Perpendicular-to-crack chloride ingress in cracked and autonomously healed concrete

Bjorn Van Belleghem[1,2,*], *Philip* Van den Heede[1,2], *Kim* Van Tittelboom[1], and *Nele* De Belie[1]

[1]Magnel Laboratory for Concrete Research, Department of Structural Engineering, Faculty of Engineering and Architecture, Ghent University, Tech Lane Ghent Science Park, Campus A, Technologiepark Zwijnaarde 904, B-9052 Zwijnaarde, Belgium
[2]Strategic Initiative Materials (SIM), Tech Lane Ghent Science Park, Campus A, Technologiepark Zwijnaarde 935, B-9052 Zwijnaarde, Belgium

Abstract. Cracks in reinforced concrete structures exposed to a marine environment or de-icing salts can cause major durability issues due do accelerated ingress of chloride ions. In this study, the influence of autonomous crack healing by means of encapsulated polyurethane on the chloride ingress perpendicular to cracks was evaluated. This was done quantitatively by determining perpendicular-to-crack chloride profiles by means of profile grinding followed by potentiometric titration and qualitatively through visualization of the chloride penetration front by means of the $AgNO_3$ spray method. The resulting chloride profiles showed that the healing mechanism was able to reduce the chloride concentrations in the direct vicinity of the crack to a large extent and to reduce the perpendicular-to-crack chloride penetration, especially further away from the exposed surface. Visualization of the chloride penetration front showed some variation in crack healing. For some healed samples almost no additional chloride ingress was found compared to uncracked samples, others showed a slightly enhanced ingress at the crack location but less perpendicular-to-crack chloride penetration compared to untreated cracked samples. Generally, the reduced amount of chlorides present in the concrete matrix due to crack healing will enhance the durability and service life of concrete structures.

1 Introduction

Crack appearance is one of the leading causes of durability problems in reinforced concrete structures. Especially for structures which are exposed to a marine environment or de-icing salts, the presence of cracks provides accelerated pathways for chlorides to enter the concrete matrix [1-4]. This then leads to an accelerated onset of reinforcement corrosion and further deterioration [5-7].

In order to prevent rapid ingress of chlorides and deterioration of structures, actions need to be taken to repair cracks as soon as possible. However, manual crack repair (e.g. by crack injection) is expensive and in some cases even impossible due to inaccessibility. Moreover, cracks are not always detected in an early stage, so manual crack repair is sometimes done when some chloride ions already entered the concrete matrix. Consequently, even after crack injection chlorides may still be present in the concrete matrix and cause initiation or further propagation of reinforcement corrosion. The ideal way of dealing with the unavoidable appearance of cracks in concrete would be to modify the concrete to give it the ability of restoring cracks by itself. This idea of creating a so called self-healing concrete grew during the last two decades. One promising approach is the embedment of brittle capsules which are filled with a healing agent in the concrete matrix [8-10]. At the moment of crack appearance, one or more of the capsules break, causing a release of the healing agent in the crack.

Previous studies have shown that this type of autonomous healing mechanism is successful in reducing the ingress of water [8, 9, 12] and chloride ions [13-16] through cracks. However, the previously mentioned studies mainly focused on the chloride ingress in the direct vicinity of the crack. Yet, chlorides also penetrate the concrete matrix perpendicular to the crack walls. Therefore, the perpendicular-to-crack chloride ingress in cracked and autonomously healed concrete is investigated in this study.

2 Materials and methods

2.1 Concrete specimens

2.1.1 Concrete mixture

A fly-ash concrete mixture containing a fly ash suitable for use in marine environments was used in this research [15]. The mix proportions are given in Table 1, the

* Corresponding author: Bjorn.VanBelleghem@UGent.be

properties of the concrete mix can be found in Table 2. Cylindrical concrete specimens with a height of 50 mm and a diameter of 100 mm were cast.

Table 1. Concrete mix proportions

Sand 0/4 (kg/m³)	696
Aggregates 2/8 (kg/m³)	502
Aggregates 8/16 (kg/m³)	654
CEM I 52.5 N (kg/m³)	317.6
Fly Ash (kg/m³)	56
Water (kg/m³)	153
Superplasticizer (ml/kg binder)	3.0

Table 2. Properties of the concrete mix

Water to binder ratio (-)	0.41
Fly ash to binder ratio (-)	0.15
Slump class	S3
Strength class	C40/50

2.1.2 Crack formation

Cracks were created in the concrete specimens in an artificial way by introducing thin plates in the fresh concrete and removing the plates after the 28 day curing period [3, 11, 12, 15, 16]. In this way, standardized cracks with a length of 60 mm, a depth of 25 mm and a width of 0.3 mm were created.

