

A Review: Novel Routes towards the Realization of Self-Healing Function in Cementitious Materials

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Abstract. Cementitious materials are the fundamental element in the field of civil construction. While due to its brittle nature, cracking of cementitious material at multi-scales could pose a threaten to the safety and durability of concrete structure. To solve this congenital problem, bio-mimic self-healing in cementitious materials was proposed and gradually demonstrated its great potential. In this review, two big categories of self-healing, autonomous and autogenous self-healing, with its corresponding up-to-date healing strategies were introduced. The merits and limits of different healing strategies were concluded. It is believed that this review could shed light to the realization of practical application self-healing concept in cementitious materials.

1. Introduction

Cementitious materials are the most commonly used construction material on this planet. Especially in China, the consumption of cement has already surpassed the cement consumption of the rest of world. However, they are susceptible to many sources of damage during their entire service life. It brings a large amount of labour-intensive maintenance work and relative cost. A recent survey conducted by European Union shows that almost 40-60% of civil engineering budget has been allocated to the maintenance and repair work [1]. Even so, as a nature of cementitious materials, micro-cracks can still exist in the cement matrix as a result of mechanical loading, environmental loading and volumetric instability. And before micro-cracks develop into macro-cracks and shown on the surface, it is hard to be inspected. Therefore, these micro-cracks pose a severe threaten to the safety, integrity, and durability of concrete structure. Meanwhile, cracks will provide a path for those harmful substances, such as moisture, carbonation, sulphate attack. These harmful substances will result in the corrosion and swelling of steel bar and finally shorten the service life of concrete structures. Conventional methods consume enormous amount of time and labour resource while only cracks on the surface of the structure can be repaired.

In recent years, inspired from biological self-healing phenomenon, a novel concept of “self-healing materials” has been proposed by many researchers and started to show its great application potential in cementitious materials [2]. Generally, the mechanism of self-healing for cementitious materials can be divided into two categories: autogenous self-healing and autonomous self-healing. Autogenous self-healing is an intrinsic self-healing property of cementitious materials. The self-healing effect comes from further hydration of un-hydrated cement particles, precipitation of carbonates and crystal grows. The most obvious advantage of this mechanism is that no extra healing agent is required to mix with concrete. Therefore, the chemical and mechanical properties of concrete will not be influenced by the



addition of substances. However, the limitations of autogenous self-healing are also significant. Firstly, autogenous self-healing can only happen for narrow crack with a crack width less than 0.2 mm. Secondly, to obtain the maximum healing performance, some special requirements on the healing conditions such as temperature, moisture and the existence of supplementary ions in the water solutions are strictly required. While, in practice, all those requirements are sometimes not available. Autonomous self-healing is another type of self-healing mechanism, in which the healing effect normally results from the additional healing agents. In this mechanism, healing agents are first sealed in a protective shell and then embedded in cementitious matrix. Once crack occurs in the cementitious structure, microcapsules that located along the path of crack will be triggered. The self-healing mechanism can be achieved through the release and reaction of healing agent with air, moisture or other stimuli in the region of crack. There advantages of autonomous self-healing are obvious. This promising application potential of autonomous self-healing in cementitious materials has stimulated researchers a great passion for further investigations. Nevertheless, there are still some drawbacks and technical issues that constricting the application of autonomous self-healing. For instant, the reliability of healing agent over time and the trigger sensitivity of shell have not attracted sufficient attention.

Although many researchers have devoted a great amount of work in this field, due to the wide diversity of required knowledge and the fast development of research progress, the difference of diverse mechanisms are not well classified and explained. Therefore, in this review, the progress of self-healing technologies which applied in cementitious materials with diverse trigger mechanism, healing agent and delivery methods will be reviewed and then classified based on (1) different types of healing mechanism and (2) different healing agent deliver methods. Besides, the strengths and weaknesses regarding different healing strategies are analyzed.

