Chapter

Self-Healing Concrete and Cementitious Materials

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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 CO_2 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

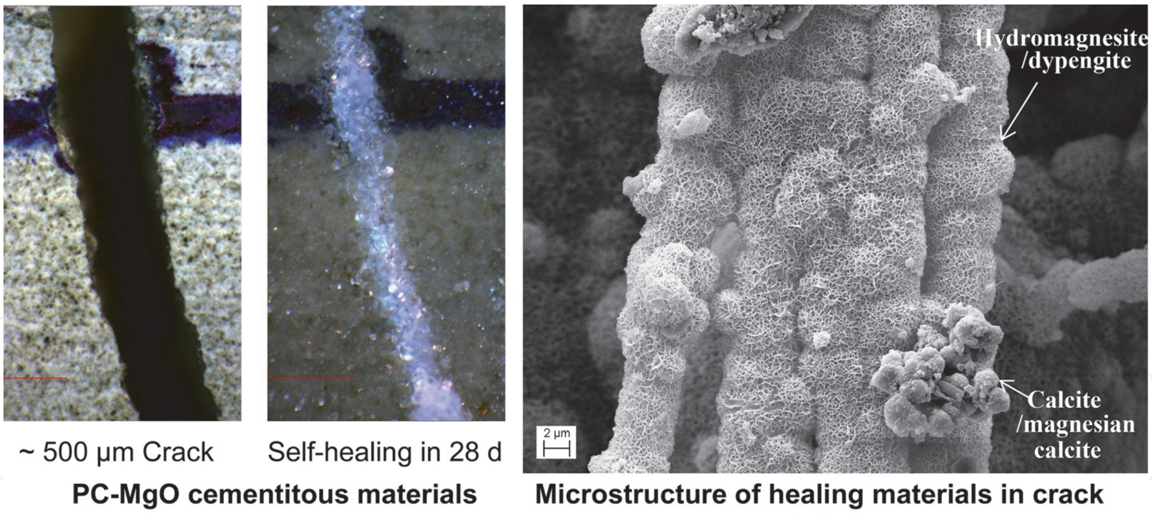


Figure 1.
Example of self-healing concrete and cementitious systems (Adopted from [3]).

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 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

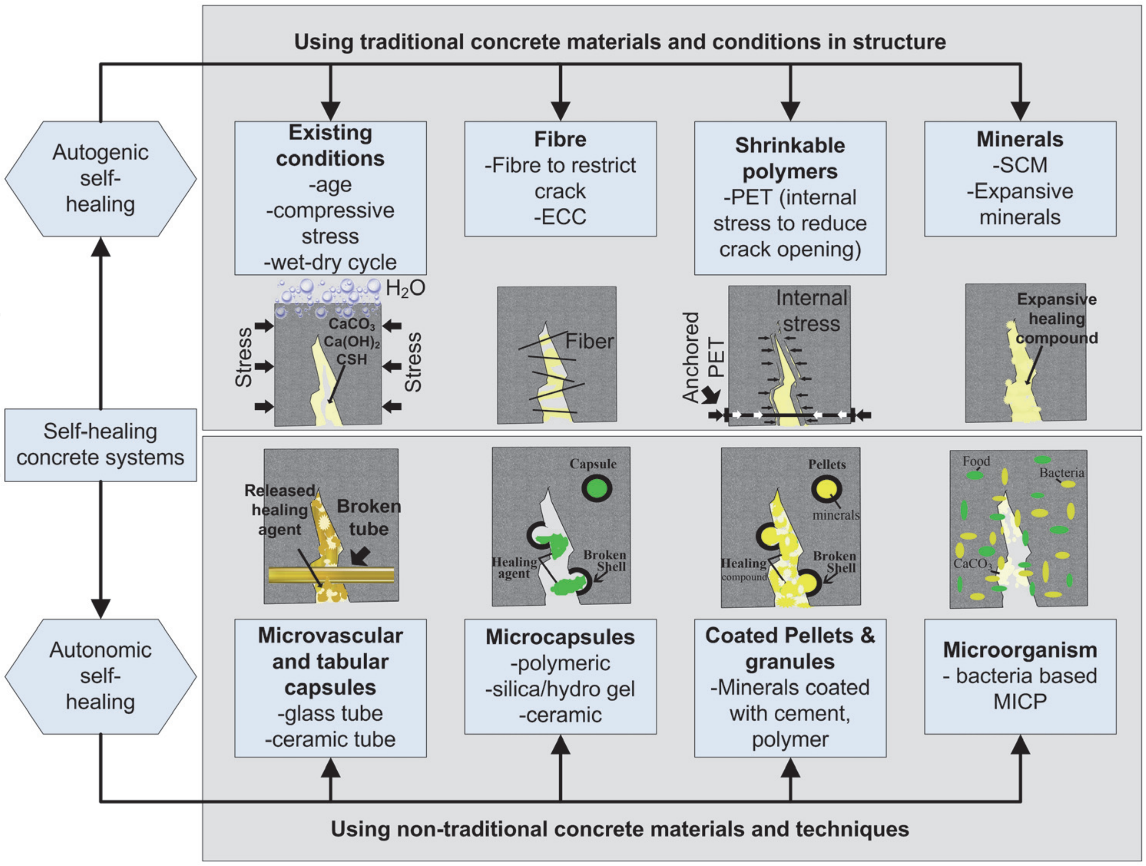


Figure 2.
Self-healing concrete systems.

