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The efficiency of self-healing cementitious materials by means of encapsulated polyurethane in chloride containing environments



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Mathias Maes, Kim Van Tittelboom, Nele De Belie*

Magnel Laboratory for Concrete Research, Faculty of Engineering and Architecture, Department of Structural Engineering, Ghent University, Technologiepark – Zwijnaarde 904, B-9052 Ghent, Belgium

HIGHLIGHTS

• Manual and autonomous methods are used to heal cracks between 100 µm and 300 µm.

- Autonomous crack healing is obtained by means of PU encapsulated in glass tubes.
- Colour change boundaries, chloride profiles and diffusion coefficients are measured.
- Autonomous crack healing has the potential to improve durability of concrete.
- The reliability of the self-healing system needs further improvement.

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ABSTRACT

Cracks in cementitious materials have a negative influence on the durability in aggressive environments, especially in marine environments since chlorides will be able to penetrate faster. Since constructions in marine environments mostly have an important social function with a high economic impact, fast repair of the cracks is desirable. However, repair costs are large and in some cases repair is impossible due to inaccessibility. A possible solution is self-healing by means of encapsulated polyurethane which has the ability to induce recovery without external intervention. From the test results it seems that chloride penetration increases when the crack width increases. Furthermore, chloride penetration at the crack tip, for crack widths between 100 µm and 300 µm, is higher than from the surface. Preliminary tests by using manual crack healing show that polyurethane is able to seal the cracks and prevent chlorides to penetrate along the crack path in 83% of the cases for initial crack widths of 100 µm and in 67% of the cases for initial crack widths of 300 µm. Based on these findings, tests were performed with autonomous crack healing by means of encapsulated polyurethane. Autonomous healing is able to seal crack widths of 100 µm and 300 µm for chloride penetration in 67% and 33% of the cases, respectively. So, autonomous crack healing by means of encapsulated polyurethane has the potential to improve durability of cementitious materials and increase the service life of constructions in chloride containing environments. Nevertheless, the reliability of the self-healing system needs further improvement.

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1. Introduction

Because of the high chloride concentration in sea water, a lot of damage is reported for constructions in marine environments. A commonly used material for such structures is reinforced concrete. However, chlorides affect the durability of reinforced concrete by initiating corrosion of the reinforcing steel. Besides, when cracks appear in the concrete structures, chlorides will penetrate faster. Since constructions in marine environments mostly have an important social function with a high economic impact, fast repair of the cracks is desirable. However, repair costs are large and in some cases repair is impossible due to inaccessibility. A possible solution is self-healing of cracks in concrete. Self-healing concrete has the ability to recover without external intervention.

Regardless the cracking method applied, a lot of other parameters influence the chloride penetration in cracked concrete. The most important parameters are the crack width and the crack depth. Apart from that, also the concrete mix composition, the aggressiveness of the environment, etc. play an important role.

Conform to the standard NBN EN 1992-1-1 [1], the allowable crack width in reinforced concrete structures depends on the

^{*} Corresponding author. Tel.: +32 9 264 55 22; fax: +32 9 264 58 45. *E-mail address*: Nele.DeBelie@UGent.be (N. De Belie).

environmental class and is in the range of $300-400 \ \mu\text{m}$. However, Win et al. [2] found that the chloride penetration depth at the crack tip (see Fig. 1) of a 100 μm wide crack was already slightly higher than the chloride penetration from the surface. Furthermore, according to Ismail et al. [3] crack widths of 200 μm and wider allow unlimited chloride diffusion perpendicular to the crack wall. Van den Heede et al. [4] suggest to limit the crack width below 50 μm in order to avoid chloride penetration. So, it seems that in marine environments, the crack widths should be limited more in order to maintain or increase the durability of the structures.

