Status-of-the-Art for Self-healing Concrete

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Abstract. Concrete is one of the most widely-used materials in construction. However, there often exist some inevitable cracks due to its brittleness. The durability and service life of the concrete structure will therefore be reduced largely. Self-healing concrete is one of the feasible and effective techniques which can respond to cracks in an astute way, and easing or even repair the cracks completely. Overviews are provided here with concrete self-healing mechanism and self-healing trigger mechanism. Based on the related principles of self-healing technology, the paper analyzes the existing self-healing technology from different aspects and forecasts the future development direction. Concrete self-healing mechanisms are classified mainly into three types as physical, chemical and biological ones. Self-healing trigger mechanisms are summed up with two aspects as physical trigger and chemical trigger respective. In recent years, concrete self-healing mainly develops to chemical, biological and composite repair mechanisms, and the trigger mechanism develops to chemical trigger such as ion trigger. Based on the recent development of technology some viewpoints about present technology improvements and major future developments are pointed out for reference.

1. Introduction

With the development of materials science, concrete materials are developing in the direction of intelligence, versatility, and high durability. Self-healing concrete as an emerging smart material can greatly improve structural durability and meet the concept of sustainable development. Self-healing concrete mimics the mechanism of repairing damaged parts by biological tissues. After the occurrence of cracks, a “reaction” is made to seal the cracks and repair the cracks. The internal crack is difficult to find and repair. The self-healing technology can stop the damage in time and prevent the crack from developing.

Concrete itself can heal cracks, mainly through the rehydration of cement to seal the cracks, but this self-healing is more demanding on the environmental conditions of the concrete, it is difficult to achieve a better heal effect in the project. Therefore, many scholars have carried out a lot of research on self-healing of concrete, and seek self-healing technology with quick healing speed, good healing effect, and simple process. At present, the research on self-healing of concrete mainly includes research on the self-healing mechanism of concrete and self-healing trigger mechanism. This paper will summarize the research results and progress of self-healing concrete from the above two aspects.

2. Research Progress on Self-Healing Mechanism

2.1. Physical Self-Healing

There are two main types of physical self-healing mechanisms. One is the bonding and sealing of cracks by adhesives such as epoxy resins. The main process of healing is that the crack development
triggers the outflow of adhesive, and the adhesive cures to heal cracks. (Fig. 1). Physical bonding self-healing research started earlier. Physical binders mainly include neoprene, α-cyanoacrylate, epoxy resin, tung oil, methyl methacrylate and the like[1-3].

![Figure 1. Diagram of physical bond self-healing.](image)

The other is the use of shape memory alloy (SMA), fibres, etc. to close or limit cracks through mechanical action. Shape memory alloy (SMA) is a type of material that has a memory function for shape, which is self-sensing, self-diagnosing, and adaptive. SMA exhibits shape memory effects or superelasticity, depending on the temperature of the material. When the temperature of the material changes, the shape memory alloy can be transformed between martensite and austenite to complete the deformation and recovery of the shape, if the transition temperature can be properly controlled, this enables the SMA to become a concrete self-healing material[4-6].

The research on the physical self-healing of concrete has been carried out very early, and many results have been obtained, but physical self-healing cannot repair the cracks twice; and its repair efficiency is low and the repair cost is high. So the current self-healing is mainly based on chemical and biological repair.

2.2. Chemical Self-Healing

2.2.1. Concrete autogenic self-healing. Extensive testing and engineering practice have shown that concrete cracks have self-healing properties when exposed to water. During the self-healing process(Figure 2a), a series of physical and chemical reactions occur in the concrete crack[7,8]: (a) Physical cause: swelling of hydrated cement paste (HCP) near the crack faces (b) Two chemical processes: the first is the continued hydration of the cement which has not reacted hitherto due to lack of water; the second chemical process is the formation of calcium carbonate and the growth of crystals on the crack faces. (c) Two mechanical causes which are contributing to self-healing: the presence of fine particles in the water which leaks through the crack, and the fracturing of small concrete particles from the crack faces. Among them, chemical causes play a major role, so the concrete autogenic self-healing of concrete is divided into chemical self-healing. The chemical reactions of calcium carbonate formation and the growth of crystals on the crack faces are as follows[9]:

\[
\begin{align*}
    \text{H}_2\text{O} + \text{CO}_2 & \rightleftharpoons \text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \rightleftharpoons 2\text{H}^+ + \text{CO}_3^{2-} \\
    \text{Ca}^{2+} + \text{CO}_3^{2-} & \rightleftharpoons \text{CaCO}_3 \quad (\text{pH}_{\text{water}} > 8) \\
    \text{Ca}^{2+} + \text{HCO}_3^- & \rightleftharpoons \text{CaCO}_3 + \text{H}^+ (7.5 < \text{pH}_{\text{water}} < 8)
\end{align*}
\]