2. Type of healing mechanism

2.1. *Bacteria based self-healing*

Inspired by Bollapudi et al. [3] who suggested that using bacteria to promote precipitation of calcium carbonate to heal crack, a bacteria-based self-healing system that using porous expanded clay immobilized bacteria particles as biotic healing agent has been described by Jonker et al [4, 5]. These works demonstrated the application potential of self-healing concrete in low-temperature marine environments using bacteria-based healing agent. In this series of studies, two-component biochemical self-healing agent was act as functional particles to partially replace regular concrete aggregates. Once crack formed in the cement matrix, the pre-embedded bacterial spores and calcium carbonate will be released and activated by the ingress water. A maximum crack width with up to 0.46mm can be healed in bacterial concrete after 100 days of submersion in water. Comparing with previous studies, the work form Jonkers seems to be more promising. Since the bacteria and mineral precursor were both embedded in and therefore protected by expand clay, the activity of bacteria and the workability of the self-healing system became more reliable. Meanwhile, this method excluded the exist of urea during the calcite precipitation process, therefore it can be more environmental friendly. In addition, J. Y. Wang et al. demonstrated the feasibility of using microencapsulated bacterial spores to self-healing crack in cementitious materials [6]. In this study, advantages that using microencapsulation technique were demonstrated. It was found that the spores were still available after it was immobilized into the melamine-based shell, comparing to the specimens without bacteria, the self-healing results shown that the specimens with microencapsulated bacteria had much higher crack healing ratio. 18% to 50% of crack area was healed in non-bacteria series and 48% to 80% of crack area was healed in the bacterial series. The maximum crack width healed in the specimens of the bacteria series was 970 μ m, which is much wider (about 4 times) than that in the specimens of non-bacteria series (max 250 μ m). The overall water permeability in the bacteria series was also lower than that in non-bacteria series. The average k-value was decreased around 10 times.

The restriction of applying bacteria based self-healing in practical field is also obvious. For example, in order to realize a fast calcite precipitation, the crack has to be long-term exposed to water

or dry-wet cycle environment. Moreover, the survivability of bacteria is another concern that needed further research.

2.2. *Polymeric adhesive agent based self-healing*

Polymeric adhesive agent-based self-healing is one of the earliest self-healing concepts in the field of cementitious material. The objective of applying adhesive agent in cementitious materials is to maintain the durability of material and structure by regaining water tightness and mechanical properties in concrete structures. Generally, there are two types of adhesive agent. They are one-component agent and two-component agent. One-component adhesive agent such as cyanoacrylate (CA) is an ideal option for self-healing as the adhesive effect of one-component agent can be functional immediately. While the durability is a big problem. Two-component adhesive agents can be stored much longer than one-component, however the trigger and mixing of these two parts agents needed a good deliver and mix of healing agent in the crack. In the following paragraphs, some available polymeric healing agent which has been used in self-healing cementitious materials will be discussed.

Cyanoacrylate (CA), also known as superglue, is a typical one-component adhesive agent. The merits of CA such as low viscosity, short harden time and super strong binding force make the CA to be a very promising adhesive agent. Li et al. [7] first introduce the application of CA into the filled of self-healing cementitious materials. In this study, superglue (CA) which served as healing chemical was sealed in hollow glass fibers. Due to the brittle nature of glass, the incorporated glass fibers can sense crack. Once the glass fibers were ruptured by the crack, the healing agent, CA, will be released into the cracks of the matrix and finally seal the crack. After that, many researchers have also explored the feasibility of using CA as adhesive agent for self-healing [8, 9]. These researches found that CA (superglue) is a suitable healing agent since the one-component agent adhesive is able to flow into and heal finer cracks. While the short shelf life and weak water resistance might be a negative factor when it was introduced into practical application.