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].

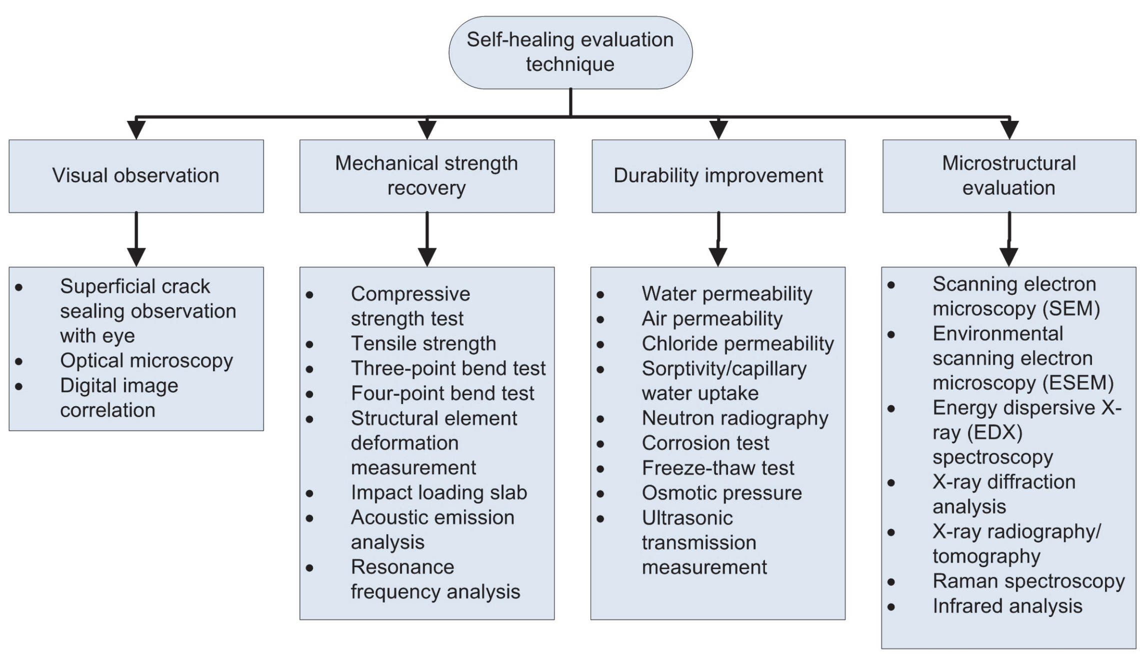


Figure 3.
Self-healing performance in concrete measurement techniques.

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, CO_2 dissolved in water from the air, and the calcium ion Ca^{2+} is derived from concrete.

$$H_2O + CO_2 \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3{}^- \leftrightarrow 2H^+ + CO_3{}^{2-} \tag{1}$$

$$Ca^{2+} + CO_3{}^{2-} \leftrightarrow CaCO_3 \ (pH_{WATER} > 8) \tag{2}$$

$$Ca^{2+} + HCO_3{}^- \leftrightarrow CaCO_3 + H^+ \ (7.5 < pH_{water} < 8) \tag{3}$$

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

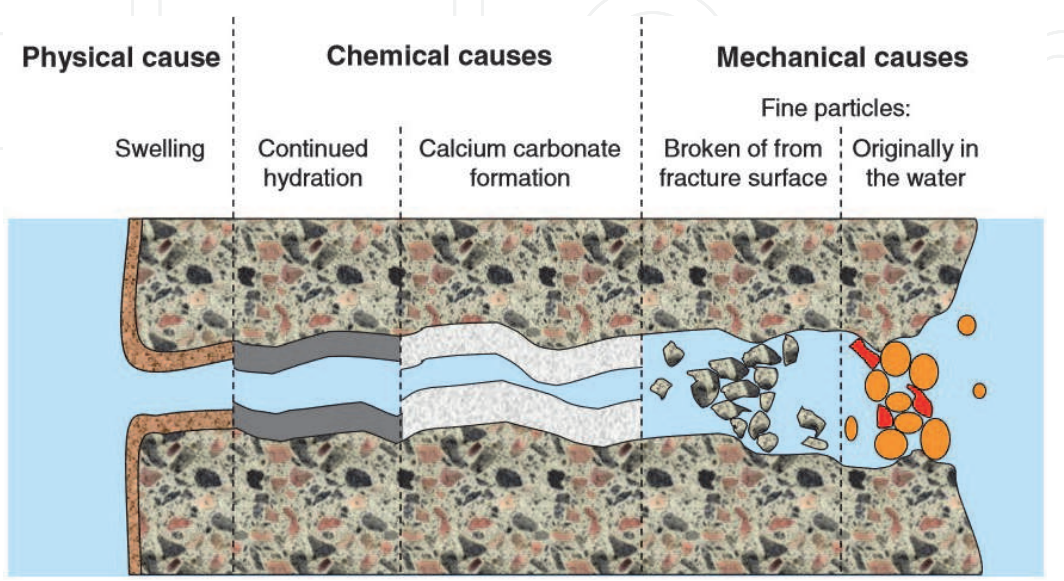


Figure 4.
A model of five steps taking place within three processes, physical, chemical and mechanical (Reproduced from [1]).