The autogenic healing of concrete cracks is a prolonged process, and usually only under ideal curing conditions can achieve better repair results, and it takes a long time[8,10-13]. The research on
concrete autogenic self-healing has been deepened. At present, the research in this area mainly focuses on the effects of different environments and mineral admixtures on the self-healing efficiency of concrete. Recent studies have shown that crystalline mixtures can enhance the self-healing ability of mortars due to delayed hydration and carbonation of lime and the reaction of the mixture with Ca (OH) 2 due to lime hydration [14].

2.2.2. Self-healing with permeable crystallization. The mechanism for the self-healing of permeation crystallization is the crystallization mechanism of the complexation-precipitation reaction[15]. The mechanism of complexation-precipitation reaction crystallization is considered to be that when the active chemical entering the concrete is in the high concentration zone of , it is complexed with the calcium ions ionized in the concrete to form a water-soluble, unstable calcium complex. Calcium complexes diffuse with water in the pores of the concrete, encounter unreacted cement, cement gels, etc., which are highly active, and the aggressive chemicals are replaced by more stable silicates, aluminates, etc., and crystallization and precipitation occur. The reaction converts into a crystal composition having a strength that fills the cracks and capillary pores in the concrete. The active chemical re-forms into free radicals and continues to migrate with water to the interior. Permeable crystallization self-healing concrete can repair cracks with a width of 0.05 mm and below[16]. At present, crystalline materials are often combined with other mineral admixtures to obtain better healing effect. Recent research shows that in the chloride ion environment, the combined use of pulverized fuel ash, silica fume, and crystalline admixtures can improve the self-healing performance of concrete more than in the distilled water environment. [17].

2.2.3. Self-healing with electrolytic deposition. Seaport concrete structures often use electrodeposition self-healing. The purpose of the electrodeposition method is to fill cracks and to coat the concrete surface with electrodeposits precipitated from cations in seawater to increase its resistance against substance penetrability[18,19].These effects are accomplished by providing a weak direct current between a reinforcing steel bar (cathode) in the concrete and an external electrode (anode) placed in seawater serving as an electrolyte solution(Figure 2b)[20].

Electrochemical deposition self-healing has excellent advantages in specific environments and is feasible for reinforced concrete structures, but this method is not universal[21, 22].Moreover, the repair effect is affected by the concentration and pH of the external solution, and has limitations in engineering applications[23,24].

2.2.4. Self-healing by other chemical reactions. The expansion agent can also be used for self-healing of concrete. The expansion agent will produce volume-expanded hydrate after hydration, which can heal cracks of 500 micrometers wide, however, the amount of expansion agent needs to be strictly controlled, and the excessive amount of expansion agent will lead to expansion cracking when concrete sets[25-27]. After decades of development, concrete self-healing is no longer limited to repair concrete cracks. Adding steel bar rust inhibitor to the repair agent to solve the problem of steel corrosion; using sodium silicate, calcium hydroxide, and other alkaline repair agents to supplement the hydroxide in the concrete; these are all in the self-healing area of concrete.
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Figure 2. Mechanisms of chemical self-healing and biological self-healing: (a) different causes that can lead to autogenic self-healing[8]; (b) Mechanisms of electrodeposition in a crack and on the concrete surface[20]; (c-d) Mechanism of biological self-healing[28].

2.3. Biological Self-Healing
Certain bacteria in the earth’s soil, such as Sporosarcina pasteurii, can gel loose sand together. It utilizes organic matter such as urea in the reaction environment and a source of calcium ions to rapidly precipitate calcium carbonate crystals with excellent gelation properties. This technology is called Microbial Induced Carbonate Precipitation (MICP). The basic principle of microbial induced calcium carbonate precipitation is that in a humid environment, microbial metabolism produces urease, which hydrolyzes urea to produce ammonium ions and carbonate ions. The negatively charged organic matter at the interface of the bacterial cell membrane continuously integrates calcium ions, and the carbonate ions formed by the hydrolysis of urea slowly mineralize to deposit crystals of calcium carbonate having gelation(Figure 2c-d)[28]. The complex chemical reactions of microbial calcium carbonate deposition can be simplified to:

\[
\text{CO(NH}_2\text{)}_2 + 2\text{H}_2\text{O} \rightarrow \text{CO}_3^{2-} + 2\text{NH}_4^+ \quad \text{(Microbial degradation)} \\
\text{Ca}^{2+} + \text{Cell} \rightarrow \text{Cell} + \text{Ca}^{2+} \\
\text{Cell} - \text{Ca}^{2+} + \text{CO}_3^{2-} \rightarrow \text{Cell} - \text{CaCO}_3 \quad \text{(Microbial cement)}
\]