2.1.3 Autonomous healing mechanism

To achieve autonomous self-repair of cracks, cylindrical capsules filled with a healing agent were embedded in the concrete matrix. The capsules, made from borosilicate glass, had an internal diameter of 3 mm, a wall thickness of 0.175 mm and a length of 35 mm. They were put through holes in the thin plates used for crack creation, cf. Van Belleghem et al. [11]. Removal of the thin plates in these self-healing specimens after the 28 day curing period resulted in breakage of the capsules followed by release of the healing agent in the crack. Further details and figures of the experimental setup of specimens with the autonomous healing properties can be found in [15].

Two types of polyurethane (PU) precursors were used as healing agents. The first PU precursor (denoted as PU_HV) is a non-commercial product with a relatively high viscosity (6700 mPas at 25°C). The second product (denoted as PU_LV) is a commercially available PU precursor with a relatively low viscosity (200 mPas at 20°C). Further details about the PU precursors can be found in [12].

2.1.4 Sample overview

Three concrete samples of each of the following series were made: uncracked samples (UNCR), samples with an untreated artificial crack (CR), samples containing an artificial crack autonomously healed by the high viscosity polyurethane (PU_HV) and samples containing an artificial crack autonomously healed by the low viscosity polyurethane (PU_LV).

2.2 Chloride exposure

The test surface of the samples was mechanically flattened by sawing off a layer with a thickness of approximately 1 mm. Thereafter, all sides of the samples except the test surface were coated with an epoxy coating and the samples were placed in a 165 g/l NaCl solution. The samples were taken out of the exposure solution after 605 days of immersion.

2.3 Evaluation methods of the perpendicular-to-crack chloride ingress

Samples from the series CR, PU_HV and PU_LV were split in half along the direction of the crack. The UNCR samples were cut in half by dry sawing.

2.3.1 Grinding and potentiometric titration

The first half of the samples was used to determine perpendicular-to-crack chloride profiles by means of grinding. Powders were ground from the crack surface at three distinct areas of 38 x 8 mm (see Fig. 1): area A (0-8 mm below the exposed surface), area B (8-16 mm below the exposed surface) and area C (16-24 mm below the exposed surface). In every area, layers with a thickness of 2 mm were ground away until a distance of 20 mm from the crack surface (or cut surface in case of the UNCR samples).

Perpendicular-to-crack chloride profiles representing the total chloride content were determined by means of an acid-soluble extraction of all obtained powders in nitric acid solution followed by potentiometric titration against silver nitrate [17].

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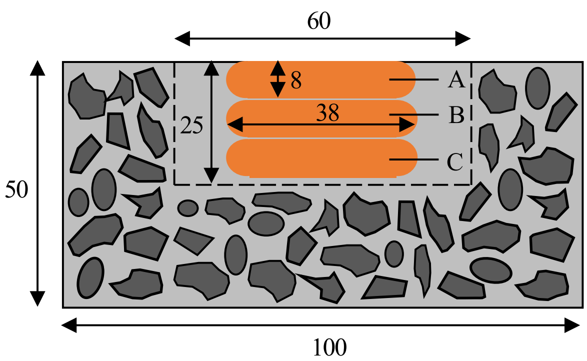

Fig. 1. Schematic view of one sample half with indication of the areas (A, B and C) on the crack surface ground for determination of perpendicular-to-crack chloride profiles.

3 Results and discussion

3.1 Perpendicular-to-crack chloride profiles

Fig. 2 shows the perpendicular-to-crack chloride profiles of the different series in the three investigated areas (A, B and C). The chloride profiles for the UNCR samples are in all three areas more or less constant and independent from the distance to the cut surface. This is logical, since there was only chloride ingress from the exposed surface which was free of cracks.

Fig. 2a shows that in the area closest to the exposed surface of the samples (area A) the influence of the presence of a crack can only be seen relatively close to the crack surface (0-6 mm away from the crack surface). It is logical that in this area the influence of a crack is rather limited, since there is a lot of influence of chloride ingress from the exposed surface. When the crack is healed by polyurethane, only in the first layer (0-2 mm distance from the crack surface) an elevated chloride concentration can be noticed compared to the UNCR series. However, this elevated chloride concentration is less than for the CR samples.