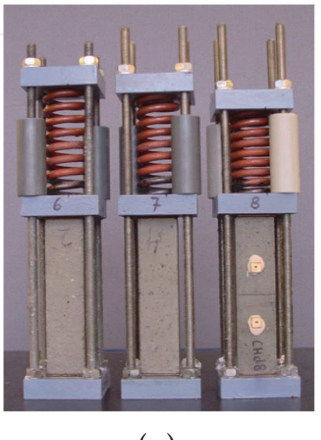
conditions, such as age, compressive stress and curing condition (e.g. wet-dry cycle); (ii) fibres to restrict cracks (e.g. ECC); (iii) shrinkable polymers to initiate internal stress after cracking to shrink the cracks and (iv) cement-compatible mineral additives.

3.1 Existing condition influence in autogenous self-healing

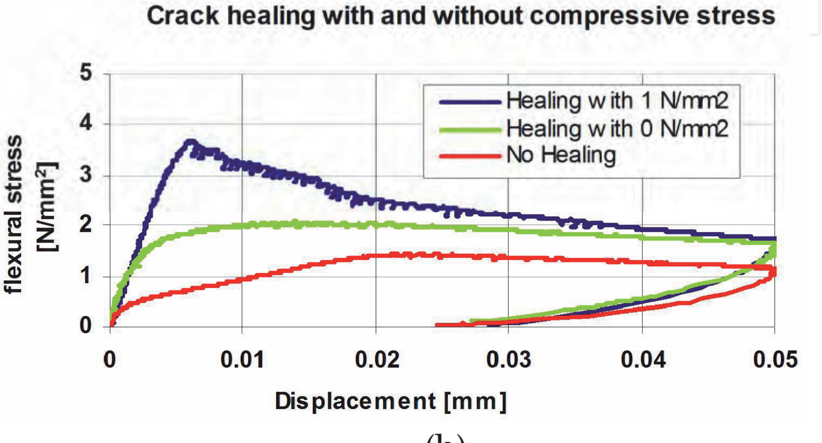
Autogenous self-healing of concrete is significantly influenced by its age, internal stress and curing conditions. Early age concrete naturally heals rapidly due to autogenous healing. Concrete prisms with cracks up to 50 μm were autogenously healed under 0.1, 1 and 2 Mpa compressive stresses [5] (**Figure 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



(a)



(b)

Figure 5.
(a) Application of compression and (b) stress-displacement curve of specimens after healing with and without applied compressive stress. (Both figures reproduced from [5]).

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 sulphoaluminate (CSA), lime, bentonite clay and crystalline additive (CA), have been mostly used for improving the concrete autogenous self-healing performance.

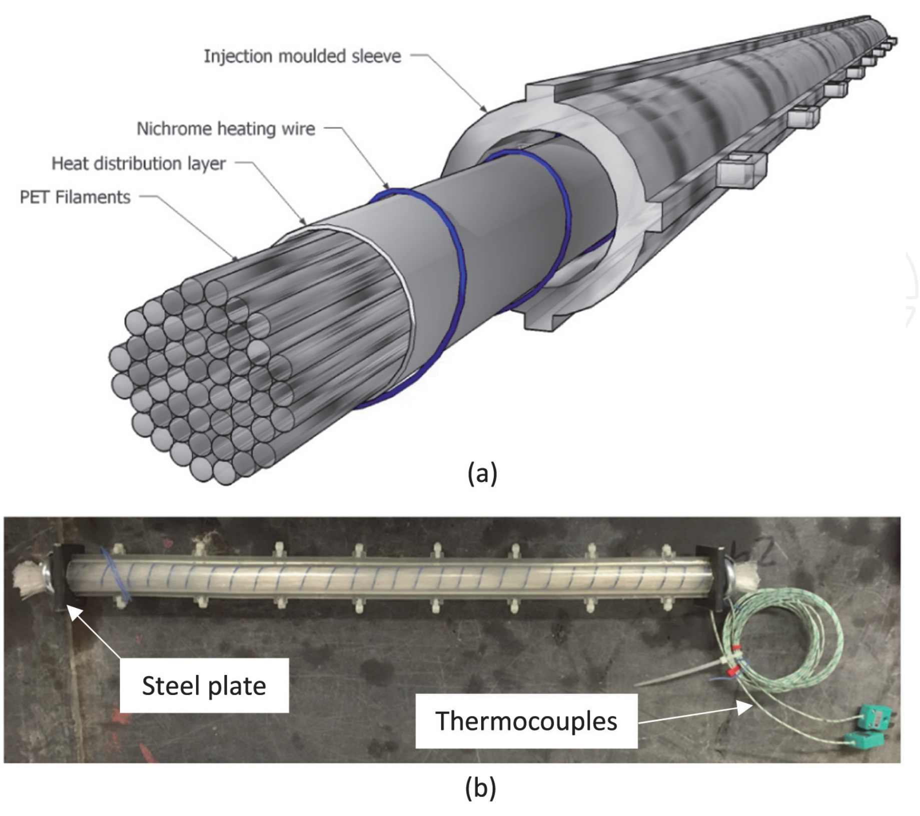


Figure 6.
(a) Schematic of shape memory PET polymer tendon, and (b) photo of the setup (Both reproduced from [7]).

