

THE EFFICIENCY OF AUTONOMOUS CRACK HEALING OF MORTAR IN CHLORIDE SOLUTIONS.

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Abstract

A lot of damage is reported for constructions in marine environments. Marine environments are very aggressive, since sea water consists mainly of chlorides. When cracks appear in the concrete structures, chlorides will penetrate faster and initiate corrosion and deterioration faster as well. A possible solution is autonomous crack healing by means of encapsulated polyurethane (PU).

Chloride resistance of autonomously PU-healed mortar was tested and compared to cracked and uncracked mortar. To do so, realistic crack widths of 100 and 300 μm were formed by means of a controlled splitting test. To obtain autonomous crack healing, glass tubes filled with a prepolymer on the one hand and an accelerator on the other hand were placed in the specimens at middle height. Upon crack formation, the tubes break and the healing agent is released. Then, the specimens were immersed for 7 weeks in a 165 g/l NaCl solution. After the immersion period, colour change boundaries as well as chloride profiles at different distances from the (healed) crack were obtained.

Based on the results, it seems that autonomous crack healing by means of PU has a beneficial influence on chloride resistance. Nevertheless, there is room for further improvement.

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 concrete by initiating corrosion of the reinforcement steel. In addition, when cracks appear in the concrete structures, chlorides will penetrate faster. So, it is important to repair these cracks and since constructions in marine environments mostly have an high economic impact, fast repair is desirable. However, repair costs are large and in some cases repair is impossible due to inaccessibility. A possible solution is self-healing concrete. Self-healing concrete has the

ability to recover without external intervention. From the literature concerning self-healing concrete/mortar, it is clear that research focuses on the general concept, the mechanical properties and water permeability. Based on the water permeability it is concluded whether harmful substances will penetrate. Specific data on degradation of self-healing concrete/mortar in aggressive environments are not available.

In former research of the authors [1] the efficiency of manually healed concrete concerning the resistance against chloride penetration was tested by means of rapid chloride migration tests. A notch method, based on the method of Audenaert et al. [2] was established to produce artificial cracks in the concrete by means of thin steel plates introduced into the fresh specimen and removed after 10 hours. When the specimens were hardened, the cracks were manually injected with polyurethane. After the migration tests chloride penetration was visualised by spraying AgNO_3 on split specimens. For cracked concrete, the chloride penetration at the crack tip increased in function of the crack width when the crack width was in the range of 0 mm (= penetration from the surface) to 300 μm . Manual healing by means of polyurethane injection increased the chloride penetration resistance. For healed concrete with a crack width of 100 μm , 83 % of the samples regained almost full resistance against chloride penetration. In the case that cracks had a width of 300 μm , 67 % of the samples regained almost full resistance. Based on these results, the authors decided to test autonomously healed mortar by means of realistic cracks, as described in this paper.

2 MATERIALS AND METHODS

2.1 Glass capsules filled with PU-healing agent

In order to carry the healing agent in the mortar specimen tubular glass capsules were used similar to the capsules used by Van Tittelboom et al. [3]. Due to a high brittleness, the tubes will easily break whenever cracks appear in the mortar matrix. Borosilicate glass tubes with an internal diameter of 3 mm and an outside diameter of 3.35 mm were used. The tubes had a length of 50 mm.

MEYCO MP 355 1K (BASF The Chemical Company) was used as healing agent. This is a commercial one-component healing agent which is applied as a two-component agent to accelerate the reaction. The main compound consists of a prepolymer of polyurethane (PU) with a viscosity of 320 mPas at 20 °C which starts foaming in moist surroundings and forms a closed cell structure. The second compound is an accelerator diluted with water. The expanding reaction of this healing agent, with a reaction time of 10-50 seconds, may lead to an increase in volume of 25-30 times.

Half of the tubes was filled with the prepolymer and the other half was filled with a mixture of accelerator and water. First, the tubes were sealed with polymethylmethacrylate at one end, then, the tubes were filled with the components of the healing agent, which were injected by means of a syringe with a needle. When all tubes were filled, the other ends were sealed and the tubes were ready to be embedded inside the mortar samples.

2.2 Mortar with(out) self-healing properties

To determine the efficiency of self-healing mortar in chloride containing environments, an Ordinary Portland Cement mortar (OPC) was prepared. The composition is based on the mix described in EN 196-1 (2005), with a water to cement ratio of 0.5 and a sand to cement ratio of 3. Cylindrical specimens with a height of 50 mm and a diameter of 100 mm were used.

