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Abstract

Concrete is one of the most used materials in the world with robust applications and increasing demand. Despite considerable advancement in concrete and cementitious materials over last centuries, infrastructure built in the present world with these materials, such as dams, roads, bridges, tunnels and buildings requires intensive repair and maintenance throughout its design life. Self-healing concrete and cementitious materials, which have the ability to recover after initial damage, have the potential to address these challenges. Self-healing technology in concrete and cementitious materials can mitigate the unnecessary repair and maintenance of built infrastructure as well as overall CO₂ emission due to cement production. This chapter provides the state-of-the-art of self-healing concrete and cementitious materials, mainly focusing on autogenic or intrinsic self-healing using fibre, shrinkable polymers, minerals and supplementary cementitious materials, and autonomic self-healing using non-traditional concrete materials such as microscale to macroscale capsule as well as vascular systems with polymeric, mineral and bacterial agents.

Keywords: concrete, autogenic self-healing, autonomic self-healing, healing process, mineral, polymer, microstructure

1. Introduction

Concrete is the most used and efficient construction material in the world. It is durable, can resist high compressive stress, is cheaper than most of the construction materials and can be moulded in a wide variety of shapes. Despite that concrete cracks due to its weakness in tension, shrinkage, fatigue loading, and under the action of environmental conditions. These microcracks can reduce concrete’s toughness, increase permeability, which can ultimately lead to the reduction of concrete’s structural integrity, durability and life span. Self-healing concrete in that context offers an actual solution.

Any process whereby concrete recovers its performance after initial damage is termed self-healing in concrete [1]. A typical self-healing in cementitious materials is presented in Figure 1. The concept of concrete self-healing has evolved from that found in biological life forms, that is, plants and animals that naturally exhibit self-healing performance when any damage appears.

According to Schlangen and Joseph (Cited in [2]), the strength of concrete gradually decreases when the first repair is required. Also, commonly, a second repair is required in concrete after 10–15 years. However, the initial repair period
can be extended considerably with the application of self-healing technology in concrete. Self-healing leads to a longer material lifetime, and it involves no repair and maintenance costs.

This chapter presents the state-of-the-art of self-healing in concrete and cement-based materials. It discusses advancements in this field and limitations. The next section (Section 2) presents the concept of self-healing in concrete and measurement techniques. Then the chapter describes major developments in different self-healing concrete field.

2. Self-healing concrete systems and measurement techniques

The self-healing system in concrete is principally divided into two types, autogenic and autonomic [1]. Autogenic self-healing in concrete is an intrinsic material-healing property wherein the self-healing process initiates from the generic materials present. For example, cementitious materials exhibit a self-repairing ability due to the rehydration property of unhydrated cement remaining on the crack surface. In contrast, a self-healing process that involves the incorporation of material components that are not traditionally used in the concrete is termed autonomic self-healing [1].

Figure 1. Example of self-healing concrete and cementitious systems (Adopted from [3]).

Figure 2 presents the developed autogenic and autonomic self-healing systems. One of the principal causes of autogenic self-healing is the hydration of unhydrated cement remaining in the matrix. Then again, the volume of healing products formed in this process is limited. Hence, the autogenic self-healing is effective within the crack width up to 50–150 μm [4]. Autogenic self-healing performance is higher in early age due to high content of unhydrated cement, and parameters such as compressive stress [5] to restrict crack and wet-dry cycles [6] can increase the healing performance. Autogenic healing performance can also be enhanced using fibres to restrict crack opening and the use of superplasticizer in engineered cementitious composite (ECC) to reduce w/c ratio [6]. Cardiff University research group introduced polyethylene terephthalate (PET) tendons [7], a shrinkable polymer activated with a heating system inside the concrete structural element to compress and close the crack enhancing the autogenous healing process. Considerable enhancement in healing performance is also possible to achieve using optimum supplementary cementitious materials (SCMs) and smart expansive minerals [3, 8–22]. Autonomic self-healing in concrete, in contrast to the autogenous healing
process, requires the release of the healing agent from reserved encapsulation or a continuous vascular network. Common encapsulating shell materials are glass [23, 24] and polymers [1, 25, 26]. Healing agents in autonomic self-healing are epoxy resins, cyanoacrylates (super glues), alkali-silica solutions [23, 24, 27, 28], methyl methacrylate [24, 28], expansive minerals [16, 29], hydrogel [30] and bacteria-based microorganisms [31–33].

Figure 2.
Self-healing concrete systems.

Figure 3.
Self-healing performance in concrete measurement techniques.
Self-healing performance in concrete is assessed using visual observation, mechanical strength recovery, permeability, durability improvement and microstructural evaluation (Figure 3). There are three fundamental factors in evaluating the self-healing: visual crack sealing and the identification of healing compounds causing it, the improvement of the durability performance and the recovery of mechanical strength properties [3, 15–21]. The mechanical strength recovery is limited in most of the concrete self-healing process. Hence, the most reliable self-healing performance is based on the physical crack closure, durability improvement, that is, permeability reduction parameters, and microstructural evaluations.