Minerals	Composition	Damage type	Curing condition	Performance (healed crack width in time etc.)	Source
CSA, [a]H, [b]A, [c]L, Mont.	Up to 10% (concrete)	3 PB, mechanical	Water	160–220 μm in 33d Calcite, CASH	[8]
CSA	4.44 and 15.24% of cement (concrete)	Tension force	Still/continuous flow water	Reduced flow in 100 μm cracks, continuous flow is efficient	[38]
CSA, CA, [a]H, [b]A, [c]L, Mont.	PC with 10% CSA and 1.5% CA	Sp. tensile test	Water	100–400 μm in 56 d Calcite	[9]
Silica, [d]CEA, bentonite, CA	8% individual combination up to 14%	Compression, sp. tensile	Water, wet-dry, air, freeze–thaw	220 μm in 2 weeks [d]CEA (individually efficient) silica, bent., CA (combination is efficient)	[11]
FA, SF, CA	OPC, OPC + 30%FA, OPC + 10%SF, OPC + 1%CA	Splitting tensile test	Water	50 μm in 12d larger cracks heal efficiently with SF	[39]
FA	15–20% with PC (paste)	Shrinkage microcracks	Water	Meso-macro pores at 91, 182 and 364 d	[40]
FA	5–15% wt. of sand (concrete)	Freeze–thaw	Water	Improve [e]DME over 90% in 28d	[41]
BFS	OPC + 50% BFS	Mechanical	Water	Product formation is three times faster for CEM I	[42]
FA, slag	30–40% of cement (mortar)	Shrinkage	Water	Improvement in compressive strength	[43]
[c]L, slag, FA	30, 50% FA; 50, 75, 85% slag (paste/mortar)	3 PB, mechanical	Water	200 μm in 42d	[12]
Slag	66% of cement (paste)	Sliced, mechanical	$Ca(OH)_2$ solution	60% of 10 μm in 240 h C-S-H, ettringite, hydrogenate etc.	[44]
Bentonite	Nanoclay in mortar as internal water reservoir	Mechanical	Water	Enhanced hydration for self-healing	[45]
Bentonite, slag, [c]L	2% PVA by vol. Length = 8 mm, dia = 40 μm	4 PB	Water, wet-dry cycle, air	Nanoclay improves the reloading deflection capacity	[46]
Quicklime, FA	(3%) on fly ash-PC cement pastes	Mechanical	Water	Increased SiO_2 solubility extra $Ca(OH)_2$	[14]
Expanded clay LWAs	Na-MFP and PC coated (mortar)	Mechanical	Water	Absorption decrease sodium, phosphorous and fluoride, CH	[47]
CSA	PVA coated, up to 10% by wt. of cement (mortar, 1:3)	3 PB	Water	<100 μm in 11d, 100–200 μm in 14d, >200 μm in 16d	[48]
CA: cement + sand + microsilica	1–2% of cement	4 PB	Water, open air	60% cracks sealed under open air condition	[49]

Minerals	Composition	Damage type	Curing condition	Performance (healed crack width in time etc.)	Source
MgO	4–12% of cement	Drying shrinkage, 3 PB	Water	<500 μm in 28d durability improved	[3]

[a]H = hauyne.

[b]A = anhydrite.

[c]L = lime/limestone powder.

[d]CEA = chemical expansive agent.

3/4 PB = Three/four-point bending, OPC = ordinary Portland cement, CASH = calcium aluminosilicate hydrate, CSA = calcium sulphoaluminate, CA = crystalline additive, FA = fly ash, SF = silica fume, [e]DME = dynamic modulus of elasticity, LWAs = lightweight aggregates, Na-MFP = sodium mono fluorophosphate (Na_2FPO_3, Na-MFP)

Table 1.
Advancement in autogenous self-healing of cementitious materials with mineral additives (Adopted from [17]).

3.4.1 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% SiO_2, 15.22% Na_2O, 1.98% Fe_2O_3, 1.93% Al_2O_3 and 1.29% MgO. Four different mixes (OPC, OPC + 30%FA, OPC + 10%SF, and OPC + 1%CA) were compared. Larger cracks (0.05–0.30 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).