First, a 20 mm mortar layer was brought into the moulds. When this layer was compacted by means of vibration, three couples of glass tubes were placed on top of it. Afterwards, the moulds were completely filled and vibrated again. The non-self-healing samples were prepared in the same way, however, samples belonging to these series contained no glass tubes.

After casting, the specimens were placed in an air-conditioned room with a temperature of 20 °C and a relative humidity higher than 95 %. Demoulding took place the next day whereupon the specimens were stored again under the same conditions until the age of 21 days. Then, the specimens were coated with epoxy at the side, this way the coating acts as reinforcement during the crack formation.

2.3 Crack formation - Splitting test

In the cylindrical mortar specimens, cracks were created at 24 days of age by means of a crack width controlled splitting test. The crack width was measured at both sides of the specimen with a LVDT (Fig. 1) and the mean value was used to control the splitting test. The crack width was increased with a velocity of 0.5 µm/s until a crack width of either 180 µm or 500 µm was reached. Then, specimens were unloaded giving rise to a final crack width of approximately 100 µm and 300 µm, respectively.

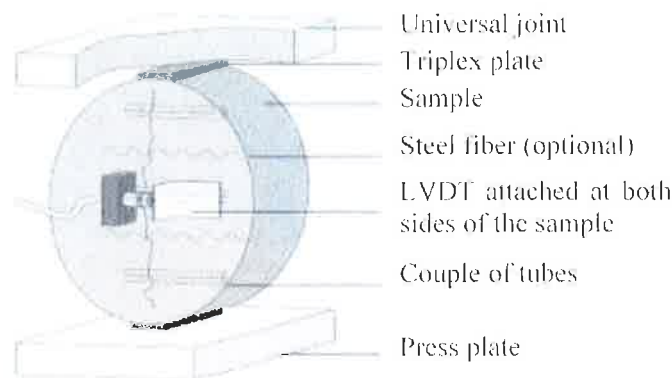


Figure 1: Splitting test to create cracks (Based on [3]).

2.4 Crack healing

Cracks in the specimens containing encapsulated healing agent were autonomously healed, as can be seen in Fig. 2.

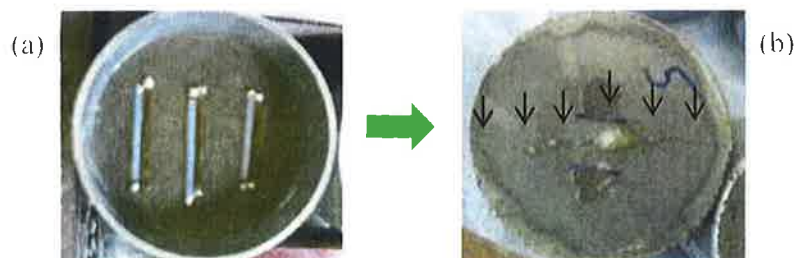


Figure 2: Self-healing mechanism by means of encapsulated PU.
(a) Placing of the glass tube couples, (b) Cracking and healing.

The embedded tubes broke during crack formation and both components of the healing agent were released. Due to capillary forces in the crack and the expanding reaction of the healing agent (cf. part 2.1), a closed cell structure is formed that fills up the crack. Cracks can be sealed completely and become air- and watertight. So, not only the low viscosity and the capillary forces in the crack but also the expansive reaction acts as the driving force for the healing agent to fill up the crack.

2.5 Diffusion test

The resistance to chloride penetration was evaluated by using the diffusion test as described in NT Build 443 (1995). The day after crack formation and healing, the specimens were coated again except for the casting surface. At the age of 28 days, the specimens were placed in a 4 g/l Ca(OH)_2 solution for 7 days until constant mass was reached. Afterwards the specimens were placed in the test solution, being a 165 g/l NaCl solution.

After 7 weeks storage in the test solution, the chloride penetration was measured by means of the colour change boundary, more specifically by spraying 0.1 M AgNO_3 on both halves of a split specimen. At least three healed samples were split per crack width. The colour change boundary was measured by means of image analysis software (ImageJ).

Next, chloride profiles were obtained by potentiometric titrations with a Metrohm MET 702 automatic titrator and a 0.01 mol/l AgNO_3 -solution. Powder to extract the chloride from was collected by grinding layers of 2 mm thickness up to a depth of 20 mm. In order to obtain information about the chloride penetration around the crack, powder was collected in a zone of 18 x 75 mm with the crack in the middle. Afterwards powder was collected from two separated zones of 18 x 75 mm both 9 mm away from the crack, see Fig. 3. Here as well, three specimens per sample type were analysed.

