

Most recent advances in the field of self-healing cementitious materials

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Keywords: Alternative binders, Fiber reinforcement, Super absorbent polymers, Encapsulated bacteria, Encapsulated liquid polymers.

ABSTRACT

While the Japanese researchers Ohama et al. [1] already mentioned in 1992 that a self-healing effect was noticed when polymer-modified concrete without hardener was made, the real pioneer in the research on self-healing concrete is Carolyn Dry from Illinois. The first time she proposed the use of encapsulated polymers to obtain self-healing concrete dates back to 1994 [2] and based on her publication output, she remained active within this field until 2003 [3, 4]. Within this timeframe, Victor Li started his research on fiber-reinforced self-healing concrete in Michigan [5]. From 2000 onwards other researchers in Japan (Mihashi, Nishiwaki et al.) [6-8], France (Granger et al.) [9], the United Kingdom (Joseph et al.) [10] and the Netherlands (ter Heide et al.) [11] started their research on self-healing cementitious materials. However, it was only in 2007, when the Dutch IOP program on self-healing was granted and the first international conference on self-healing materials was organized in the Netherlands, that self-healing concrete gained world-wide attention and all over the world research groups started working on this topic. One year later, in Belgium or more specifically at the Magnel Laboratory for Concrete Research of Ghent University, research on self-healing concrete started. In this keynote, an overview of the most recent developments within the Magnel Laboratory will be given.

1. INTRODUCTION

Self-healing in cementitious materials can be classified broadly into two groups: (improved) autogenous healing and autonomous healing. (Improved) autogenous healing refers to the recovery process where healing is caused by material components that could also be present when the concrete is not specifically designed for self-healing. The term autonomous healing is used when healing is caused by engineered additions which would otherwise not be found in concrete. In the following paragraphs different approaches of each mechanism will be discussed.

2. (IMPROVED) AUTOGENOUS HEALING

Autogenous crack healing can be mainly attributed to: hydration of unhydrated cement particles and dissolution and subsequent carbonation of calcium hydroxide ($\text{Ca}(\text{OH})_2$). In addition to these mechanisms, swelling of the matrix and blocking of the crack due to debris present in the ingress water or loose concrete particles resulting from cracking, may also cause autogenous healing. While the overall contribution of these mechanisms in autogenous healing remains a matter of debate,

researchers agree that autogenous healing can be improved when the amount of reactive binder agents is increased (Figure 1), crack widths are restricted (Figure 2) or additional water is supplied in the crack region (Figure 3).

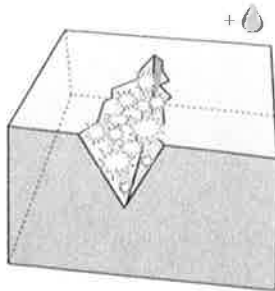


Figure 1. Improved autogenous healing (upon contact with water) due to an increased amount of reactive binder.

While partial cement replacement by blast furnace slag or fly ash, waste products of the steel industry and coal-combusted power stations respectively, results in more environmentally friendly concrete, their use may also cause additional advantages. Their slower reaction rate may result in a higher amount of unhydrated particles and thus an improved possibility for ongoing hydration. However, as the reaction of both binder materials needs to be activated/initiated by Ca(OH)_2 , resulting from cement hydration, less Ca(OH)_2 will be available for possible crack healing by carbonation.

Calorimetric measurements on mixes of crushed cement paste and water showed that the cumulative heat production of series in which cement was partly replaced by slag or fly ash was higher compared to series containing only cement. Among both, blast furnace slag resulted in the highest heat production and thus probability of further hydration upon contact with water. This corresponds to the higher crack healing efficiency of slag and fly ash mixes which was noticed when measuring the water permeability over time of cracked samples [12].

For calcium carbonate (CaCO_3) precipitation to occur, both water and carbon dioxide (CO_2) need to be present. Microscopic investigation of the crack width evolution during wetting and drying cycles allowed to study the effect of the mix composition on the amount of autogenous healing by CaCO_3 precipitation. In this experiment, mixes containing only Portland cement proved to have the best healing efficiency. As more Ca(OH)_2 is available within this composition, more Ca(OH)_2 can react with CO_2 from the air to form CaCO_3 crystals within the crack. In addition, it was shown that only cracks below 200 μm could close due to CaCO_3 precipitation at the crack faces [12].

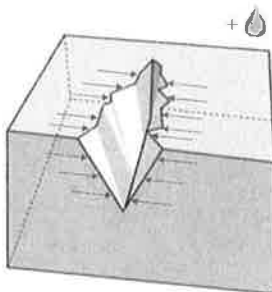


Figure 2. Improved autogenous healing (upon contact with water) due to restriction of the crack width.