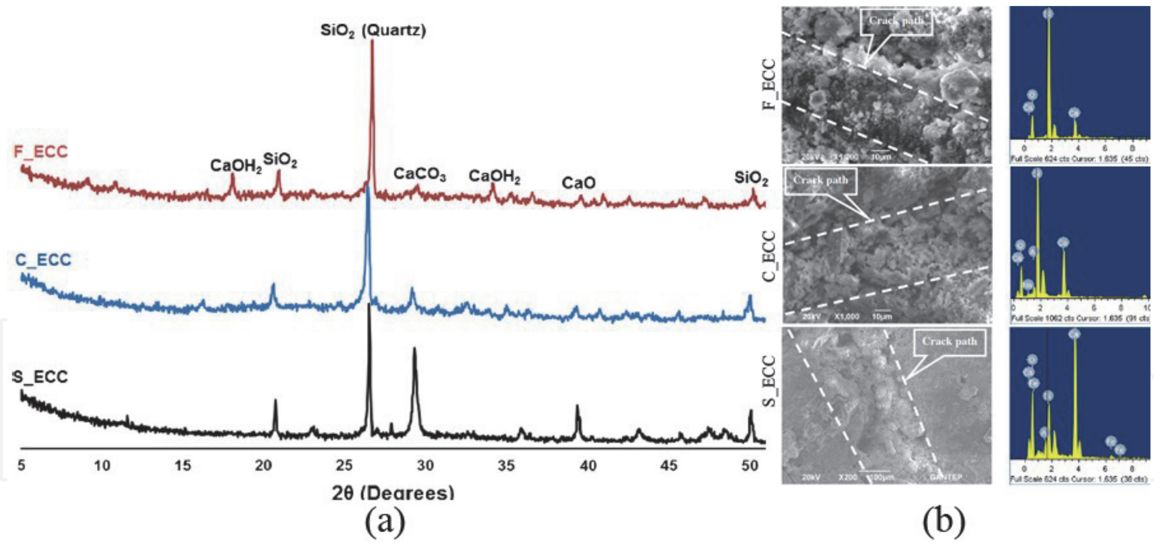


Figure 7.
Self-healing materials, (a) XRD and (b) SEM image with EDX element detection (Both reproduced from [50]).

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 sulphoaluminate (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 [$Na_{0.6}Al_{4.70}Si_{7.32}O_{20}(OH)_4$] (15.4%) along with various types of carbonates such as $NaHCO_3$, Na_2CO_3 and Li_2CO_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 μm 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-μm 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

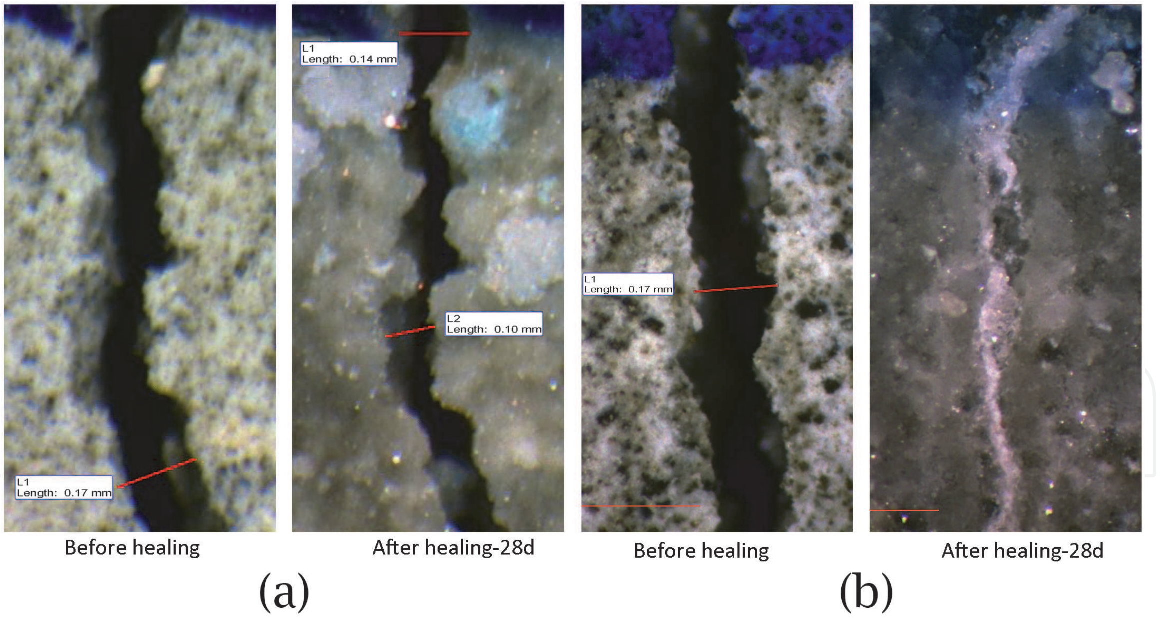


Figure 8.
The typical crack sealing pattern in 28 days: (a) 100% PC cement mix and (b) cement with expansive minerals (Reproduced from [17]).