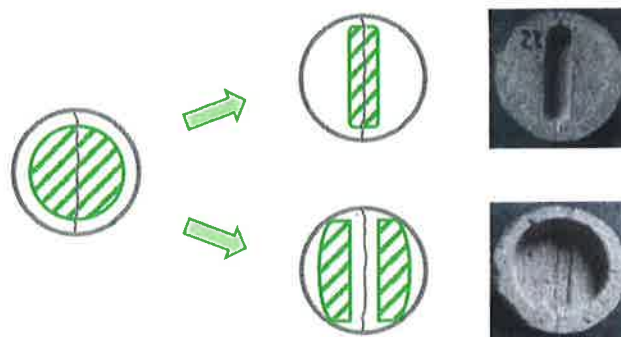


Figure 3: Grinding method to collect powder around the crack.

The extraction of chlorides from the powder was based on the method described by Maes et al. [4]. In this paper, the acid-soluble chloride content, which is the total chloride content, is measured. By using the titrated volumes of AgNO_3 , chloride contents were calculated using Eq. 1.

$$C_i = \frac{10 \times 100 \times 35.45 \times 0.01 \times \text{Vol. AgNO}_3}{1000 \times 2} \quad (1)$$

where c_i represents the total chloride concentration (wt.%-concrete); 10 the dilution factor; 35.45 the atomic mass of chlorides (g/mol); 0.01 the concentration of the titration solution (mol/l); Vol.AgNO₃ the titrated volume of silver nitrate (ml); and 2 the mass of the concrete powder in the extraction solution (g).

Non-steady-state diffusion coefficients D_{nssd} and chloride surface concentrations were obtained by fitting Eq. 2, which is the error function solution of Fick's second law, to the measured chloride profiles, using a non-linear regression analysis in accordance with the least squares method.

$$C_i(x,t) = C_s - (C_s - C_i) \cdot \operatorname{erf}\left(\frac{x}{\sqrt{4 \cdot D_{nssd} \cdot t}}\right) \quad (2)$$

where $c_i(x,t)$ is the chloride concentration at depth x and time t (wt.%-concrete), C_i the initial chloride concentration (wt.%-concrete), C_s the chloride concentration at the surface (wt.%-concrete), D_{nssd} the non-steady-state diffusion coefficient (m²/s), x the distance from the surface until the middle of the considered layer (m) and t the exposure time (s). Compared to the mass of concrete, it is reasonable to assume that the initial chloride concentration C_i in Eq. 2 equalled 0%. The first layer was excluded from the regression analysis, since the measured chloride concentration in the first layer is generally considered not representative.

3 RESULTS

3.1 Colour change boundaries

In order to evaluate the healing effect with regard to the resistance against chloride penetration after 7 weeks immersion in the 165 g/l NaCl solution, four healing categories are defined based on the colour change boundary, see Fig. 4: (1) Totally healed (no Cl⁻ penetration around the crack), (2) Partially healed (Cl⁻ penetration until the tubes), (3) Partially healed (Cl⁻ penetration beyond the tubes (< crack length)) and (4) No effect (similar to cracked concrete).

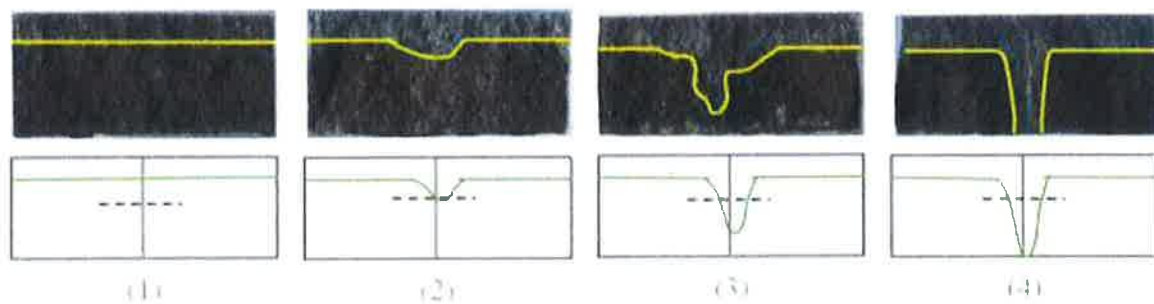


Figure 4: Visual indication of four categories to evaluate healing based on the chloride penetration depth around the crack measured by means of the colour change boundary.