3. Autogenous self-healing of cement and concrete

Autogenous self-healing in cement was spotted early in the twentieth century by Lauer and Slate [34], and the concept was gradually established by different researchers [35, 36]. The crystallisation of calcium carbonate within the crack is the primary process in autogenous self-healing of matured concrete [35]. Reactions involved in the deposition of calcium carbonate are presented in Eqs. (1)–(3). In those reactions, CO₂ dissolved in water from the air, and the calcium ion Ca²⁺ is derived from concrete.

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

Reasons for autogenous self-healing proposed by different researchers [36] are: (i) Further reaction of the unhydrated cement, (ii) expansion of the concrete in the crack flanks, (iii) crystallisation of calcium carbonate, (iv) closing of the cracks by fine particles existing in the water and (v) closing of the cracks by spilling off loose concrete particles resulting from the cracking. This five action model is schematically presented in Figure 4.

The understanding and improvement of autogenous self-healing have developed in four major directions (Figure 2). These are: (i) manipulation of existing
conditions, such as age, compressive stress and curing condition (e.g. wet-dry cycle); (ii) fibres to restrict cracks (e.g. ECC); (iii) shrinkable polymers to initiate internal stress after cracking to shrink the cracks and (iv) cement-compatible mineral additives.

3.1 Existing condition influence in autogenous self-healing

Autogenous self-healing of concrete is significantly influenced by its age, internal stress and curing conditions. Early age concrete naturally heals rapidly due to autogenous healing. Concrete prisms with cracks up to 50 μm were autogenously healed under 0.1, 1 and 2 Mpa compressive stresses [5] (Figure 5a). The crack face comes into contact by the impelled compressive stress. Hence, the concrete specimens cured under any amount of compressive stress healed much better than specimens cured under no compression stress (Figure 5b). Only a specific amount of compression is required to keep the crack faces in contact. Samples that are submerged in water during curing recovered their strength. In contrast, specimens stored in 95% RH for 3 months did not heal at all. This is due to insufficient hydration in the high humid condition, which is not enough to trigger the healing process.

3.2 Fibre action in autogenous self-healing

Fibres can restrict the propagation of crack width, and smaller crack width is favourable for enhanced autogenous healing in concrete. Fibre is a common feature in Fibre-Reinforced Composite Concrete (FRCC) and ECC. Randomly distributed fibres can bridge over cracks, which can decrease the crack width and block the migration of aggressive agents (e.g. chloride ions and CO$_2$) [6, 37]. These properties improve the autogenous self-healing capacity of concrete and composites. A series of wetting and drying cycles on ECC was carried out by [6] to mimic self-healing performance in outdoor environments. Through self-healing, crack-damaged ECC recovered 76–100% of its initial resonant frequency value and attained a distinct rebound in stiffness. The tensile strain capacity after self-healing recovered close to 100% that of virgin specimens without any preloading. This was found even for the specimens deliberately pre-damaged with microcracks by loading up to 3% tensile strain. It takes about four to five wet-dry cycles to attain the full benefit of self-healing. The use of high cement content, low water-to-cement ratio also increases the autogenous self-healing capacity of ECC. However, FRCC, ECC and

![Figure 5](http://dx.doi.org/10.5772/intechopen.92349)
HFRCC are costly and maintaining homogeneity of fibres in the matrix for consistent self-healing is challenging.

### 3.3 Shrinkable polymers action in autogenous self-healing

The shrinkable polymers such as PET can shrink when activated by heating in a specific condition. This shrinkage stress can be used for pre-stressing the concrete thus bringing crack-tip closure for efficient healing. Cardiff University self-healing research team is working with the original crack-closure system for cementitious materials using shrinkable polymer tendons [7]. The system involves the incorporation of unbonded pre-oriented polymer tendons in cementitious beams (Figure 6). Crack closure is achieved by thermally activating the shrinkage mechanism of the restrained polymer tendons (PTs) after the cement-based material has undergone initial curing. Upon activation, the polymer tendon completely closes the preformed macrocracks and imparts significant stress across the crack faces. This enhances the autogenous self-healing process in concrete.

### 3.4 Mineral admixture in autogenous self-healing

Supplementary cementitious materials (SCMs) and expansive minerals compatible with cement can improve the self-healing capacity of concrete. Depending on minerals, it can serve either or both functionalities, that is, to remain considerably un-hydrated after the initial mixing stage, and to produce compatible expansive hydrated compounds that can heal cracks [19]. Both these functionalities contribute to the autogenous healing process. A summary of mineral additives use for self-healing is illustrated in **Table 1**. SCMs such as fly ash, silica fumes and blast-furnace slag, and expansive minerals such as MgO, calcium sulphaaluminate (CSA), lime, bentonite clay and crystalline additive (CA), have been mostly used for improving the concrete autogenous self-healing performance.