Microbial self-healing concrete is more intelligent than other self-healing technologies and is the future direction of development. Moreover, after experimental research, microbial repair of concrete cracks is feasible, but the survival rate of microbial spores is a technical difficulty of this method[29]. PH value, temperature, nutrient solution, etc. all affect the self-healing effect of microorganisms[30]. Microbial self-healing is often combined with fiber, capsule and other repair methods to improve the survival rate and repair efficiency of bacteria[31]. Fiber-reinforced concrete has an ideal self-healing ability. Some fibers have hydrophilic properties (such as polyvinyl alcohol fibers), which can provide a nucleation site for the formation of self-healing products at the cracks, and promote the formation and growth of self-healing products. By using fiber to control crack width and provide crystallization point for self-healing products, coupled fiber and bacteria can obtain a better healing effect. PVA fiber
and carbonic anhydrase alkali-resistant bacteria are incorporated into concrete, and PVA can effectively limit the crack width while providing bacteria with a crystal nucleation point of calcium carbonate. The incorporation of fibers greatly improves the leaching and utilization efficiency of calcium ions in concrete, thereby promoting bacteria to precipitate more calcium carbonate on the fibers. In addition, the incorporation of PVA fibers increases the size of calcite; fiber-based bacterial coupling repair improves the recovery rate of flexural strength (Figure 3) [32]. The future development of self-healing concrete is also a combination of multiple healing mechanisms, thereby improving healing efficiency.

Figure 3. PVA fiber with bacteria [32]

3. Research Progress on Trigger Mechanism of Self-healing

The triggering mechanism of the self-healing process of concrete is another essential factor to realize the self-healing function, and it is the key to achieve the “intelligence” of concrete. The self-healing trigger mechanism is mainly divided into two categories: physical trigger and chemical trigger. Capsule physical triggering mainly includes four main forms: mechanical rupture, phase change, altered porosity and thermal decomposition. The chemical triggering self-healing process is also mostly used in the capsule encapsulation system. The chemical reaction is used to control the release of the wall material from the core material. According to the wall material control mechanism, the chemical triggering is further divided into conversion reaction, chemical bond cleavage, and depolymerization reaction.

At present, the self-healing mechanism of concrete is gradually developed to intelligent triggering, in which ion triggering is a triggering method with high healing efficiency. The microcapsules are made of PH-sensitive materials. When the concrete carbonization pH value is lowered, the microcapsule wall is cracked, and calcium hydroxide is released to supplement the hydroxide consumed by the carbonization of the concrete (Figure 4a) [33]. In addition, the pre-storage of the core material of the self-dissolving concrete of the capsule wall is also a more advanced self-healing triggering method. The mineral-soluble organic membrane protects the mineral material from being prematurely consumed in the early stage, and the alkali solution is based on the hardening of the concrete. Dissolution occurs and the mineral material is dormant. When cracks are generated and developed, water that penetrates the cracks will excite the mineral material for repair (Figure 4b) [34].
Figure 4. Different mechanisms of trigger: (a) PH value trigger microcapsule[33]; (b) Fundamental concept of autolytic self-healing method for cementitious materials[34].

4. Summary and Future Perspectives
(A) The self-healing mechanism of concrete is mainly based on chemical and biological repair. The future development direction is to improve the healing efficiency of concrete by combining multiple healing mechanisms; (B) Crack healing is the origin of concrete self-healing technology. However, the application of self-healing technology will be more and more extensive, and it has gradually involved concrete deterioration problems such as concrete carbonation, reinforcement bar corrosion and harmful ion erosion. (C) The technological breakthrough of the self-healing trigger mechanism is the key to achieve intelligence to heal cracks, chemical triggering methods such as ion triggering are the mainstream of future development; (D) Self-healing concrete conforms to the concept of sustainable development and green environmental protection. However, from the selection of materials to the evaluation of restoration effects to the application of practical engineering, there are still many deficiencies in self-healing technology, and a lot of research work is needed.

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