CHAPTER 25

Bio self-healing nanoconcretes

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Abstract

Concrete as the most widely used construction material is susceptible to crack when exposes to stresses. Various types of passive techniques have been introduced to fill the generated cracks, however the majority of them are not permanent, effective, and environmentally friendly. Over recent years, the embedment of an active mechanism called “self-healing mechanism” in concrete has been proposed as an alternative approach to the ineffective passive techniques. Among the investigated self-healing mechanisms, bio self-healing approach has drawn considerable attention as it can address the cracking issues by inducing calcium carbonate in a sustainable way. However, the effectiveness of bio self-healing concrete highly depends on the successful protection of bacteria in concrete matrix. So far, various types of micro-scale and recently nano-scale protecting careers have been tested to evaluate the effectiveness of bio self-healing concrete. In this chapter, the latest nanobiotechnological self-healing approaches for protection of bacteria in a harsh concrete pH are discussed.

Keywords

nanotechnology; nanoconcrete; bio self-healing; microbially induced calcium carbonate precipitation; bacteria
1 Introduction

Concrete is a composite material made up of coarse and fine aggregates bonded together with a paste of cement. Mixing aggregates with water and dry cement results in the formation of slurry that is poured or moulded easily into the desired shape; a hard matrix is formed from the reaction of the cement with water binding materials together into a stone-like durable material [1]. Concrete has become the most important material in modern construction because of its many benefits and advantages, including being cost-effective and affordable, being flexible enough to be cast into any shape, and being capable of hardening at ambient temperature [2]. In addition, concrete has excellent water and temperature resistance properties and also requires very low maintenance [3]. Concrete can be applied multi-modally and its fairly similar coefficient of thermal expansion to steel makes it a very suitable material for reinforcing with steel bars for even stronger structures [4]. Because of these features, concrete is the most widely used construction material in the world and has been used in construction of bridges, buildings, highways, dams, sidewalks, infrastructures, and even sculptures [3]. Despite its benefits and numerous applications, concrete has some undesirable properties, among them cracking, which is the focus of this chapter. Cracks are induced in concrete for a number of reasons, such as having excess water in the concrete mix, rapid concrete drying, miscalculation and excreting a higher stress to the concrete, and absence of control joints, as well as the formation of corrosion precipitation [5, 6]. Concrete continues to experience cracking, even in situations where there was strict observance of specification in design, supply, placing, and curing of the concrete structure and components [7].

When problems with concrete cracking occur, investigations typically focus on the factors and practices resulting in the cracking or those that cause excessive dry shrinkage. In the short term, concrete cracking results in loss of aesthetic value. In the interim, cracks in concrete are normal as
the natural hardening process of concrete causes them. Concrete cracks because of plastic shrinkage that forces cracks to relieve tension within the drying concrete. Expansion where the weather is hot will also result in cracking by concrete, while factors such as heaving and settling, as well as premature drying and overload can result in concrete cracking [8]. In the long term, concrete cracking will aggravate the carbonation and chloride attack processes that result in the reinforcement rusting, thereby creating weaknesses and adversely affecting the structures’ durability [9]. This not only results in structural destruction, but also the longevity of the structure is also reduced. Furthermore, the functional aspects of the structure or building are adversely affected in the long term due to cracking. If cracks occur, they should be repaired appropriately at the earliest opportunity.

Concrete cracking cannot be prevented, but it can be controlled to minimize cracking. Drying shrinkage, a common cause for concrete cracking in restrained concrete where temperature decrease and shrinkage, creates tensile stresses that can exceed the tensile strength of concrete, causing cracking can be prevented or controlled by considering the many factors contributing to dry shrinkage. The thermal coefficient of concrete, stiffness, rate of shrinkage, and creep and flow rates are affected by the grading of aggregate, the mineral composition, and the shape surface texture. The common approach to repairing cracked concrete is through manual repairs, such as sealing. However, this is a costly and cumbersome process that has other disadvantages, including degradation of structure integrity and strength. Despite the current practices in minimizing the crack formation, there is no way to eliminate the formation of crack in a concrete matrix. Therefore, incorporating self-healing mechanisms inside the concrete can be a promising solution to address these issues.
2 Self-healing concrete