![Figure 6](image)

**Figure 6.** (a) Schematic of shape memory PET polymer tendon, and (b) photo of the setup (Both reproduced from [7]).
### Minerals Composition Damage type Curing condition Performance (healed crack width in time etc.) Source

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Composition</th>
<th>Damage type</th>
<th>Curing condition</th>
<th>Performance</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSA, H, A, L, Mont.</td>
<td>Up to 10% (concrete)</td>
<td>3 PB, mechanical</td>
<td>Water</td>
<td>160–220 μm in 33d</td>
<td>[8]</td>
</tr>
<tr>
<td>CSA</td>
<td>4.44 and 15.24% of cement (concrete)</td>
<td>Tension force</td>
<td>Still/continuous flow water</td>
<td>Reduced flow in 100 μm cracks, continuous flow is efficient</td>
<td>[38]</td>
</tr>
<tr>
<td>CSA, CA, H, A, L, Mont.</td>
<td>PC with 10% CSA and 1.5% CA</td>
<td>Sp. tensile test</td>
<td>Water</td>
<td>100–400 μm in 56 d</td>
<td>[9]</td>
</tr>
<tr>
<td>Silica, CEA, bentonite, CA</td>
<td>8% individual combination up to 14%</td>
<td>Compression, sp. tensile</td>
<td>Water, wet-dry, air, freeze-thaw</td>
<td>220 μm in 2 weeks</td>
<td>[11]</td>
</tr>
<tr>
<td>FA, SF, CA</td>
<td>OPC, OPC + 30%FA, OPC + 10%SF, OPC + 1%CA</td>
<td>Splitting tensile test</td>
<td>Water</td>
<td>50 μm in 12d larger cracks heal efficiently with SF</td>
<td>[39]</td>
</tr>
<tr>
<td>FA</td>
<td>15–20% with PC (paste)</td>
<td>Shrinkage microcracks</td>
<td>Water</td>
<td>Meso-macro pores at 91, 182 and 364 d</td>
<td>[40]</td>
</tr>
<tr>
<td>FA</td>
<td>5–15% wt. of sand (concrete)</td>
<td>Freeze-thaw</td>
<td>Water</td>
<td>Improve DME over 90% in 28d</td>
<td>[41]</td>
</tr>
<tr>
<td>BFS</td>
<td>OPC + 50% BFS</td>
<td>Mechanical</td>
<td>Water</td>
<td>Product formation is three times faster for CEM I</td>
<td>[42]</td>
</tr>
<tr>
<td>FA, slag</td>
<td>30–40% of cement (mortar)</td>
<td>Shrinkage</td>
<td>Water</td>
<td>Improvement in compressive strength</td>
<td>[43]</td>
</tr>
<tr>
<td>1L, slag, FA</td>
<td>30, 50% FA; 50, 75, 85% slag (paste/mortar)</td>
<td>3 PB, mechanical</td>
<td>Water</td>
<td>200 μm in 42d</td>
<td>[12]</td>
</tr>
<tr>
<td>Slag</td>
<td>66% of cement (paste)</td>
<td>Sliced, mechanical</td>
<td>Ca(OH)₂ solution</td>
<td>60% of 10 μm in 240 h</td>
<td>[44]</td>
</tr>
<tr>
<td>Bentonite</td>
<td>Nanoclay in mortar as internal water reservoir</td>
<td>Mechanical</td>
<td>Water</td>
<td>Enhanced hydration for self-healing</td>
<td>[45]</td>
</tr>
<tr>
<td>Bentonite, slag, L</td>
<td>2% PVA by vol. Length = 8 mm, dia = 40 μm</td>
<td>Mechanical</td>
<td>Water, wet-dry cycle, air</td>
<td>Nanoclay improves the reloading deflection capacity</td>
<td>[46]</td>
</tr>
<tr>
<td>Quicklime, FA</td>
<td>(3%) on fly ash-PC cement pastes</td>
<td>Mechanical</td>
<td>Water</td>
<td>Increased SiO₂ solubility extra Ca(OH)₂</td>
<td>[14]</td>
</tr>
<tr>
<td>Expanded clay LWAs</td>
<td>Na-MFP and PC coated (mortar)</td>
<td>Mechanical</td>
<td>Water</td>
<td>Absorption decrease sodium, phosphorous and fluoride, CH</td>
<td>[47]</td>
</tr>
<tr>
<td>CSA</td>
<td>PVA coated, up to 10% by wt. of cement (mortar, 1:3)</td>
<td>3 PB</td>
<td>Water</td>
<td>&lt;100 μm in 13d, 100–200 μm in 14d, &gt;200 μm in 16d</td>
<td>[48]</td>
</tr>
<tr>
<td>CA: cement + sand + microsilica</td>
<td>1–2% of cement</td>
<td>4 PB</td>
<td>Water, open air</td>
<td>60% cracks sealed under open air condition</td>
<td>[49]</td>
</tr>
</tbody>
</table>
SCMs to enhance autogenous self-healing

Fly ash (FA) and silica fume (SF) and blast furnace slag (BFS) are mostly used as SCMs in the OPC system to improve concrete self-healing performance [12, 13, 37–43]. The substitution of FA 15–20% in OPC paste system has increased the volume of C-S-H gel and reduced meso-macropores, increasing the autogenous self-healing performance [40]. Watanabe et al. [41] replaced about 5–15% wt. of sand with FA in concrete and found a better dynamic modulus of elasticity recovery at 5% replacement and improving trend at 15% under the non-destructive ultrasonic test method. While freezing and thawing decreased dynamic modulus to 80% of the initial state, curing in water recovered it to over 93–98% after 28 days.