Epoxy is another type of adhesive agents which has also been used in concrete repairment for a long time. In recent years, the application of epoxy on crack sealing and mechanical regaining of concrete has been extended to the self-healing concrete [2, 10]. Two-component epoxy repairing system is the most popular adhesive agent in the literature. In their application, microencapsulated epoxy and its hardener were first embedded in cementitious material. When the crack intersects the encapsulated epoxy and its hardener, the epoxy will flow out and be cured by the hardener. While, in the practice, the proper mixing of epoxy and its hardener became a barrier to the realization of self-healing function. To solve this problem, one-component epoxy microcapsules was developed to increase the efficiency of self-healing [11, 12]. Recently, Wenting et al. [13] demonstrated the work which employing one-component epoxy filled microcapsules to achieve mechanical restoration of cementitious materials. To decrease the viscosity of epoxy, they also proposed using benzylalcohol (BA) to adjust the viscosity of epoxy into an ideal value. However, the longevity of one-component epoxy microcapsules has to be addressed properly.

Beside the abovementioned adhesive agents, the feasibility of many other different types of adhesive agents such as acrylate-encapped, urethane-based precursor [14] and commercial available healing agent MEYCO MP355 1K have also explored [15].

2.3. *Water swelling agent based self-healing*

Water swelling agent such as polyurethane (PU) [15] and superabsorbent polymer (SAP) [16, 17] is a newly emerging type of healing agent. The focus of this type of healing mechanism is mainly targeting on the reduction of water permeability. The application of PU-based healing agent in self-healing cementitious materials was investigated by Kim Van Tilleboom [18]. The healing agent they used, MEYCO MP 355 1K, is a commercial product. This type of PU starts foaming when it encounters with moist environment. The foaming reaction of this healing agent may lead to an increase of the volume of PU up to 25-30 times bigger than it before. In addition, a function of chloride diffusion

resistance for crack widths around 100 μ m - 300 μ m was found in this study. Nevertheless, due to the weak resistance of PU to water and alkali, the reliability of the PU self-healing system needs further improvement.

The first application of superabsorbent polymer (SAP) particles in cementitious materials is designed for the prevention of self-desiccation during the hardening process of cement-based materials. Recently, the potential of applying SAP for self-healing and self-sealing cementitious materials has also studied. H. X. D. Lee et. al. [19] reported that, by adding SAP less than 1vol.%, the flow rate of cracked sample through a 340 μ m wide crack is reduced substantially. After that, Snoeck et al. [20] demonstrates that the combination of microfibers and SAP enables the cracked cementitious materials samples to be healed in an environment with a relative humidity of more than 60%. A recent study shown that, comparing to control samples with similar crack widths, the peak flow rate and cumulative flow through of SAP embedded samples decreased by up to 85% and 98%. However, inevitably, the use of SAP often results in a drastic decrease in strength. For example, the addition of 5% SAP by weight was found to reduce the compressive strength by 80%. Figure 2.1 demonstrates the working mechanism of self-sealing cracks using SAP. As can be seen from Figure 2.1a, during the period of cement hydration, the SAP will loss water and begin to shrink due to the unbalance of moisture, leaving pores and holes in the cement matrix. When crack occurs during the service life of cementitious materials, the pores will be act as macro defect and the crack is likely to propagate through them (Figure 2.1b). Once the cracked cementitious materials exposure to water, the SAP will swell up immediately. The swollen SAP can fill the crack and decrease or even stop further infiltration of water (Figure 2.1c).

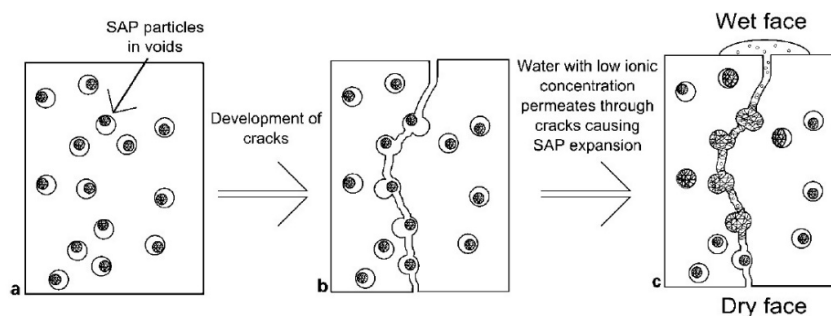


Figure 1. Schematic showing potential mechanism of self-sealing cracks using SAP (Ref).