Table 2 gives an overview of the ability to regain resistance against chloride penetration due to autonomous healing by means of encapsulated polyurethane. The percentages represent the part of the samples belonging to the specific category. To classify them, colour change boundaries were measured and compared.

Table 2: Influence of autonomous crack healing in OPC mortar with regard to chloride penetration, after 7 weeks immersion in a 165 g/l solution. Classification based on Fig. 4.

Healing category	OPC	
	100 μm	300 μm
(1)	50 %	-
(2)	17 %	33 %
(3)	-	17 %
(4)	33 %	50 %

According to the measured colour change boundaries, it seems that 67 % of the autonomously healed mortar specimens with an initial crack width around 100 μm regain almost full resistance against chloride penetration (categories 1 and 2). Besides, specimens with initial crack widths around 300 μm can be healed almost totally in only 33 % of the cases (category 2). For 33 % and 50 % of the autonomously healed mortar specimens with 100 μm and 300 μm cracks, respectively, no effect was observed.

3.2 Chloride penetration profiles

Fig. 5 shows the chloride profiles for healed, unhealed and uncracked specimens with crack widths of 100 μm and 300 μm . Each profile is the average of three individual profiles obtained in different zones (cf. Fig. 3), namely in the zone around the crack for healed specimens (PU – C), in the zone around the crack for unhealed specimens (CR – C) and in the zones next to the healed crack (PU – R) which gives an indication of uncracked samples (REF). The number in the specimen codes refers to the initial crack width.

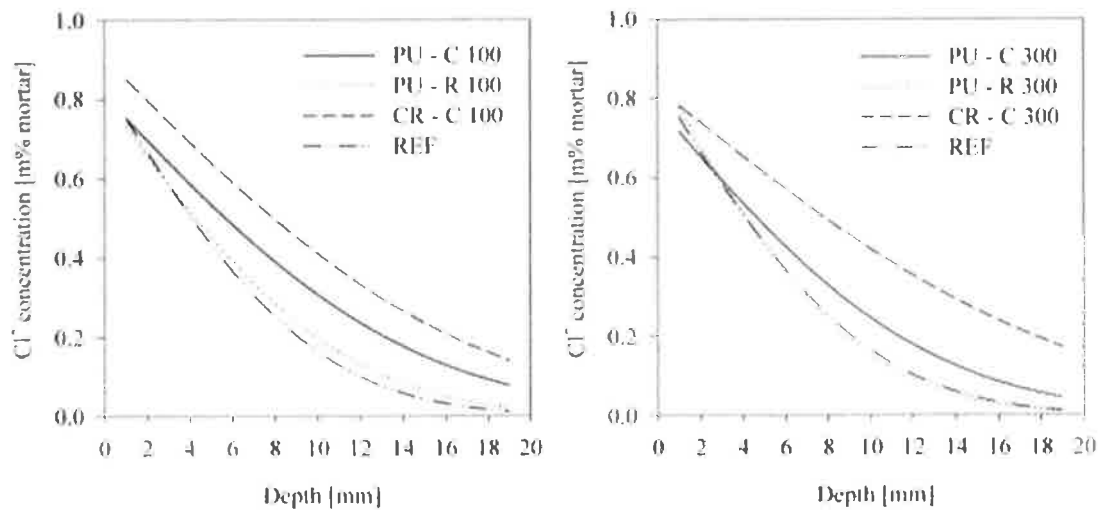


Figure 5: Average chloride profiles obtained after 7 weeks immersion in a 165 g/l NaCl solution, with initial crack widths of 100 μm on the one hand and 300 μm on the other hand.

Based on the average chloride profiles, it seems that autonomous crack healing has a beneficial influence on the resistance against chloride penetration. The chloride concentrations at different depths around healed cracks (PU-C) are clearly lower than in cracked samples without healing (CR-C). Although they are still higher than in uncracked

mortar. So, based on these findings it can be concluded that autonomous crack healing by means of encapsulated PU has a beneficial influence on chloride diffusion, regardless the crack width, but uncracked concrete performs better. Nevertheless, it should be mentioned that these are average profiles. A more detailed inspection of the values of the individual chloride profiles per specimen, as can be seen in Fig. 6, learns that for specimens with a 100 μm crack as well as for specimens with a 300 μm crack only two of the three tested specimens were (almost) totally healed while one showed no healing effect. This is in accordance with the findings based on the inspection and categorisation of the colour change boundaries.