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

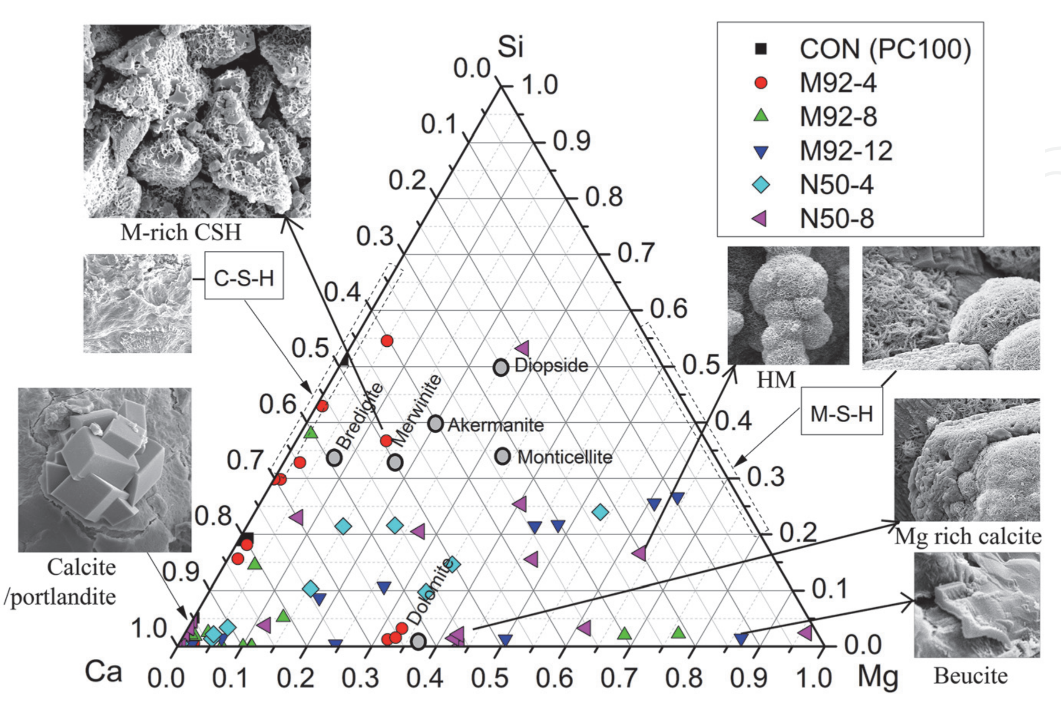


Figure 9.
Ternary diagrams of healing compounds EDX computed atomic mass percentage formed in PC-MgO cement mixes (Reproduced from [2]).

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.

		Shell material	Core material	Øi (μm)	Øo (μm)	Wall thickness (μm)	Length (mm)	Mixed in
Capsule for self-healing	Spherical	Expanded clay	Na_2FPO_3	x	4000	x	x	√
		Expanded clay	Bacteria	x	1000–4000	x	x	√
		Expanded clay	$CaC_6H_{10}O_6$	x	1000–4000	x	x	√
		Diatomaceous earth	Bacteria	x	_	x	x	√
		Gelatin	Acrylic resin	—	125–297	—	x	—
		Gelatin	Epoxy	—	50	—	x	√
		Gelatin	Tung oil	—	50	—	x	√
		Gelatin	$Ca(OH)_2$	—	50	—	x	√
		Wax	Retarder agent	—	120	—	x	√
		Paraffin	Water	—	900	—	x	—
		Cement + paraffin	SAP	—	—	—	x	—
		UF	Epoxy	—	120	4	x	√
		UFF	Epoxy	—	20–70	—	x	—
		PU	Na_2SiO_3	—	40–800	—	x	√
		Silica gel	MMA/ TEB	—	4.15	—	x	√
		Silica	Epoxy	—	—	—	x	√
		Silica	Na_2SiO_3	–	5000	–	x	/
		Gelatin + acacia gum	Mineral oil+ Na_2SiO_3	–	300–700	5–20	x	√
	Cylindrical	Glass	CA	800	1000	100	100	/
		Glass	CA	800, 1500, 3000	—	—	75, 75, 100	/
		Glass	epoxy	3000–4000	5000–7000	—	250	/ –

		Shell material	Core material	Øi (μm)	Øo (μm)	Wall thickness (μm)	Length (mm)	Mixed in
		Glass	CA	3200	4000	400	200	/
		Glass	CA	—	100	–	63.5	√
		Glass	CA, epoxy, polyacrylate, PU, bacteria	2000–3000	2200–3350	100	20–80	/
		Ceramics	PU	2500–3500	3000–4000	250	15–50	/
		Perspex	Epoxy	—	—	—	—	/
		Plant fibre	—	—	40–188	—	—	—
		PP with wax	MMA	–	–	–	–	/
		concentric glass capsule	MgO, bentonite, lime	6150	11,400	450	–	√
	Pellets	Cement	Na_2FPO_3, Na-MFP	–	~4000	–	x	√
		PVA	MgO	–	600–4000	10–50	x	√
		PVA	CSA	–	500	12–73	500	√
Vascular network for self-healing	Tubular	Glass	Alkali silica, epoxy	800	2000	600	x	/
		Glass	CA	3000	4000	500	x	/
		Glass	Epoxy	4800	6000	600	x	/
		Glass	CA	3200	4000	400	x	/
		Glass	Foam, epoxy, silicon, CA	1500	—	—	x	/
		Spiral twisted wire with EVA	Epoxy	2000	3400	700	x	/
		Porous concrete	Epoxy	—	25,000–35,000	—	x	/

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]).

(a) (b)

Figure 10.
(a) Vascular network in concrete slab panel and (b) vascular network combination with PET in field trial (Reproduced from [56]).

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 CO_2 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.