2.4. Autogenous self-healing

Differ to the autonomous self-healing autogenous self-healing refers to the intrinsic healing ability of materials itself. As the earliest self-healing mechanism noticed in cementitious materials, the first literature report about this can be traced back to the end of nineteenth century [21]. Following that, more systematic studies were conducted to investigate the effect of autogenous self-healing on various aspects of cementitious materials.

The influence of autogenous self-healing on permeability has been studied by many researchers [22, 23]. The mechanism and the chemical/physical process for the autogenous self-healing were investigated theoretically and experimentally. It was believed that the formation of calcite in the crack is the cause for the autogenous healing while the concrete composition has no influence on autogenous healing. As expected, an obvious self-sealing effect can be found on cracked cementitious material when it exposure to water. Furthermore, the enhancement of mechanical properties of cementitious materials due to the autogenous self-healing has also been investigated. Lauer and Slate first demonstrated that the tensile strength of cementitious materials can be enhanced by the autogenous self-healing of crack [24]. Recently, Yingzi Yang et. al. demonstrated the autogenous self-healing effect on Engineered Cementitious Composite [25]. The researcher found that, up to 100% of the tensile strain capacity can be recovered for those specimens pre-damaged by loading up to 3% tensile

strain. Besides, the reduction of chloride ingress or reinforcement corrosion due to the autogenous self-healing was also investigated [26].

Nevertheless, limitations of the autogenous self-healing are still pending for improvement. For example, the self-healing process must be triggered under a long-term water immersion. Meanwhile, depending on the curing conditions, the self-healing can only be effective for narrow crack less than 300 μm .

2.5. Mineral mixture based self-healing

It is known that the autogenous healing mechanism is largely depends on further hydration of unhydrate cement particles. While for typical hardened concrete, autogenous self-healing is not very promising as the unhydrate products in cement is not sufficient enough. To compensate this drawback, adding mineral admixtures in cementitious materials seems to be a good option to promote the autogenous self-healing performances. Till now, the effect of various mineral additives i.e., silica-based materials [27], calcium sulfoaluminate based expansive agents [28] and crystalline components [29] on promoting the autogenous self-healing of cementitious has been investigated. For example, the maximum crack width of around 400 μm found to be healed with expansive powder minerals contained glass capsule system. In this system, two layers glass macrocapsules was employed as healing agent container. The expansive powder minerals are positioned in first layer of capsules, water is positioned in inner capsules. When the concentric glass macrocapsules are cracked, the released healing agent will interacts with [28] water and CO_2 and then different hydrated and carbonated products are formed, to seal and heal the cracks. The result shows that the addition of mineral admixture can promote the effect of autogenous self-healing in cementitious materials. Meanwhile, it was found that the healing efficiency of cementitious materials can be further improved by utilizing a combination of minerals rather than a single mineral. Nevertheless, there are still existing some drawbacks when applying mineral admixtures as self-healing agent to promote healing process. Directly adding mineral admixture into the concrete without any protection may result in an immediately reaction when the add mineral admixture encounter with water. Moreover, the addition of expansive agent in concrete matrix could cause damage of concrete structure due to the expansion effect [30].

3. Healing agent delivery methods

The physical and chemical condition in cementitious materials is complicate and relatively harsh. For instance, the mixing process of cement and aggregate could produce a strong shear force. Following that, at the initial stage of cement hydration, large amount of $\text{Ca}(\text{OH})_2$ could be generated as a hydration product of the tricalcium silicate (C_3S). The produced $\text{Ca}(\text{OH})_2$ can dissolve in the water of cement paste, resulting in a fast increase of pH value ($\text{pH}_{\text{max}} > 13$). Meanwhile, during the curing and hardening period of cementitious materials, water or saturated humidity will always be present. All these factors post a great threaten to the survive of almost any types of the aforementioned healing agent. Therefore, in order to deliver the healing agent to the crack more efficient and effective, it is ideal that the healing agent could be preserved properly until it comes into effect. Till now, several methods have been developed to protect the healing agent from being influenced by the harsh condition and to deliver the healing agent to the place where it needed. In the following paragraphs, three typical deliver methods of healing agent with its corresponding strengths and weaknesses have presented.