Self-healing material refers to the material that are capable of repairing itself back to its original state. For cementitious materials, the concept of self-healing can naturally occur over time (autogenic) but in limited quantity. The autogenic self-healing concrete concept can be seen in old structures that remain strong and standing despite these structures having limited maintenance. The conclusion is that the cracks in these structures’ concrete partially self-heal when there is interaction between moisture and non-hydrated clinker within the cracks [10]. Modern construction methods, nevertheless, result in lowered cement quantities. As a result of this action, the available non-hydrated cement becomes less, and the consequence is a reduction in natural self-healing effect [11]. Natural cement healing ability phases start with cement hydration; followed by calcium carbonate (CaCO$_3$) precipitation, and lastly, blocking of flow paths due to the deposition of water impurities, or movement of some bits of concrete that become detached through the process of cracking [12]. The natural self-healing of cement is subject to various factors including degree of damage, temperature, concrete age, freeze-thaw cycles, and the state of the mortar.

Man-made processes to achieve self-healing in concrete have been developed, with the first process being put forth in 1994 through the use of an adhesive as a healing agent; the adhesive is encapsulated into micro capsules and upon formation of cracks, the micro capsules break and release the healing agent that then heals the crack [13]. The adhesives can be stored either in longer tubes or in short fibre. Mechanisms that are more effective were then developed afterwards to enhance or speed up concrete healing through man-made initiatives.

Self-healing concrete has immense benefits, both structural and aesthetic, as well as economical. Self-healing concrete ensures the need for concrete rebar is reasonably reduced as the cement self-
heals; usually, the cracks in cement let water in resulting in steel reinforcement corrosion that causes structural weaknesses, and/ or failure. While the initial costs involved in using self-healing concrete are higher than normal concrete, the self-healing concrete becomes more cost-efficient in the longer term due to low maintenance costs, longer life span, and higher durability. Self-healing concrete also enables self-healing of structure without any external input and also leads to significant increments in flexural and compressive strength of the concrete compared to normal concrete [10]. Self-healing concrete also enhances the resistance of the concrete towards freeze-thaw attacks while also reducing the concrete’s permeability. Self-healing concrete results in increased safety and strength because it ensures safety is automatically assured in concrete structures [14]. Because cracks in self-healing concrete are easily closed at no extra cost, the safety of a particular structure is increased as the concrete will gain 25% of its original strength; this is significantly higher than the strength gain achieved by modern methods of sealing concrete cracks which is 15%. Self-healing concrete enhances the durability of structures since self-healing concrete has a greater density, and hence greater durability compared to normal concrete [15]. Self-healing concrete has positive effects on design and architecture because increasing the life span of structure using self-healing concrete will require architects to reconsider the potential function in a specific structure/ building and the future urban space function surrounding certain buildings. These concerns will lead to designs that are highly flexible so that function can be changed easily. Further, the self-healing concrete results in reduced emissions given that the cement industry is among the top contributors to CO₂ emissions [2].
3 Different approaches for designing self-healing concrete

3.1 Chemical approaches

Use of fly ash (limestone powder- LP) and blast furnace slag (BFS); these have a significantly high self-healing capacity, although initially they are inferior in terms of strength development and early stage micro structure development [16]. The slag and fly ash particles have a low degree of hydration and when there is a crack, the unreacted particles are reactivated resulting in the crack being close as they regain strength and water impermeability. A test on the effectiveness of BFS and LP with relatively high ratio of water/binder done using four point bending tests on a pre-cracked beam after 28 days was done [17]. Water submerged specimens, the deflection capacity recovered between 65-105% from virgin specimens, a significantly higher percentage compared to air cured specimens. The micro-cracks in the water submerged specimens attained healing with significant CaCO$_3$ amounts due to continuous hydration of the cementitious materials [18]. BFS and LP have various advantages in self-healing concrete including reducing hydration heat of cement, reducing alkali aggregate permeability and reaction, increases resistance to sulphate attack and corrosion, and improving concrete workability. Further, using fly ash reduces the amount of needed cement that results in reduced costs [19]. Disadvantages of BFS and LP include negative effects on the concrete if of poor quality, causing slow setting of cement when used (fly ash), unacceptable freeze-thaw performance of the concrete, and causing slow setting and early low strength of the concrete [20].