In area B (Fig. 2b) the influence of a crack in the concrete matrix is more clear: at the crack surface of the CR samples the chloride concentration is more than three times higher than for the UNCR samples. Furthermore, an elevated chloride concentration is noticed until a distance of 14 mm away from the crack. Healing of the crack with both PU’s is very similar in this area. The chloride concentration at the surface of the crack is reduced nearly by half and compared to the UNCR series, there is an elevated chloride concentration only until a distance of 4 mm from the crack surface. The perpendicular-to-crack chloride ingress in the CR specimens is most clear however in area C (Fig. 2c). First of all, the chloride concentration at the crack surface remains very high in this area (about 7 m%/binder) while the mean chloride concentration in the UNCR samples is only about 0.35 m%/binder. The chloride content is thus 19 times higher at the crack location. However, it should be mentioned that the very high values of the chloride concentrations near the crack surface might be caused by the fact that artificial cracks were used in this study. Consequently, the crack surface is a cast surface and has a higher paste content.

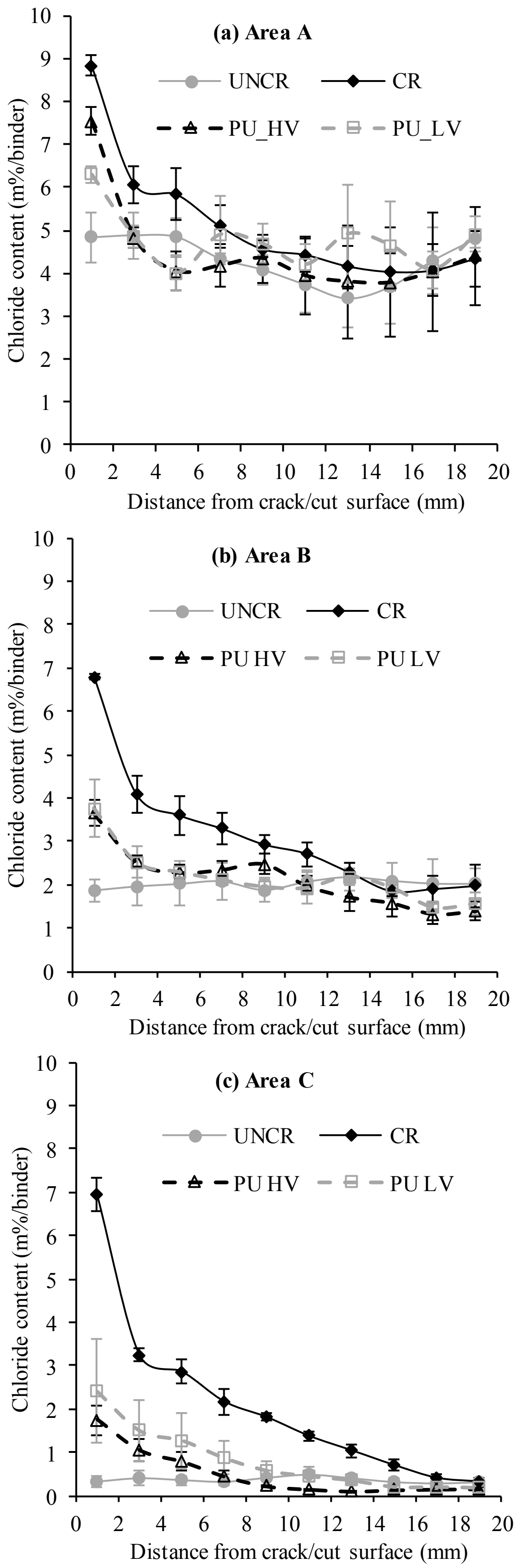

Fig. 2. Perpendicular-to-crack chloride profiles in uncracked, cracked and healed samples for areas (a) A, (b) B and (c) C. Error bars represent the standard error on the mean values.

Nevertheless, elevated chloride concentrations in the CR samples were noticed until a distance of 18 mm from the crack surface. Also, the chloride concentration in this area decreases nearly linearly with the distance from the crack.

Healing of the crack reduced the chloride penetration perpendicular to the crack significantly in area C. For the PU_HV series, the chloride concentration at the crack surface was four times lower compared to the CR series. At a distance of 6 mm from the crack surface, the chloride concentrations were already comparable to the concentrations found in the UNCR samples. Crack healing with PU_LV showed slightly worse results compared to crack healing with PU_HV. Also, more variation was noticed between the three investigated specimens (noticeable by the larger standard errors on the mean values in Fig. 2c). Nevertheless, from a distance of 10 mm from the crack surface onwards the chloride concentrations were comparable to the concentrations found in the UNCR samples and for every distance the chloride concentrations were lower compared to the CR samples.

3.2 Chloride penetration front

The chloride penetration front of one sample of each series is shown in Fig. 3. The crack surface (or cut surface for the UNCR sample) is always shown at the right side of the photos in Fig. 3.

The UNCR samples generally showed a uniform penetration front from the exposed surface (see Fig. 3a) with a mean penetration depth of 18.8 ± 2.3 mm.