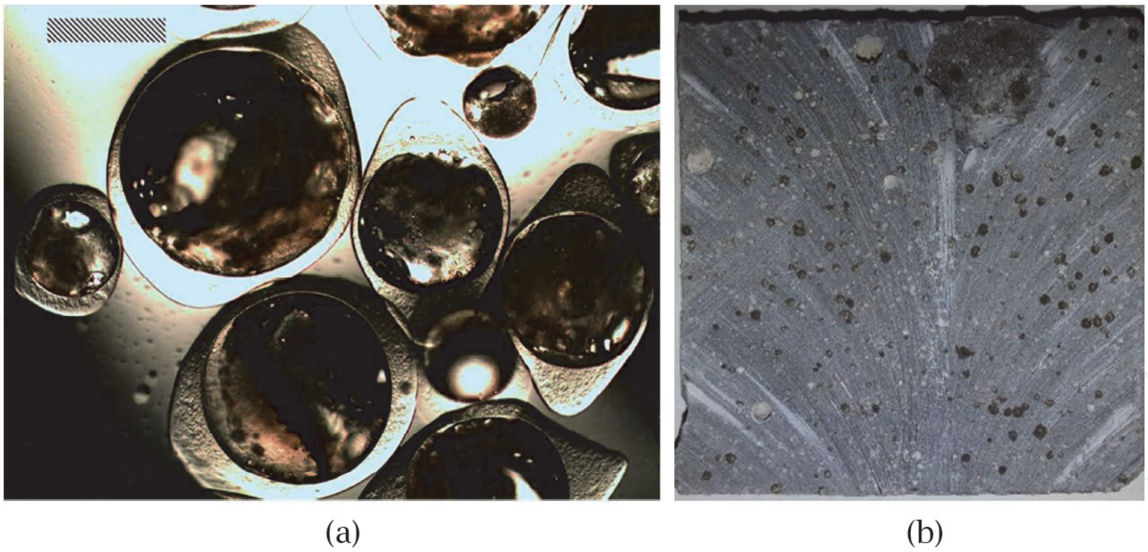


Figure 11.
(a) Microscopic image of microcapsules (scale bars correspond to 500 μm) and (b) ruptured microcapsules appearing as 'wet' spots on the digital image of the split face (Both reproduced from [60]).

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 filed trail 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_2FPO_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

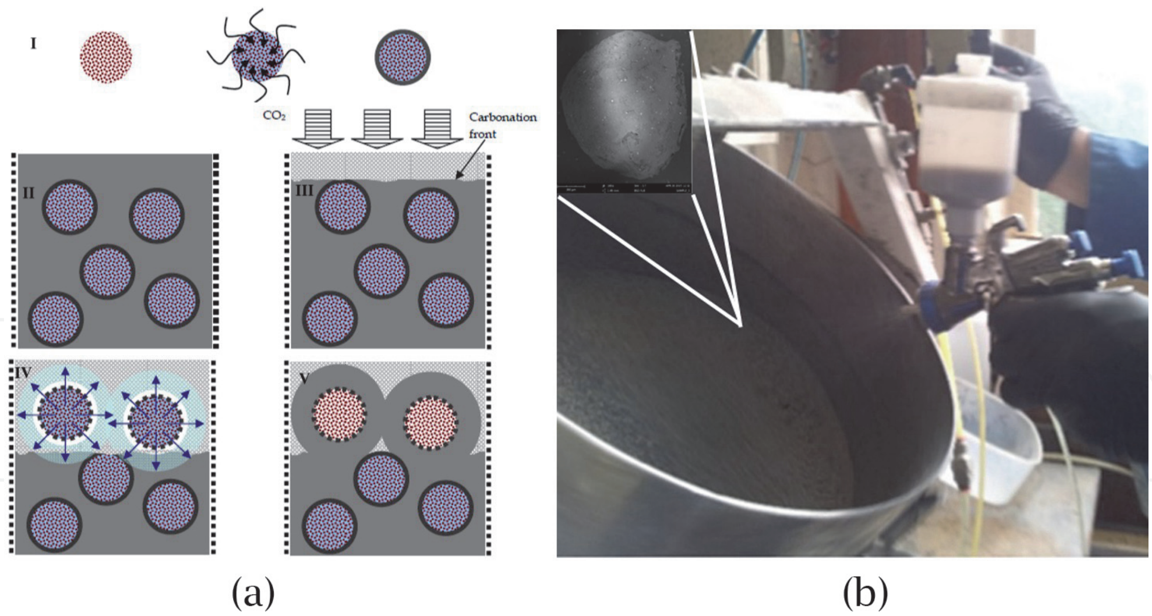


Figure 12.
(a) Impregnation of LWAs to prepare pellet and self-healing concept: I-V (Reproduced from [49]), and (b) spraying PVA coating solution on the MgO pellets in the disc pelletizer and a microscopic image of a pellet covered by PVA (Adopted from [29]).

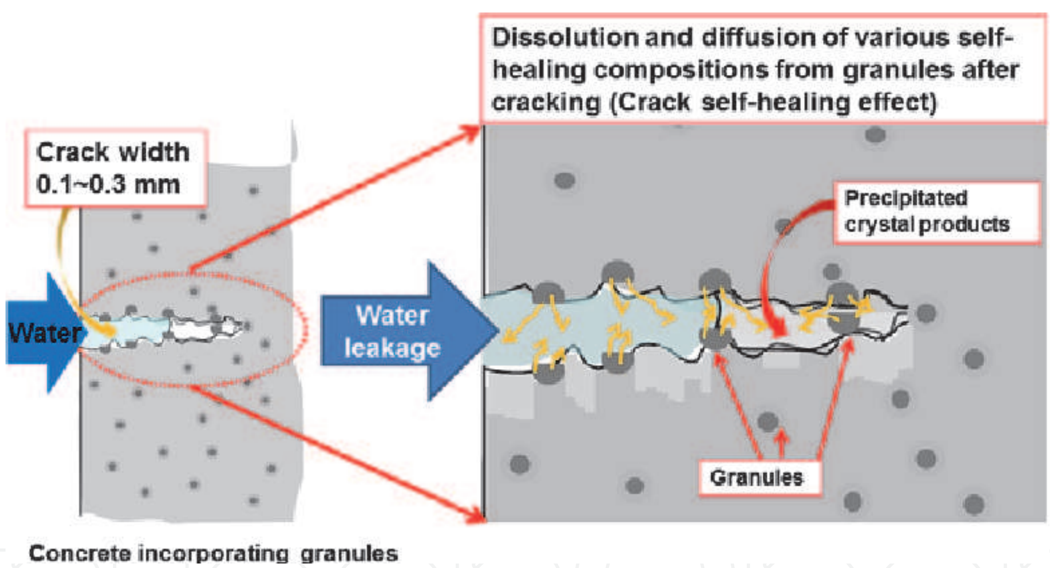


Figure 13.
Concept of self-healing concrete with granules containing expansive mineral agents (Reproduced from [64]).