3.2 Use of polymers

3.2.1 Encapsulated polymers

In this approach, when a crack appears, the capsules break releasing the embedded polymers such as methyl methacrylate contained in the gap caused by crack. Through capillary action, the agent
flows into the crack, causing bonding together of the crack faces and sealing the crack [21, 22]. Different healing agents can be used, for instance polyurethane which helps reduce the water permeability of the cracked surface. Brittle glass and ceramic tubes have also been utilized as encapsulation materials; however, the capsules must survive the concrete mixing process where poly vinyl alcohol fibres are used in encapsulation [10].

3.2.2 Superabsorbent polymers (SAP)

Superabsorbent polymers (SAP) materials can be used to create self-healing concrete because of a unique property they possess where hydrogels can take up large amounts of fluid of up to 500 times of their weight and retain it within their structures without dissolution. When cracks occur, SAPs become exposed to the humid environment causing them to swell and this partly seals cracks, especially from harmful intruding substances [23]. Upon swelling, the SAP particles desorb, providing the surrounding matrix with fluid for internal curing, precipitation of CaCO$_3$, and further hydration and this can completely cause the cracks to close. Concrete pH usually drops from 12.8 to between 9 and 10 when cracks occur. pH sensitive hydrogels should be used carefully as they only swell when there is fresh water penetration [24]. Advantages of using SAPs include their ability to be used to heal concrete and reverse cracks once or multiple times without external input as SAP undergo repeated swelling when exposed to moisture. This method also ensures the appearance of concrete does not change, is cost effective and requires no external input, and expands the reliability and life of the concrete, and therefore, the structure [25]. Disadvantages of this approach include possible weakening of concrete strength when many glass tubes are used that results in low recycling rate of such cement with polymers.
3.3 Biological approaches

Bio self-healing concrete is a product that produces limestone through biological processes capable of repairing itself back to the original state and heal cracks appearing on concrete structures surfaces. The generation of self-healing concrete is made possible by the addition of Bacillus genus bacteria, along with a calcium-based nutrient; further, phosphorus and nitrogen source can be added to the ingredients when concrete is being made. Different biological approaches can be employed to design bio self-healing concrete which were extensively discussed in previous studies [2, 26-28]. Various bacterial forms can precipitate CaCO$_3$ in both laboratory and natural conditions. The following factors govern CaCO$_3$ precipitation; (i) the concentration of calcium, (2) pH values, (3) nucleation sites, and (iv) dissolved Inorganic carbon (DIC) concentration. The bio-agents can remain dormant within the concrete for two millennia; however, whenever there is a damage to the concrete and water/moisture starts seeping in through the developed cracks, the bacteria spores germinate on getting into contact with the water that is also aided by the nutrients [29]. This causes the limestone on the cracked surface to solidify, sealing the crack. During the bacterial conversion of the calcium lactate to create limestone, there is oxygen consumption, and this has an extra advantage as far as the self-healing is concerned [30]. Oxygen is an essential element in steel/iron corrosion and when all or most of it is consumed through the bacterial conversion and this reduces the chances of rust while increasing the durability of the steel reinforcement. Calcium carbonate is among the materials most compatible with concrete and its production is induced through a biological process using bacteria to cause self-healing of concrete [31]. The presence of water results in rapid germination and multiplication of the bacterial spores where they convert the nutrient to limestone within days, although this can take place over weeks in cold temperatures. The advantages of using bacteria for self-healing concrete include the ability to repair cracks with no need for external input, increases in durability, resistance to freeze thaw.
attacks, reduction in concrete permeability, and reduced steel corrosion that would occasion rebar in addition to the bacteria being harmless to human health. Disadvantages of the approach include high costs of the concrete, almost double that of regular concrete, bacterial growth which is not good in any media, the matrix holding the bio-agent can become shear fault zones in the concrete given they take up about 20% of the concrete volume [32].