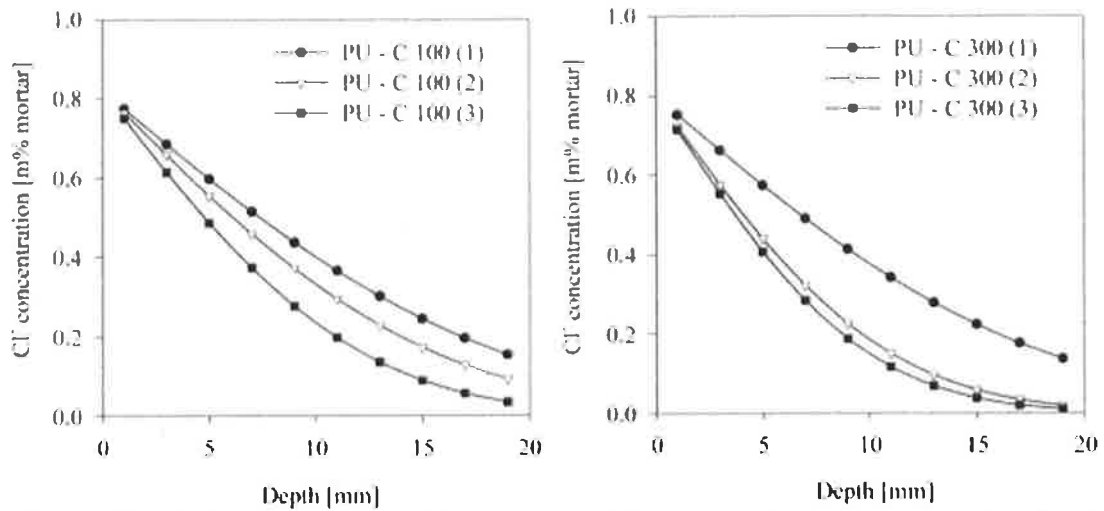


Figure 6: Individual chloride profiles obtained after 7 weeks immersion in a 165 g/l NaCl solution, with initial crack widths of 100 μm on the one hand and 300 μm on the other hand.

3.3 Chloride diffusion coefficients

By fitting Eq. 3 to the measured individual chloride penetration profiles, diffusion coefficients are calculated. Table 3 gives the average chloride diffusion coefficients with an indication of the standard deviations. Three specimens were examined per test configuration.

Table 3: Total chloride diffusion coefficients.

Zone	$D_{\text{nssd}} [10^{-12} \text{ m}^2/\text{s}]$	
	100 μm	300 μm
CR-C	21.1 ± 3.0	26.9 ± 3.1
PU-C	12.7 ± 9.3	11.7 ± 8.7
PU-R	7.0 ± 2.3	6.3 ± 0.8
REF	7.0 ± 0.2	

In general the diffusion coefficients in the zone around an unhealed crack (CR-C) are higher than those in the zone around a healed crack (PU-C) and those for uncracked concrete (REF and PU-R), regardless the crack width. It is also clear that the mean values obtained for healed cracks are closer to the values for uncracked concrete than to those for cracked

concrete, indicating the beneficial influence of PU-crack healing. However, the standard deviations for the diffusion coefficients obtained around a healed crack show a large scatter. This finding is in accordance with former results and findings in this paper and can be explained by the fact that only a part of the PU-healed cracks are really sealed and filled up with PU. The latter is probably due to falling short of the healing mechanism rather than the fact that chlorides penetrate through the PU-foam since previous tests [3] showed that the closed cell structure of the used PU is watertight. Visual inspection of the specimens and the glass tubes after splitting shows that in the autonomously healed specimens without improved resistance against chloride penetration, the healing agents were still (partially) in the tubes. Possible explanations are that the crack formation was insufficient to trigger the healing mechanism or that the tubes were shifted during the moulding process, which made it not possible for the two components to react properly. Another possible explanation is the influence of the capillary forces [5]. The capillary forces in the tubes can be higher than in the crack, especially because long tubes (50 mm) and quite large cracks (up to 300 μm on average) were used in this research. So, additional tests are performed in order to obtain more certainty with regard to the results of autonomous crack healing of mortar.

4 CONCLUSIONS

Autonomous crack healing of mortar by means of encapsulated PU has a beneficial influence on the resistance against chloride diffusion, regardless the crack width. If the healing mechanism works properly and the crack is sealed well, (almost) no chlorides will penetrate along the crack. However, based on chloride penetration depths, chloride profiles and chloride diffusion coefficients, it can be concluded that in 33 % of the cases crack healing has no effect on the resistance against chloride penetration. Nevertheless, autonomous crack healing is able to increase the durability of mortar/concrete structures in chloride-containing environments.

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