This brings us to the second mechanism which can be used to improve autogenous crack healing: restriction of the crack width through the addition of fibers. Fibers are usually added to the concrete mix in order to improve the structural strength, ductility, freeze-thaw resistance, resistance to spalling,... However, it was shown that they can also improve autogenous healing by enhancing multiple crack formation and limiting the crack width.

The efficiency of natural flax fibers and synthetic polyvinylalcohol (PVA) fibers was compared. Measurements of the regain in mechanical properties as well as microscopic investigation of cracked samples subjected to wetting and drying showed that the healing efficiency did not depend on the type of fibers used. However, it was noticed that healing was determined by the initial crack width. Cracks narrower than 30 μm closed completely while cracks with a width between 30 μm and 150 μm only showed partial closure [13].

In both of the afore mentioned approaches (increasing the amount of reactive binder or restricting the crack width), autogenous healing was improved although healing only started at the moment the cracked samples were brought into contact with water. As water is a crucial factor for autogenous healing to occur, autogenous crack healing can be largely improved when additional water is provided. Super absorbent

polymers (SAP) can serve this purpose. SAP are cross-linked polymers which can absorb a disproportional large amount of liquid and swell substantially to form a soft and insoluble gel. SAP particles are currently added to the concrete mix in order to cause internal curing. In addition, SAP particles can result in improved autogenous healing.

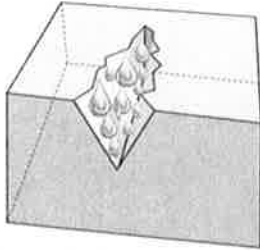


Figure 3. Improved autogenous healing due to additional water supply.

When cracks arise in the concrete matrix, ingress of moisture via the cracks causes the SAP particles to swell, thus leading to a direct physical blocking effect. In addition, SAP will release their water content again during dry periods, improving the reactions leading to autogenous crack healing.

It was noticed that for the types of SAP used in this study (commercial products obtained from BASF), both the mechanical properties and the water tightness were regained after samples were exposed to wetting and drying. Bigger SAP particles ($\pm 500 \mu\text{m}$) seemed to promote self-healing better compared to smaller ones ($\pm 100 \mu\text{m}$). Even without submersion of the samples, just upon exposure to a relative humidity of 90% or even 60%, partial healing of the cracks took place when SAP particles were included [14].

3. AUTONOMOUS HEALING

Autonomous healing of cracks in cementitious materials can be obtained following different approaches. A subdivision can be made based on the type of healing agent used. At one hand bacteria, which precipitate CaCO_3 , can be applied. These bacteria are available, in a dormant state, within the concrete matrix. Once cracks appear and water intrudes into these cracks, the bacteria become active and start to consume the available nutrients resulting in the formation of CaCO_3 crystals which fill the crack. On the other hand, polymer-based, liquid healing agents can be provided in the matrix to cause crack healing. In the latter case, crack formation results in the release of the liquid agent which starts reacting inside the crack and results in this way in crack healing. For each of these approaches, carriers are needed. In the first case the carrier serves as protection mechanism for the bacteria against the high pH in the cementitious matrix. In the second case the main goal of the carrier is to preserve the liquid healing agent until the moment of crack appearance. In both cases an additional function of the carrier is to act as trigger mechanism. At the moment of crack appearance, breakage of the carrier should activate the healing process.

In the approaches mentioned hereafter, *Bacillus sphaericus* (BS) bacteria were used for the precipitation of CaCO_3 crystals. BS is an alkaline spore-forming strain which has a high carbonate production capacity and can precipitate CaCO_3 in alkaline (pH 9-10) environments. However, as the pH in concrete is even higher (pH 12-13) different carriers were investigated in order to protect the bacterial spores.

A first carrier which was used to protect the spores is diatomaceous earth (DE) (Figure 4). DE consists of fossilized remains of diatoms, a type of hard-shelled algae. Some of these algae have a hollow inner structure and can maintain the spores inside, however in most of the cases, the bacteria will be attached to the surface of the diatoms as the surface pores are only between 0.1 and 0.5 μm . The particles themselves have sizes ranging from 4-20 μm [15].

Although, most spores were not within the diatoms, an obvious protective effect was noticed upon combination of the spores with DE. While only 5% of nutrient (urea)

decomposition was noticed when bacteria were added to a high pH solution without protection, this percentage increased to more than 70% when the bacteria were previously combined with DE. Moreover, the addition of DE and BS did not have a negative effect on the mechanical properties of the cementitious matrix [15].