FA and SF, and a crystalline additive (CA) mineral were used for improving the self-healing performance of concrete [39]. CA was composed of 35.58% CaO, 16.81% SiO₂, 15.22% Na₂O, 1.98% Fe₂O₃, 1.93% Al₂O₃, and 1.29% MgO. Four different mixes (OPC, OPC + 30%FA, OPC + 10%SF, and OPC + 1%CA) were compared. Larger cracks (0.05–0.20 mm) healed better with SF additives. Microcracks in the range of 0–0.05 mm in CA additive mixes completely healed within 12 days.

The blast furnace slag (BFS) was used individually and in combination with FA and other minerals for improving self-healing properties. Fibre-reinforced cement composition with a local waste BFS and limestone powder (LP) in a mix proportion of 1:1:2.2 (C:BFS:LP), 0.5 w/b-ratio and 0.018% total mass of superplasticizer demonstrated improved self-healing performance [13]. The specimens cured under water recovered 65–105% deflection capacity compared to virgin specimens, while specimens cured in the air recovered only 40–60%. Small 25-μm cracks were healed efficiently, while larger cracks such as 60 μm were not healed completely. A higher proportions of BSF (50%) substitution in OPC decreases the formation of the healing material at an early age, which alters after 22 days [42]. However, optimum self-healing ability for the mixing content of slag and FA were 30 and 40%, respectively [43].

A considerable proportion (up to 70% of total weight) of slag and two classes fly ash (FA) were used as SCMs in ECC for improving autogenous self-healing performance [50]. Microscopic observation showed that slag-ECC healed up to 100-μm width crack. On the other hand, both F- and C-Class FA containing ECC sealed up to 50- and 30-μm width cracks, respectively. A microstructural investigation on the self-healed materials revealed that it was mostly composed of calcite and C-S-H gels and that composition varied with the supplementary minerals used (Figure 7).
A higher amount of healing products of slag-ECC formed due to the higher pH value of pore solution and CaO content.

3.4.2 Expansive minerals to improve autogenous self-healing

Several types of expansive minerals can enhance autogenous self-healing performance of concrete. Calcium sulfoaluminate (CSA) is one of the popular expansive minerals used for improving healing capacity in concrete [8, 9]. A self-healing agent (SHA) composed of silicon oxide (71.3%) and sodium aluminium silicate hydroxide \(\text{Na}_{0.6}\text{Al}_{4.70}\text{Si}_{7.02}\text{O}_{20}(\text{OH})_{4}\) (15.4%) along with various types of carbonates such as \(\text{NaHCO}_3\), \(\text{Na}_2\text{CO}_3\) and \(\text{Li}_2\text{CO}_3\) (etc.), and minerals such as bentonite clay (montmorillonite), feldspar and quartz was also used as an expansive self-healing agent [8]. Cracks of about 150 \(\mu\)m were healed within 33 days in the concrete with SHA, forming alumina silicate and modified gehlenite phases (CASH: calcium aluminosilicate hydrate). The reported healing mechanism was a swelling effect initiated by montmorillonite, and then expansion and re-crystallisation triggered by aluminosilicate with calcium ion. Ferrara et al. [51] used an active silica-based crystalline admixture (CA) as an expansive agent in cement and sand to improve the self-healing potential of raw concrete structures. Crack sealing of over 70–80% was required for reasonable mechanical performance to be recovered, such as stiffness (larger than 20%). The healing compounds formed by the crystalline admixture are similar to cement hydration products such as ettringite and calcium silicate hydrates.

Magnesium oxide (MgO), bentonite clay and quicklime were used in different proportions to enhance the autogenous self-healing capacity of concrete and cementitious materials [3, 16–21]. Substitution of PC with up to 12.5–15% by a mix of the three expansive mineral agents, MgO 5–7.5%, bentonite clay 2.5–5%, and quicklime 2.5–5%, results in optimum enhancement of the autogenous self-healing in the cement mix [17, 18]. A typical crack healing image is presented in Figure 8 that shows how efficiently the expansive mineral containing PC mix sealed 170-\(\mu\)m crack in 28 days. The flexural strength recovery and crack sealing efficiency of early age (1 day) cracked specimen was enhanced up to 48 and 39%, respectively, in an expansive mineral containing cement mix, compared to the 100% PC cement mix. The permeability (gas permeability coefficient) decreased by about 70% in the

![Figure 7.](image)

**Figure 7.**
Self-healing materials, (a) XRD and (b) SEM image with EDX element detection (Both reproduced from [50]).
expansive mineral containing mix compared to the 100% PC cement mix. Besides common healing compounds, calcite, portlandite, ettringite and C-S-H, MgO formed brucite, other magnesium hydro-carbonate products. Although, the healing capacity of cementitious materials decreases with the increase in the age of cement paste mix at crack formation, expansive minerals improved the autogenous self-healing capacity of PC mixes at all ages compared to the 100% PC paste [18].

