures were taken of the specimens every 1.5 hours in order to monitor visual changes on a regular base. Figure 7 shows the different stages of deterioration which were noticed. The first stage corresponded to the point where the moisture front, caused by NaCl ingress through the artificial crack, reached the reinforcement level. The second stage corresponded to the point at which the corrosion process had started, resulting in tensile stress formation and leading to a horizontal crack through the mortar at the reinforcement level. The last stage was represented by the formation of a vertical crack above the reinforcement bar.

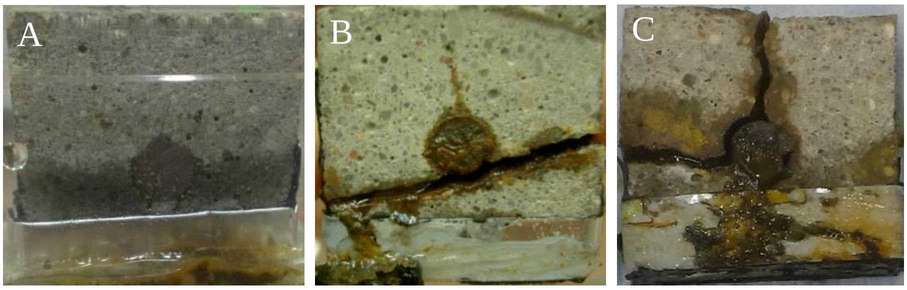

Figure 7. Observed stages within the corrosion process: A. Moist matrix up to the reinforcement level; B. Horizontal crack formation in the mortar matrix; C. Vertical crack formation in the mortar matrix.

In Figure 8 the time at which one of the three above mentioned stages was observed is shown. In agreement with the outcome of the current evolution, samples of the UN, B and SF series performed very well and exhibited none of the three aforementioned stages. After completion of the test, it appeared that for one sample of the UN series a small transverse crack at the bottom surface was present in one of the samples. This was probably present from the start which could explain the higher current measured at 7 hours compared to the other samples of this series. In general, the samples of the CR series showed a faster evolution in deterioration compared to the less performing treated samples. In less than 10 hours of exposure to the accelerated corrosion test all samples of the CR series showed moisture ingress, followed by horizontal and vertical crack formation in the mortar matrix due to formation of expansive corrosion products. Also for the samples of the S and the N series, moisture ingress and horizontal crack formation was noticed. However, it seemed that due to the treatment the damage due to corrosion was less severe compared to the series with untreated cracks (CR) and vertical cracking could be prevented. Moreover, for the series treated with sodium nitrite only two out of the three samples showed some degradation.

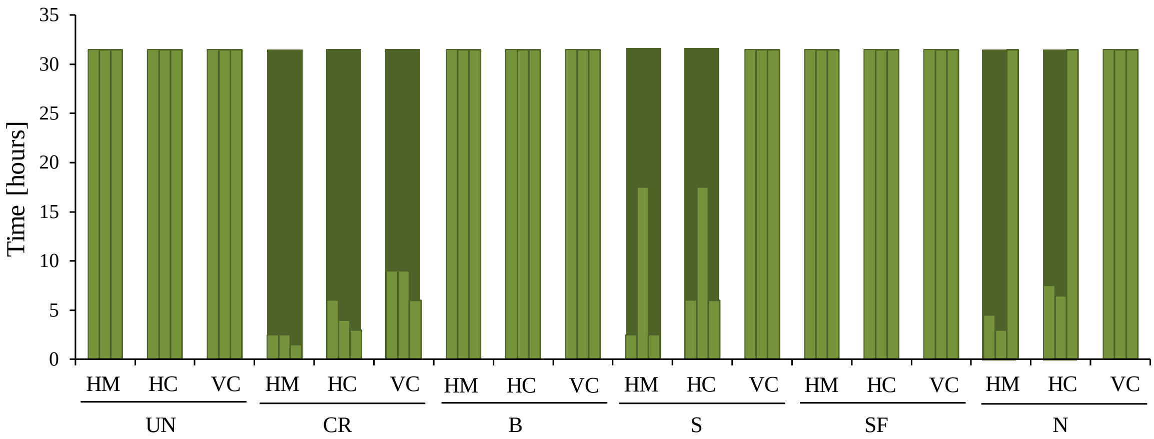

Figure 8. Time of appearance of the different degradation stages for the samples of all test series (light green colour indicates that the degradation stage was not yet noticed; as soon as a certain degradation mechanism was noticed, the colour changes to dark green, HM = horizontal moisture front, HC = horizontal crack and VC = vertical crack).

4. CONCLUSIONS

The autogenous healing property of concrete, a mechanism that includes further binder hydration and calcium carbonate precipitation, may close cracks of up to 100 µm completely. In marine infrastructure, the presence of magnesium sulfates may aid the crack sealing through brucite precipitation. However, as soon as the remaining crack width is above 10 µm, chlorides will penetrate faster through these cracks into the matrix, impairing the service life of reinforced concrete structures. Incorporation of autonomous healing mechanisms can then provide a solution. Self-healing by encapsulated polyurethane based agents, is characterised by a self-healing efficiency above 75% towards chloride diffusion in the presence of 300 µm wide cracks. Neutron radiography images obtained during a capillary sorption test indicated that in-situ healing in wet conditions was favourable for the polyurethane reaction and improved the crack sealing. Finally, also the incorporation of water repellent agents and/or corrosion inhibitors, effectively delayed reinforcement corrosion during accelerated corrosion tests on cracked, manually treated mortar samples.

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