Microorganisms attain calcium precipitation through two main pathways, namely (i) the sulphur cycle in which sulphur reduction is done by sulphur reducing bacteria in anoxic environments; (ii) through the nitrogen cycle where urea/ uric acid and amino acid oxidative determination occurs to cause degradation using ureolytic bacteria in aerobic environments as well as in anaerobic nitrate reduction conditions [33]. Urea hydrolysis is among the most common microbially induced CaCO$_3$ precipitation (MICP) through urease enzyme in calcium abundant environments. This method leads to a hike in inorganic dissolved carbon concentration and high pH [34]. The hydrolysis of urea is propelled by urease in bacterial environment to form ammonia and carbon dioxide leading to the pH and carbonate concentration rising. A single mole of urea creates a single mole of ammonia and a single mole of carbonate through intracellular hydrolyzation that in turn forms an extra one mole of ammonia and carbonic acid. This process has various advantages, including significantly influencing concrete strength positively, results in concrete of lower permeability than normal concrete, and provides greater resistance to freeze-thaw effects [35].

3.4 Bio self-healing concrete preparation and limitation

Bacteria as the main components of bio self-healing concrete are directly mixed with other concrete ingredients that is extremely alkaline environment for the bacterial growth and metabolism. This is one of the limitations of directly using bacteria in concrete as a means of creating self-healing concrete as the highly alkaline environment is very harsh and the bacteria
will or may not survive to achieve its intended use for self-healing. The other limitations in designing bio self-healing concrete are the excreted shear stresses to the bacteria during mixing and a very dry condition of hardened concrete. In these conditions, most organisms cannot survive and if do, they barely induce calcium carbonate.

One method entails the use of micro scale materials like silica when using ureolytic bacteria to make self-healing concrete that involves the process of blending ureolytic cells that have been freeze dried with an aqueous solution to create a base mixture. The base mixture is then mixed with silicate forming compounds to create a blend of silica that encapsulates the ureolytic cells which is then freeze dried (the encapsulated ureolytic cells) [36]. This method will ensure the ureolytic cells remain viable and can survive the harsh alkaline environment which is created when concrete is made (mixing water and cement). Further, the silica will ensure the hardened concrete does not damage the ureolytic cells and prevent their premature inactivation before cracks occur.

Despite the usefulness of microscale materials as the protective career for bacterial agent, it has been reported that the addition these materials can weaken the integrity of concrete matrix as the binding efficiency significantly decreases [26, 28]. The problems associated with the harsh environment of concrete for microorganisms can be solved using nano technologies in which nano materials are used to encapsulate/adsorption the various bacteria. Using a novel approach with a combination of nano technologies can ensure better protection of bacterial agent in concrete structures through using innovative capsulation techniques.

4 Nanomaterials for self-healing concrete

Nanotechnology refers to the technical understanding of the physical world at a very miniscule scale and it is concerned with constituents or particles or nano-scale dimensions with sizes ranging
from 1 to 100 nm [37, 38]. These materials have been, and are being actively researched for their application in construction in the development of high-performance concrete [39]. Nano products can manipulate structure at nano-scale level resulting in multifunctional, tailored, cementitious composites that have superior durability and mechanical performance to be generated. Such composites have better features, including self-cleaning, self-sensing capabilities, self-healing, self-control of cracks, and high ductility. Nanotechnology is achieved in concrete through the incorporation of nano-scale materials such as nano-TiO₂, nano-SiO₂, nano-Al₂O₃, nano-clays, and nano-Fe₂O₃, use of nanotube fibres such as carbon nanotubes (CNT) and carbon nano fibres (CNF) [40]. Nanotechnology gives useful insights on how nano-materials can be used in concrete to achieve benefits that include protection against ingress, concrete restoration, moisture control, structural strengthening, resistance to chemicals, increased resistivity, passivity preservation, cathodic control and protection [38]. Carbon nanotubes, for instance, have a tensile strength of nearly 20 times higher than steel, making them an ideal reinforcements in structural applications such as high rise buildings and in bridges [41]. These novel approaches have been tested experimentally and show promising initial results [42]. Nanotubes and Nano-fibers based on polymers are highly promising nano materials that hold much promise for applications in the building construction sector [43].