3.1. Microencapsulation

Microencapsulation technique has been widely applied in the field of agriculture, drug manufacture, food etc. In recent years, this technique has also been introduced to a new emerging field, self-healing materials. The first application of using microcapsules as a vessel to deliver and protect healing agent was demonstrated in polymer [31]. In this application, microcapsules with urea-formaldehyde (UF) shell containing dicyclopentadiene (DCPD) were synthesis by in-situ polymerization technique. Inspired from that, the microcapsule-based self-healing concept has also shown its great application

potential in extending the lifetime of cementitious materials [32]. Once the incorporated microcapsules are ruptured by the stimuli such as force [33], ions [34] pH [35] etc., the self-healing action is realized through the release and reaction of repairing chemicals in the region of crack.

The properties of microcapsules are important in realizing the self-healing effect in cementitious materials. A good design of microcapsules not only directly determines the self-healing efficiency but also have a positive influence on the mechanical properties of the cementitious materials as a whole. Depending on the shell materials, the microcapsules for the use of cementitious materials self-healing can be grouped into two categories, polymeric shell microcapsule and inorganic shell microcapsules. Polymeric microcapsules employ organic materials such as urea-formaldehyde resin, melamine-formaldehyde resin (MF) [36], polystyrene (PS) [37] etc. as shell materials to protect and deliver healing agent to the crack. Microencapsulation techniques including spray drying, interface polymerization and polymer phase separation are normally used fabricate polymeric microcapsule. The benefit of using polymer as shell materials is it has good sealing function to the healing agent, which is believed as a crucial factor for most of healing agent that would lose effect when it encounters with high alkaline solution. Inorganic microcapsule is another category of microcapsules that employing inorganic materials such as silica particles [38], glass capsules [39], expanded clay [4] as shell materials. Due to the similar properties of materials, the advantage of inorganic microcapsules is the relatively good bonding strength with cementitious matrix, which is believed to have a influence on the trigger efficiency of microcapsules.

3.2. Vascular system

Vascular system is the earliest method that was employed to deliver healing agent to the crack in cementitious materials. Early in 1994, Dry proposed the work that using hollow fiber containing chemical healing agent to seal matrix cracks and restore the strength in damaged areas [8, 40]. In this study, embedded tubes with healing agent were used in concrete matrix to transport drugs. The advantage of this system is that more healing agent can be contained in the vascular and transport to the crack. The schematic of vascular self-healing system is illustrated in Figure 2.2. Hollow glass fibers were first embedded in the cementitious matrix. The healing agent and cure agent (only for two channels vascular system) are stored or injected separately in different fiber. Once the glass fibers are broken by the crack propagation, the healing agent will be released and seal the crack.

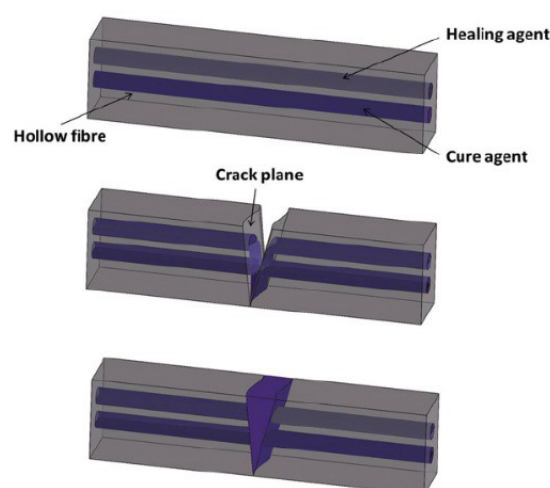


Figure 2. Schematic representation of hollow fibers self-healing concept.