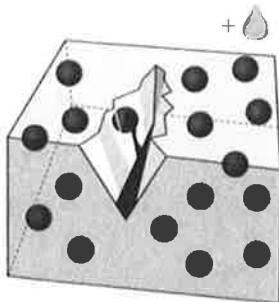


Figure 4. Autonomous healing (upon contact with water) by encapsulated (spherical capsules) bacteria.

While nutrients were already added to the mixing water when making the samples with DE protected spores, more precipitation of CaCO_3 crystals was noted inside the crack when the samples were submerged in a nutrient solution during the time span of healing compared to the submersion in water. Only when the cracked samples were submerged in a nutrient solution, complete filling of the 150-200 μm wide cracks was noted after 40 days. The efficiency of this approach was also proven by a reduced capillary water absorption of cracked samples when DE and BS were included. Here again, an additional beneficial effect was noted when samples were submerged in a nutrient solution instead of water [15].

A spherical carrier which has been used to protect the bacteria are melamine-based microcapsules (Figure 4). The capsules had diameters ranging from 5-10 μm . This type of microcapsules were able to survive the mixing process of cementitious materials. Moreover, after release from the capsules, the bacterial spores were still able to decompose urea and thus to precipitate calcium carbonate. A drawback of this approach, however, is that the addition of nutrients to the mix and the presence of the capsules reduced the mechanical properties of the cementitious matrix. Nevertheless, the matrix porosity was also reduced [16].

The efficiency of this approach was evaluated by means of microscopic investigation of cracked samples. All samples, even when no or empty capsules were added to the mix, showed some crack filling, except those which were stored at a high relative humidity instead of being submerged in water or a nutrient solution. However, while for series without bacteria only cracks with a width up to 250 μm were able to close completely (due to autogenous healing), when bacteria loaded capsules were provided even 1 mm wide cracks were able to heal completely [16].

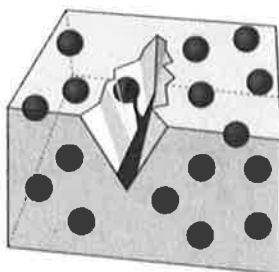


Figure 5. Autonomous healing by encapsulated (spherical capsules) bacteria.

As the bacterial spores need water in order to become active, the previous bacteria-based mechanisms are only activated when samples are submerged periodically or continuously in water or a watery nutrient solution. In order to be able to activate the mechanism in dry state, the bacteria can be incorporated in SAP particles (Figure 5). In this case, the main function of the SAP during crack healing is to facilitate the germination of the spores and bacterial ureolytic activity by supplying water. In addition, the SAP will retain their earlier crack blocking effect due to their swelling reaction and improve autogenous crack healing by providing water for further hydration and CaCO_3 precipitation.

Both the bacterial spores and the nutrients were provided inside the SAP during synthesis of the SAP particles in the laboratory. The bacterial spores were still viable and kept their ureolytic activity after synthesis of the polymers and subsequent processing steps (grinding of the polymer). These bacterially loaded SAP particles were, together with some additional nutrients, added to the mortar mixture upon preparation [16].

After crack formation it was shown that samples with bio-SAP particles, which were subjected to wetting and drying, showed a higher crack healing efficiency in view of the healing rate and maximum healed crack width. In case SAP with spores and nutrients were provided healing ratios of more than 70% were still noticed for cracks with widths until 700 μm [16].

This beneficial effect was only noted for samples subjected to wetting and drying while it was aimed for that healing would now also take place at high or medium relative humidity. The self-synthesized SAP used in this study showed 25 times less water absorption when the relative humidity decreased from 100% (wet state) to 90% and even about 2000 times less when the relative humidity further decreased to 60%. It is thus obvious that the fact that wetting and drying was still needed is caused by the poor behaviour of the specific SAP. Further research therefore aims at the combination of the bacteria with better performing SAP types [16].

While for the bacteria-based approaches mostly spherical capsules or carriers have been used, up to now polymeric agents were mostly embedded inside cylindrical capsules as they have the advantage that the probability of a crack going through is higher. Within the cylindrical capsule-based approach, a subdivision can be made between capsules with one compartment (Figure 6), which are usually filled with one-component healing agents, and capsules with two or more compartments (Figure 7) which are filled with multi-component healing agents.

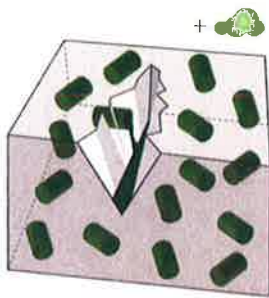


Figure 6. Autonomous healing (upon contact with moisture) by encapsulated (tubular capsules) one-component healing agents.