Recently, nanotechnological approaches have been also used in designing bio self-healing concrete. Researchers have successfully fabricated magnetic iron oxide nanoparticle (Fe₃O₄) to be used for efficient protection of bacteria when they are mixed with concrete ingredients [31, 44]. They used solid-state fermentation to trigger biomineralization of calcium carbonate once a crack occurs. To achieve self-healing concrete, the researchers immobilized bacteria with nanoparticles of iron to aid the bacteria become more active and increase their tolerance to harsh environments,
such as those found in concrete that make microbial growth difficult. The negative net charge in bacterial cell walls due to the availability of functional groups (carboxyl or phosphate groups) in teichoic acids, provides a promising microenvironment for adsorption of nanoparticles [45]. As shown in Figure 1, the physical adsorption is governed by covalent binding/ or electrostatic forces between magnetic nanoparticles and the bacterial cell walls.

Figure 1 Schematic view of iron oxide nanoparticle (ION) adsorption on gram positive bacterial cell wall [45].

To study the bacterial growth and capability to induce CaCO$_3$ precipitation, Seifan et al. [31, 44] fabricated two types of nanoparticles namely naked Fe$_3$O$_4$ and amino acid coated Fe$_3$O$_4$. Their results indicated that amine-modified nanoparticles could effectively promote bacterial growth, while the presence of naked particles significantly increased the production of CaCO$_3$. To evaluate the effect of magnetic immobilized bacteria on self-healing characteristic of concrete, the optimum concentration of designed bio-agent was mixed with concrete and the healing process was
monitored within 28 days incubation. As illustrated in Figure 2, the utilization of nanobiotechnology could successfully improve the self-healing efficiency.

![Figure 2 Stereomicroscopic images of: (a–b) crack healing process in bio-concrete specimen before and 28 days after water exposure, and (c–d) induced CaCO$_3$ precipitation in crack and pore after treatment [46].](image)

Apart from self-healing characteristics, the effect of nano bio-agent on mechanical properties of concrete is also an important factor to be considered. It has been shown that the presence of immobilized bacteria with nanoparticles can significantly reduce the concrete water absorption [8, 45]. This phenomenon is mainly attributed to the production of CaCO$_3$ crystals by microorganism that fills the pores and microcracks in concrete.

The functional properties of cement-based composites modified with nanoparticles, in particular Fe$_3$O$_4$ nanoparticles, have been previously described [47]. In addition, it was evidently shown that the implementation of nanotechnology could successfully address the limitations associated with
the production of self-healing concrete. However, there are still few challenges in the large-scale production of bio self-healing concrete modified with nanoparticles which need to be overcome. The first challenge is the relatively high costs of nanomaterial fabrication in comparison to the price of concrete. The main source of costs is related to the instrument used for nanoparticle synthesis because of the complexity of the process. The implementation of alternative techniques such as plant-mediated nanoparticle synthesis method can be a solution to reduce the production costs of nanomaterials. The relatively high cost of bio-agent preparation (nutrients and microbial growth) is another limitation need to be addressed. To reduce the cost of bio-agent preparation, the utilization of nutrients from industrial waste can be helpful. The long performance of bio self-healing nanoconcrete under various environmental conditions is another critical aspect needs to be considered. Therefore, future research should be focused on such challenges to develop bio self-healing nanoconcrete in the near future.
References


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