Expansive minerals combination, that is, MgO, bentonite clay and quicklime can improve the autogenous self-healing capacity of drying shrinkage cracks in the cementitious materials. The maximum healable drying shrinkage cracks width in

Figure 8.
The typical crack sealing pattern in 28 days: (a) 100% PC cement mix and (b) cement with expansive minerals (Reproduced from [17]).

Figure 9.
Ternary diagrams of healing compounds EDX computed atomic mass percentage formed in PC-MgO cement mixes (Reproduced from [2]).
100% PC and PC-expansive minerals mixes were up to 160 and 400–500 μm, respectively, after 28 days healing in water [3, 19]. Contained expansive minerals, such as reactive MgO can enhance healing compounds within the crack (Figure 9) to effectively heal the crack.

Expansive minerals can also improve the self-healing capacity of ECCs [46, 52]. Bentonite (Na-Montmorillonite) as a nanoclay was mixed with slag and limestone powder and used in ECC to improve its self-healing performance [46]. An ECC-MgO system resulted in higher flexural strength recovery of pre-cracked prismatic specimens cured under accelerated autoclaved conditions compared to their pre-cracked ECC without MgO [52]. The combined effect of fibre to restrict crack and the expansive minerals to heal the crack is promising.

4. Autonomic self-healing system in concrete

In the autonomic self-healing system, different kinds of active healing agents are encapsulated into the concrete or composites. Popular encapsulation systems are microvascular glass tube network [23, 24] and microcapsules [1, 25, 26]. Table 2 presents an overall conception of encapsulation materials and technical developments for the autonomic self-healing process. Typically a mobile liquid healing agent is always required. Less viscosity of healing agents is expected so that it can enrich a longer crack path in the damage zone, including microcracks [54]. Healing agents also should possess the ability to make a strong bond between the crack faces.

4.1 Autonomic microvascular and tabular capsules for self-healing

Capillary glass tubes are a popular choice for the microvascular network or tabular system to carry the healing agent into the concrete matrix [23, 24, 27, 28]. Diameters of the glass tubes typically range from 0.8 mm [23] to 4 mm [55]. A cyanoacrylate (<5 cP viscosity) enclosed in capillary tubes (0.8 mm inner diameter and 100 mm length), with 50 μl capacity and sealed the end with silicon considerably recovered flexural stiffness in beams [23]. Mihashi et al. [28] used embedded glass pipes with two types of healing agent, alkali-silica based and two-part epoxy resin. Considerable strength recovery performance was noted with both types of the healing agent within the crack range between 300 and 500 μm. Nevertheless, efficient mixing of two-component resin inside the crack was a challenging issue.

Cardiff University researchers have investigated the type of healing agent, delivery technique, mortar mix design and the quantity of steel reinforcement used [27]. They used three popular healing agents, (i) epoxy resins following [28], (ii) cyanoacrylates following [23] and (iii) alkali-silica solutions following [28]. During the first and second loading cycles under a three-point bend test, both primary and secondary healing occurs. Low-viscosity (typically 5 cP) single-agent cyanoacrylate adhesive resulted in optimum self-healing due to its efficient infiltration into microcracks. However, healing agents carried into the cracks are limited due to the capillary action [27]. This limitation can be eliminated with the use of an open-ended system.