For the samples of the CR series, an increase in chloride penetration near the location of the crack was found. This can be seen in Fig. 3b by the deeper location of the chloride penetration front near the crack (right side of the photo). The mean penetration depth from the exposed surface at the location of the crack for the CR samples was 37.5 ± 1.3 mm. Since the crack depth was 25 mm, this means that there is a clear penetration of chlorides beyond the crack tip (indicated by the vertical arrow in Fig. 3b). Also, the penetration of chlorides perpendicular to the crack surface is visible in Fig. 3b (indicated by horizontal arrows).

Crack healing with PU_HV generally resulted in a relatively 'good' healing behaviour. Two out of three specimens showed nearly no increase in chloride penetration near the crack location (Fig. 3c). One specimen did show a chloride penetration beyond the crack tip, but the penetration perpendicular to the crack was much less compared to the CR samples.

Samples where cracks were healed with PU_LV showed more variation in healing behaviour. One of the samples was healed well and showed almost no additional chloride penetration compared to UNCR samples (Fig. 3d). A second sample showed a slight increase in chloride penetration at the crack location, but less than what was found for the CR samples. The chloride penetration front in the third sample however was more similar to the front found in the CR samples. As mentioned before, this variation in healing behaviour was also noticeable in the results of the perpendicular-to-crack chloride profiles (Fig. 2c).

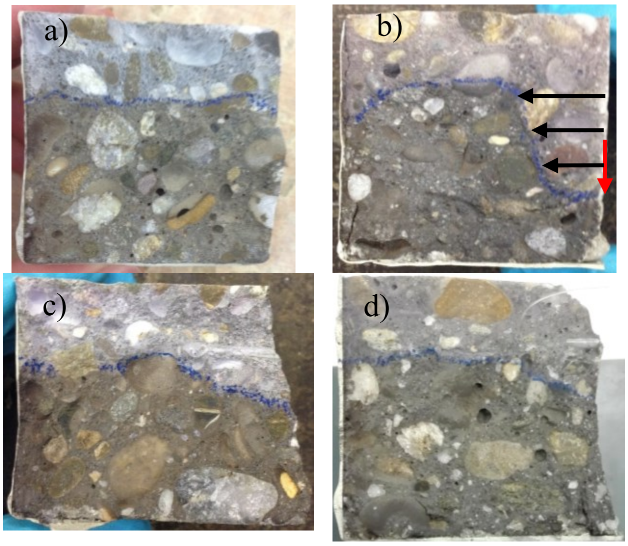

Fig. 3. Example of the chloride penetration front for one sample of the series a) UNCR, b) CR, c) PU_HV and d) PU_LV.

4 Conclusions

Perpendicular-to-crack chloride profiles taken from concrete samples containing an artificial crack showed a very high chloride concentration at the crack surface along the whole crack depth. Furthermore, clear penetration perpendicular to the crack walls was noticed. An increase in chloride concentration due to the presence of a crack was found up to a distance of 18 mm away from the crack. This shows that not only at the crack location there is a possible risk for onset of reinforcement corrosion and further concrete deterioration, also at a certain distance away from the crack elevated chloride concentrations can have a negative effect on the durability of a concrete element. By visualization of the chloride penetration front, a significant chloride penetration beyond the crack tip and perpendicular to the crack surface was noticed for all cracked samples.

Concrete samples where the crack was autonomously healed by encapsulated polyurethane showed an improved behaviour regarding the chloride ingress. The hardened polyurethane inside the crack formed a (partial) barrier against immediate chloride ingress through cracks. Especially at larger depths below the exposed surface, crack healing was able to cause a significant decrease of the chloride concentration in the close vicinity of the crack as well as further away from the crack. Visualization of the chloride penetration front showed that two out of three samples where the crack was healed by PU_HV were able to almost completely prevent additional chloride ingress at the location of the crack. The remaining sample did show a slight increase in the chloride front near the crack, but still showed an improved behaviour compared to the CR samples. Crack healing with PU_LV resulted in more variation in healing behaviour. While one of the samples nearly showed no improvement, another sample was nearly perfectly healed, successfully blocking the chloride ingress at the crack location.

Visualization of the chloride penetration front by $AgNO_3$ spray is a fast and easy method to provide a first indication of the potential of a healing agent to reduce ingress of chlorides in cracked concrete. Potentially interesting healing agents can be selected based on the results of this method and subsequently a more detailed analysis can be made by means of chloride profiling.

Generally, autonomous crack healing by encapsulated polyurethane can reduce the chloride concentration in the direct vicinity of the crack and cause a reduction of the chloride penetration perpendicular to the crack. This will have important benefits for the durability of reinforced concrete structures in chloride-containing environments.

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