An example of a one-component healing agent which has been used is cyanoacrylate (Figure 6). This agent is characterized by a very low viscosity and a rapid strength development upon contact with moisture in the air. While this rapid strength development can be seen as an advantage, since crack repair can be done within a few seconds, it was merely experienced as a disadvantage. At first, due to the high reactivity of this agent, hardening of the agent in some cases already occurred within the glass capsules, before capsule breakage. In addition, due to the short reaction time limited outflow of the agent into the crack was noticed. As a result, the obtained strength regain always remained lower than 50% of the original value [17].

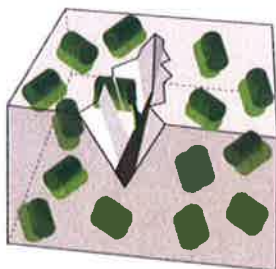


Figure 7. Autonomous healing by encapsulated (tubular capsules) multi-component healing agents.

The advantage of using a multi-component healing agent is that premature hardening of the agent inside the capsules should not be feared as the reaction only becomes possible when both agents contact each other after capsule breakage (Figure 7). An additional difficulty in this approach, however, is that the different components of the healing agent need to find each other before the reaction can start. As for epoxy resins the mix ratio of the different components is very important in order to have a complete polymerization reaction, multi-component epoxy resins were found not to suit as healing agent inside self-healing concrete [17]. The noticed strength regain always remained lower than 20%. A multi-component

agent which did seem appropriate was a polyurethane-based adhesive.

The polyurethane-based adhesive consists of two components which react upon contact with each other irrespective the mix proportion. One component is a prepolymer of polyurethane, the second component is a mix of accelerator and water. Both components of this agent were embedded inside cylindrical capsules with a

diameter ranging from 2 to 3 mm and made from glass or ceramics. Both materials are very brittle and thus break easily at the moment of crack appearance. To increase the probability that both components contact each other, capsules filled with each of the components were fixed next to each other [18].

Up to 60% of the original strength was regained upon reloading previously cracked samples which contained encapsulated polyurethane. Even when the samples were reloaded for a second time up to 25% of the original strength was regained due to a second healing action. For cracked samples containing encapsulated polyurethane it was possible to reduce the water permeability coefficient with a factor 10^2 to 10^3 when glass capsules were used and even with a factor of 10^3 to 10^4 when ceramic capsules were embedded [18].

4. CONCLUSIONS

Among the earlier mentioned self-healing approaches, those relying on improved autogenous healing are most close to practical application. This is of course because these mechanisms are caused by components which are nowadays already added to the concrete mix for other purposes.

Self-healing by bacteria embedded in DE, microcapsules or SAP is also quite close to practical application as these agents can survive the mixing process and can thus easily be added upon concrete manufacturing. However, some work will have to be dedicated to the reduction of the cost of the bacteria and thus to allow upscaling of the bacteria production. In addition, work is needed to make sure that the decrease in strength due to the presence of the nutrients and carriers, remains limited.

Most work will still be needed to apply the polymer-based self-healing system within a realistic concrete structure. The biggest bottleneck for this approach is to develop a suitable encapsulation material which is flexible enough to survive the mixing process but then becomes brittle enough to break upon crack formation. Also the long term behaviour of the encapsulated liquid healing agent is a topic which needs further attention.

Of course, even when completely ready for application in practice, these self-healing approaches will only be applied in specific types of concrete structures. More exactly those for which the added value due to self-healing is higher compared to the added cost for implementation of the self-healing approach.

For example, for underground structures, such as parking garages and tunnels, additional treatments are already needed before delivery to seal water transporting cracks caused by shrinkage. As in this specific case, water is available within the cracks, the addition of fibers can help to limit the width of the shrinkage cracks and to improve autogenous healing while added SAP particles can help to block the crack immediately and prevent leakage. If a permanent crack barrier is needed (also when the water level goes down) SAP particles can be combined with bacteria to block the crack permanently with CaCO_3 .

For non-water transporting cracks, for example cracks in reinforced bridge ledgers, it will be an advantage when the mechanism does not need water or moisture for its activation. In this case, polymer-based self-healing can be the ideal mechanism to prevent high repair costs. While the use of elastic healing agents holds the advantage of allowing dynamic movements of the healed crack, high modulus healing agents will create a strong bond between the crack faces and possibly allow multiple crack healing as new cracks will appear at another location where the healing agent is not yet exhausted.

While it is not yet clear for which type of structure self-healing will be most promising, we hope that in the near future self-healing will be introduced in at least some of the mentioned applications.

ACKNOWLEDGEMENTS

Financial support from the Research Foundation Flanders (FWO-Vlaanderen) for these studies (Project No's. G.0157.08 and 3.F.0229.02) as well as from the Ghent University Research Fund (BOF) is gratefully acknowledged.

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