The most recent advancement of a vascular network system in concrete was used in a filed trail of a road improvement scheme by Materials for Life (M4L) project [56]. The vascular network systems with shape memory polymer tendons (PET) were combined in large-scale structural elements (Figure 10). The self-healing performances were promising in this field trial.
<table>
<thead>
<tr>
<th>Capsule for self-healing</th>
<th>Shell material</th>
<th>Core material</th>
<th>Øi (μm)</th>
<th>Øo (μm)</th>
<th>Wall thickness (μm)</th>
<th>Length (mm)</th>
<th>Mixed in</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spherical</td>
<td>Expanded clay</td>
<td>Na$_2$PO$_4$</td>
<td>x</td>
<td>4000</td>
<td>x</td>
<td>x</td>
<td>√</td>
</tr>
<tr>
<td></td>
<td>Expanded clay</td>
<td>Bacteria</td>
<td>x</td>
<td>1000-4000</td>
<td>x</td>
<td>x</td>
<td>√</td>
</tr>
<tr>
<td></td>
<td>Expanded clay</td>
<td>CaC$<em>6$H$</em>{10}$O$_6$</td>
<td>x</td>
<td>1000-4000</td>
<td>x</td>
<td>x</td>
<td>√</td>
</tr>
<tr>
<td>Diatomaceous earth</td>
<td>Bacteria</td>
<td></td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>√</td>
</tr>
<tr>
<td></td>
<td>Gelatin</td>
<td>Acrylic resin</td>
<td>—</td>
<td>125-297</td>
<td>—</td>
<td>x</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>Gelatin</td>
<td>Epoxy</td>
<td>—</td>
<td>50</td>
<td>—</td>
<td>x</td>
<td>√</td>
</tr>
<tr>
<td></td>
<td>Gelatin</td>
<td>Tung oil</td>
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<td>50</td>
<td>—</td>
<td>x</td>
<td>√</td>
</tr>
<tr>
<td></td>
<td>Gelatin</td>
<td>Ca(OH)$_2$</td>
<td>—</td>
<td>50</td>
<td>—</td>
<td>x</td>
<td>√</td>
</tr>
<tr>
<td></td>
<td>Wax</td>
<td>Retarder agent</td>
<td>—</td>
<td>120</td>
<td>—</td>
<td>x</td>
<td>√</td>
</tr>
<tr>
<td>Paraffin</td>
<td>Water</td>
<td></td>
<td>—</td>
<td>900</td>
<td>—</td>
<td>x</td>
<td>—</td>
</tr>
<tr>
<td>Cement + paraffin</td>
<td>SAP</td>
<td></td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>x</td>
<td>—</td>
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<tr>
<td></td>
<td>UF</td>
<td>Epoxy</td>
<td>—</td>
<td>120</td>
<td>4</td>
<td>x</td>
<td>√</td>
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<td>UFF</td>
<td>Epoxy</td>
<td>—</td>
<td>20-70</td>
<td>—</td>
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<tr>
<td></td>
<td>PU</td>
<td>Na$_2$SiO$_3$</td>
<td>—</td>
<td>40-800</td>
<td>—</td>
<td>x</td>
<td>√</td>
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<tr>
<td></td>
<td>Silica gel</td>
<td>MMA/ TEB</td>
<td>—</td>
<td>4.15</td>
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<tr>
<td></td>
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<td>Epoxy</td>
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<td>—</td>
<td>—</td>
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<tr>
<td></td>
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<td>Na$_2$SiO$_3$</td>
<td>—</td>
<td>5000</td>
<td>—</td>
<td>x</td>
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<td>Silica</td>
<td>Mineral oil$_1$, Na$_2$SiO$_3$</td>
<td>—</td>
<td>300-700</td>
<td>5-20</td>
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<tr>
<td>Cylindrical</td>
<td>Glass</td>
<td>CA</td>
<td>800</td>
<td>1000</td>
<td>100</td>
<td>100</td>
<td>/</td>
</tr>
<tr>
<td></td>
<td>Glass</td>
<td>CA</td>
<td>800, 1500, 3000</td>
<td>—</td>
<td>—</td>
<td>75, 75, 100</td>
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</tr>
<tr>
<td></td>
<td>Glass</td>
<td>epoxy</td>
<td>3000-4000</td>
<td>5000-7000</td>
<td>—</td>
<td>250</td>
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<tr>
<td>Shell material</td>
<td>Core material</td>
<td>Øi (μm)</td>
<td>Øo (μm)</td>
<td>Wall thickness (μm)</td>
<td>Length (mm)</td>
<td>Mixed in</td>
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<td>Glass</td>
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<td>3200</td>
<td>4000</td>
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<td>200</td>
<td>/</td>
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<td>Glass</td>
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<td>—</td>
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<td>—</td>
<td>63.5</td>
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<tr>
<td>Plant fibre</td>
<td>—</td>
<td>40-188</td>
<td>—</td>
<td>—</td>
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<tr>
<td>PP with wax</td>
<td>MMA</td>
<td>6150</td>
<td>11,400</td>
<td>450</td>
<td>—</td>
<td>/</td>
<td></td>
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<tr>
<td>concentric glass capsule</td>
<td>MgO, bentonite, lime</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>√</td>
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</tr>
<tr>
<td>Pellets</td>
<td>Cement</td>
<td>Na2FPO3, Na-MFP</td>
<td>~4000</td>
<td>—</td>
<td>x</td>
<td>√</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PVA</td>
<td>MgO</td>
<td>600-4000</td>
<td>10-50</td>
<td>x</td>
<td>√</td>
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</tr>
<tr>
<td></td>
<td>PVA</td>
<td>CSA</td>
<td>500</td>
<td>12-73</td>
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<table>
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<th>Vascular network for self-healing</th>
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<tr>
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</tr>
<tr>
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<td>Epoxy</td>
</tr>
<tr>
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<td>CA</td>
</tr>
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<td>Glass</td>
<td>Foam, epoxy, silicon, CA</td>
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<tr>
<td>Spiral twisted wire with EVA</td>
<td>Epoxy</td>
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<tr>
<td>Porous concrete</td>
<td>Epoxy</td>
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</table>