Joseph et al. [9] demonstrated vascular healing system that using embedded borosilicate glass tubes as a way to deliver healing agent. However, only a small amount of healing agent was found can flow

into the crack after the crack formation. To increase the transport distance and amount of healing agent, additional healing agent was provided inside a tank which connected to the outer end of the hollow fiber [41]. While there are two main drawbacks that using glass fiber to form vascular system. First, the glass fiber may not survive in the system during the set up and concrete mixing process. In addition, the alkali-silica reactions may shorten the long-term service of glass vascular system. As a replacement, Pareek et al. [42] set up a container free vascular system. To introduce hollow ducts in concrete structures, steel bars with smooth surface were first embedded during casting and then pulled out after the concrete cured for 24 hours. Recently, Minnebo et al. [43] demonstrated work using alternative brittle materials: polymethyl methacrylate (PMMA), starch, alumina and inorganic phosphate cement to replace the commonly used vascular material, glass. The results obtained from mechanical test shown that the self-healing is possible to realize with the vascular healing network they proposed.

Overall, to design and optimize the vascular system, researchers have to comprehensively assess the size (diameter and thickness) of fiber, the viscosity and the polymerization kinetics of healing agent. Meanwhile, the choice of healing agent has to make on the basis of crack widths that need to be repaired.

3.3. Porous network

Inspired by the fracture healing behavior of creature's bones, the idea of porous network healing concrete system was proposed by Sangadji and Schlangen [44]. Figure 3.1 shows the schematics of the conceptual working principle of healing agent transport in the porous concrete. This system installed a concrete vascular structure without using extra delivery method. The porous network system consists of two parts, the prefabricated porous core and the concrete main body. Once the crack emerged in the concrete system, the cracks can approach those porous structures so that the healing agent can be transported via the porous structure to the cracks and then heal the cracks. Both polymer and bacteria-based healing agent can be employed in their structure. When using epoxy as healing agent, the crack zone was sealed and the crack faces were glued, showing a tendency to recover strength and stiffness of crack specimens. When applying bacteria-based healing agent as a healing solution, despite the limited function in mechanical regain, a liquid tightness was achieved on cracked porous network self-healing system. More efforts are still needed to investigate the reusability and up-scaling ability of this system.

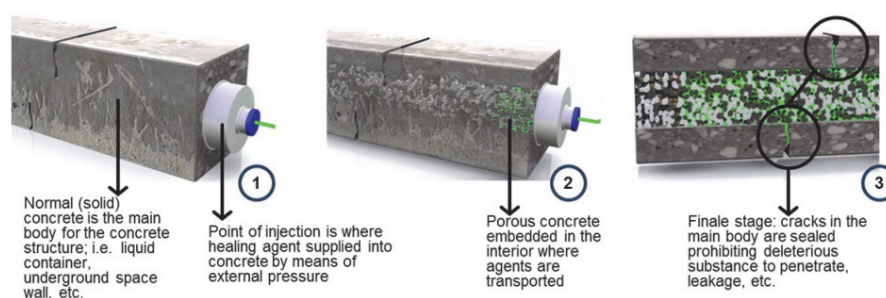


Figure 3. Schematics of the conceptual working principle of healing agent transport in the porous concrete.

4. Conclusion

In this paper, literatures about self-healing in cementitious materials with diverse healing agent and its corresponding delivery methods are reviewed. The advantages and disadvantages of different self-healing strategies are analyzed. Generally speaking, no single healing strategy is universal applicable. The selection of healing agent and strategy has to take the application condition and environmental situation into consider. Last but not least, it has to be pointed out that self-healing cementitious

materials is an interdisciplinary research topic which involves subjects such as chemistry, material science, structural engineering and microbiology etc. For further development of this field of research work, a good communication and cooperation between researchers from different background will be strongly recommended.

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