The influence of the crack width on chloride penetration has been mainly studied by means of chloride diffusion (by means of immersion) and chloride migration (migration cell or rapid chloride migration). Afterwards chloride penetration depths were measured by means of the colorimetric method (by spraying AgNO₃) onto a split specimen) and chloride diffusion or chloride migration coefficients were calculated. However, these parameters are misused sometimes. A lot of papers mention the chloride diffusion coefficient while the chloride migration coefficient is calculated. In the following part, the description of the coefficient is done based on the used test method instead, however a different name could have been used in the original paper. Djerbi et al. [5] found a bilinear relation between the chloride migration coefficient, obtained by migration cell tests, and the crack width. Cracks were created by means of a controlled splitting test which means that the cracks were through going. For crack widths between 0 µm and 100 μ m, the migration coefficient increased with increasing crack width, and for crack widths between 100 μ m and 200 μ m this increase was less clear and the migration was rather constant. Similarly, Audenaert et al. [6] found a bilinear relationship between the chloride penetration depth measured after rapid chloride migration tests and the crack width for cracks induced non-destructively. Ye et al. [7] investigated chloride profiles after chloride diffusion tests for specimens with realistic crack widths ranging from 50 µm to 200 µm, obtained by 3-point bending tests, from which it was clear that the chloride concentrations increase at certain depths from the exposed surface, when the crack width increases. Comparable to this. Kwon et al. [8] found for on-site drilled cores that chloride diffusion coefficients kept increasing with crack widths from 100 µm to 300 µm. In accordance, Jang et al. [9] found a linear relationship between crack widths up to 206 µm and chloride migration coefficients, by performing migration cell tests. They used realistic through-going cracks obtained by a splitting test. In addition, they also found that the chloride migration coefficient, does not increase with increasing crack widths up to the critical crack width, namely approximately 55 µm. Yoon et al. [10] define the critical crack width as a threshold crack width above which chloride penetration from the surface is faster than in sound concrete. Yoon et al. [10] themselves concluded, based on rapid chloride migration tests, that the critical crack width is about 12 µm. In their experiments, they created realistic not through



Cl⁻ penetration (a) At the crack tip

- (b) Perpendicular to the crack
- (c) From the surface

Fig. 1. Chloride penetration around a crack.

going cracks by applying tensile stresses on metals plates attached at the surface of the specimen. According to the chloride diffusion profiles obtained by Ismail et al. [3], the critical crack width is maintained at 30 μ m. Ismail et al. [3] created cracks using the expansive core method. Next, Sahmaran [11] found that the effect of realistic crack widths below 135 μ m on the chloride diffusion coefficient is marginal, however, this is not a critical crack width. Furthermore, he concluded that when the crack width increases, the diffusion coefficient increases as well, and this effect was more pronounced when the crack width was larger than 135 μ m.

From the literature it seems that quite some research has been done on chloride penetration in cracked concrete. However, somehow the conclusions are contradictory. Nevertheless, it is clear that cracks promote the chloride ingress and thus impair the durability of cementitious materials. Notwithstanding, very little research has been done on the efficiency of self-healing concrete in chloride containing environments. From the literature concerning self-healing cementitious materials, it is clear that research on self-healing of cracks focuses on the general concept, the regain in mechanical properties and in water permeability after crack healing. Based on the water permeability it is concluded whether harmful substances will still penetrate after healing or not [12].

In general, self-healing in cementitious materials is classified in two main groups: intrinsic healing and capsule based healing [12]. The first group, intrinsic self-healing materials, exhibits self-healing properties due to the composition of the cementitious matrix. To achieve this so-called autogenous healing the presence of water is crucial to obtain calcium carbonate precipitation and hydration of unhydrated cement particles. According to Jacobsen et al. [13], after three months storage in water, autogenous healing of cracks in OPC concrete leads to a reduction in the rate of chloride migration. The reduction amounts to 28-35% compared to migration in freshly cracked specimens. This effect is in accordance with the findings of Sahmaran [11], who observed a significant amount of autogenous crack healing, with initial crack widths less than 50 um, resulting in a reduced chloride diffusion coefficient and a slower chloride penetration rate. Although, autogenous crack healing seems to have a beneficial influence on chloride penetration it is a rather slow mechanism which is only suitable for small cracks in humid environments. Therefore, current research focusses on autonomous healing based on introduced capsules, with polymeric or biogenic healing agents, to obtain fast crack repair. In the case of possible chloride ingress fast healing is required and autonomous crack healing seems more appropriate, since the healing mechanism is triggered by the crack formation and cracks are filled up almost immediately. Capsule based healing sequesters a healing agent inside discrete capsules. When a crack appears, the capsules break and the healing agent is released in the region of damage. Since Van Tittelboom et al. [14] concluded that polyurethane is a very appropriate healing agent to obtain self-healing properties in cementitious materials, glass tubes with encapsulated polyurethane were used as healing mechanism in this research. However, spherical capsules offer more opportunities to be used in practice because they are easier to mix them in. Nevertheless, compared to spherical capsules, cylindrical tubes have a high probability of crack going through because of the higher surface to volume ratio and because of the fact that the ends are somewhat anchored within the matrix. For spherical capsules the bond strength between capsules and the matrix needs to be stronger than the strength of the capsule to avoid the crack going around [15,16]. In addition, Mookhoek [17] showed that cylindrical tubes can provide enough volume of healing agent to heal the crack, while spherical capsules are rapidly exhausted. In order to evaluate efficiency of the autonomous crack healing in this research, damage is concentrated in the zones where the self-healing mechanisms in incorporated. Up to now only a limited amount of examples is Download English Version:

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