Table 2. Autonomic self-healing: Encapsulation materials and techniques used (‘−’ means ‘not reported’, ‘x’ means ‘not applicable’, ‘√’ means ‘yes’ and ‘/’ means ‘no’). (upgraded from [53]).
4.2 Autonomic microcapsule self-healing system

Microcapsules are developed to avoid challenging issues in tubes-based capsulation systems incorporation in bulk concrete production. In this healing technique, microcapsules preserving reactive healing agents are ruptured by the forces imposed on capsules’ shell due to the cracks propagation in the matrix. The released healing agent then reacts with the cementitious matrix crack surface to form healing compounds that bridge the gap and eventually heal the cracks.

The compatibility of microcapsules with bulk concrete depends on a wide variety of factors. Major influencing factors are the size and volume fraction of microcapsules used, the capsules’ mechanical properties and interlock properties between the capsules and the surrounding materials [57]. The shape of the embedded capsule is another major factor that should be considered for compatibility issues. Spherically shaped capsules provide a more controlled and enhanced release of the healing agent upon breakage. It also reduces the stress concentrations around the void left from the empty capsule. However, a tubular capsule can cover a larger internal area of influence on the concrete for the same volume of a healing agent (higher surface area to volume ratio).

Yang et al. have investigated methyl methacrylate (MMA) as a monomer and triethylborane (TEB) as the healing agent and the catalyst [25]. In the investigation, about 50.2 and 66.8% reduction in permeability has been achieved within 3 and 30 days, respectively. Microscopic imaging confirms that some ruptured microcapsules existed and filled the cracks of the sample after 80% ultimate compressive strength at 28 days.

About 2% crystalline sodium silicate in polyurethane-encapsulated microcapsules with a diameter ranging from 40 to 800 μm increased 24% mechanical load recovery compared to 12% in the control samples [58]. However, the compressive strength of the composite reduced by 12% compared to that of the control mix. In the concrete containing microcapsules, sodium silicate reacts with calcium hydroxide of cement and produces a calcium-silica-hydrate (C-S-H) gel that heals the cracks partially. The C-S-H further reacts with dissolved CO₂ in water and sodium oxide, which produced calcium carbonate. This is similar to the main hydration phase of cement, which causes strengthening.

Sodium silicate encapsulated in double-walled polyurethane/urea-formaldehyde (PU/UF) was reported in [59]. The addition of 2.5 and 5% microcapsules resulted in about 24 and 35% healing efficiency based on the crack depth measurements.
Further advancement with sodium silicate encapsulated in gelatin and gum arabic shell materials (Figure 11) was found in recent studies [57, 60]. These microcapsules survive mixing with cement and rupture successfully upon crack formation and release sodium silicate solution. Although increasing microcapsules volume fractions in a ~24% reduced the mechanical properties, the crack sealing was just under 100%. Besides, the crack depth and sorptivity coefficient were decreased by 70 and 54%, respectively. These microcapsules were also successfully implemented in the field trial of a road improvement scheme by M4L project [61].

The colloidal silica solution capsules up to 16 vol% in PC grout increased the sealing efficiency from ~20% for the only PC to ~85% in 28 days [62]. However, monodisperse photo-polymerised acrylate shell with hydrophilic mineral core microfluidic droplets are further advancement in the self-healing microcapsule field [63].

4.3 Coated minerals (pellets and granules) for self-healing

Although the direct addition of potential minerals to the concrete mix improves autogenous self-healing performance, protecting those minerals in initial mixing may further enhance the healing process. With this in mind, pellets of potential healing mineral agents have been used for improved concrete self-healing. Sisomphon et al. [47] used expanded lightweight clay aggregates (LWAs) impregnated with a solution of sodium mono fluorophosphate (Na$_2$FPO$_3$, Na-MFP) and coated by cement paste layers. The entire mechanism is schematically presented in Figure 12a. Pellets with expansive minerals such as a reactive MgO were spray-coated (10–50 μm) with polyvinyl alcohol (PVA) to produce PVA-coated MgO pellets for self-healing concrete applications (Figure 12b). A PVA-coated granulated CSA (calcium sulpho aluminate)-based expansive mineral was used for improving the self-healing performance of cementitious materials [48]. Replacement of CSA pellets was up to 10% by wt. of cement and mortar was prepared with 1:3 cement-to-sand ratio and w/c = 0.5. Cracks in the range of 0.1–0.2 mm were healed completely within 14 days whereas larger crack >0.2 healed within 16 days.

Granules of expansive self-healing agent coated with an extra layer of cement compounds were investigated by [64]. The self-healing concept is schematically
presented in Figure 13. The fundamental concept is that the surface of the coating may hydrate during initial production and mixing while the core healing mineral agent remains unhydrated; this may then dissolve and diffuse into the crack surface after crack propagation and form new products for self-healing.

4.4 Bacteria-based self-healing in concrete (bioconcrete)

Alkali-resistant endospore-forming bacteria that precipitate calcite through biological metabolism are used for self-healing in concrete. Examples of these bacteria are *B. cohnii*, *B. pseudofirmus* and *B. sphaericus*. The process involved in calcite production is termed as microbiologically induced calcite precipitation (MICP) [32]. There are two conventional MICP processes: firstly, the urease system, which
is initiated by the hydrolysis of urea by the bacteria, secreted enzyme urease (urea aminohydrolase) as a catalyst [33] and secondly, calcium lactate-based MICP [65].

In the urea-based MICP process, hydrolysis of urea with urease results in ammonia and carbonate ions, which increase the pH value into the bacteria cell. Researchers have experimented with urea as a mineral precursor for biocementation using bacteria [33, 66]. In the presence of CaCl₂ as a source of \( \text{Ca}^{2+} \), high pH content bacteria cause CaCO₃ crystal precipitation from the solution. Typically, bacteria shell made with various ions are negatively charged to attract positive cautions \( \text{Ca}^{2+} \) ions surrounding the cell wall, which reacts with CO₃²⁻ and precipitate CaCO₃ around the cell [66].

Calcium lactate (\( \text{CaC}_6\text{H}_{10}\text{O}_{6} \)) is a crystalline salt, typically produced from the reaction of lactic acid with calcium carbonate or hydroxide. This was used as an alternative of urea-CaCl₂, as a precursor for bacterial metabolism in concrete to avoid ammonia production in hydrolysis reactions. According to [65], metabolic absorption and breakdown of calcium lactate with bacteria lead to the precipitation of CaCO₃.

Bacteria cannot survive long if they are mixed directly with fresh cement. The survivability of bacterial spores was optimized in [65], through the technique of packing bacterial spores and organic mineral precursor compounds in porous expanded clay particles before mixing in the concrete matrix. The pellets (2–4 mm) were principally made with the three components of a solid mixture, and they were used as a replacement of some of the similar size coarse aggregate. A high concentration of calcite precipitation has been found in concrete specimens with bacteria incorporated expended clay particles, which efficiently acted in crack-plugging and reduced permeability (Figure 14). About to micron sized (0.15 mm width), cracks were sealed. However, the main drawback in the bacterial pellet process is the

![Figure 14.](image)

*Figure 14.* Microscopic images of bacteria based self-healing concrete, (a) Stereomicroscopic image of crack sealing, (b) Stereomicroscopic close-up image of massive columnar precipitate (c–e) ESEM images of top part of massive columnar precipitate indicated in image by dotted square (Reproduced from [65]).
negative impact on the mechanical performance of concrete. About 50% of the total aggregate volume requires replacing with bacterial pellets for satisfactory self-healing performance, which negatively impacts the mechanical strength of concrete.

An encapsulation of bacterial spores inside microcapsules is a recent advancement in this field [26]. These microcapsules were reported flexible in humid/water conditions and becoming brittle in the dry environment. With their bacterial encapsulation systems, about 970-μm width cracks were healed successfully, which was four times greater than for non-bacterial mixes. Nevertheless, bacterial activity reduces dramatically with the increase in the pH (>12) value in concrete.

5. Conclusions

Concrete being one of the most-used construction development materials, early damage and failure within a structure’s design lifetime is a threat to infrastructure industries. A self-healing concrete has great potential to mitigate this challenge. Self-healing in concrete can be broadly classified into two categories: autogenic and autonomic healing [1].

The autogenous self-healing capacity of concrete could be enhanced through restricting crack growth, wet-dry cycle, using SCM’s such as GGBS, fly ash, and silica fume, and using expansive minerals such as MgO, bentonite clay, quicklime, CSA and crystalizing mineral agents. However, the effectiveness of autogenous self-healing is considerably dependant on the remaining unhydrated cement or mineral in the concrete. This is hitherto restricted to smaller healable crack widths, more extended healing periods and the strength recovery.

Autonomic healing in concrete, in contrast to autogenous healing, requires the release of the self-healing triggering agent from reserved encapsulation or a continuous supply network. This is to further improve the self-healing efficiency of concrete compared to the autogenous healing process. Popular autonomic self-healing systems are microencapsulation, microvascular and pellets with different autonomic healing agents such as epoxies, cyanoacrylates, methyl methacrylate, alkali-silica solutions, minerals and microorganisms.

The self-healing concrete technology can be adopted in developing smart and resilient infrastructure development. Different self-healing concrete technology can be utilized depending on different applications. The greatest challenges of all self-healing technology in the concrete industry remain the difficulties in widespread uptake, the additional costs involved and the validation of long-term durability performances. Field trials such as those initiated by the University of Cambridge, Cardiff University and the University of Bath through Materials for Life (M4L) and Resilient Materials for Life (RM4L) research projects are significantly crucial for self-healing concrete validation in large scale.

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Conflict of interest

There is no conflict of interest.
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