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 dissolute 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 bio-cementation using bacteria [33, 66]. In the presence of $CaCl_2$ as a source of Ca^{2+}, high pH content bacteria cause $CaCO_3$ crystal precipitation from the solution. Typically, bacteria shell made with various ions are negatively charged to attract positive cautions Ca^{2+} ions surrounding the cell wall, which reacts with CO_3^{2-} and precipitate $CaCO_3$ around the cell [66].

Calcium lactate ($CaC_6H_{10}O_6$) 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-$CaCl_2$, 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 $CaCO_3$.

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

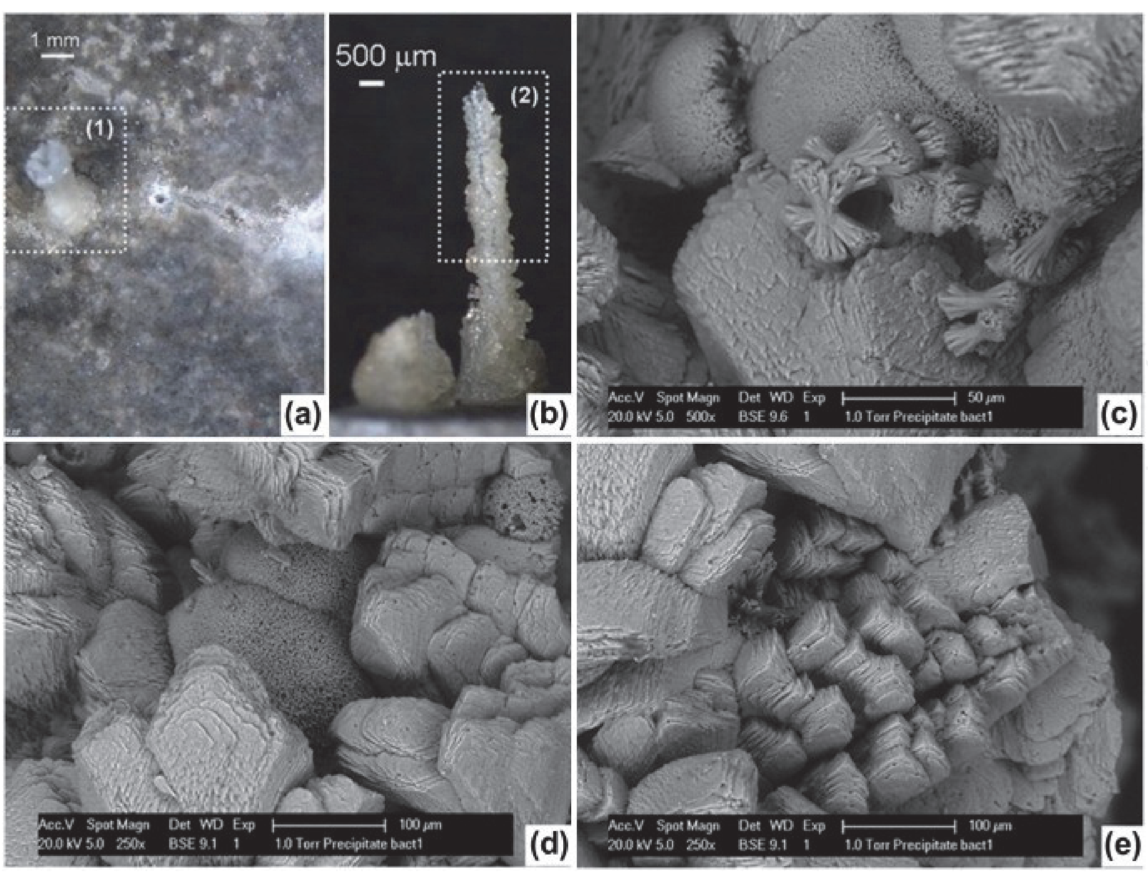


Figure 14.
Microscopic images of bacteria based self-healing concrete, (a) Stereomicroscopic image of crack sealing, (b) Stereomicroscopic close-up image of massive columnar precipitate (c–e) ESEM images of top part of massive columnar precipitate indicated in image by dotted square (Reproduced from [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.

Acknowledgements

The authors are grateful for collaboration and support from the Engineering and Physical Sciences Research Council (EPSRC) research projects 'Materials for Life (M4L)' and 'Resilient Materials for Life (RM4L)'.

Conflict of interest

There is no conflict of interest.

DOI: http://dx.doi.org/10.5772/intechopen.92349

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References

[1] de Rooij M, van Tittelboom K, de Belie N, Schlangen E, editors. Self-Healing Phenomena in Cement-Based Materials: State-of-the-Art Report of RILEM Technical Committee 221-SHC: Self-Healing Phenomena in Cement-Based Materials. Vol. 11. Springer Science & Business Media; 2013. ISBN: 978-94-007-6624-2

[2] Erik S, Joseph C. Self-healing processes in concrete. In: Self-healing materials: Fundamentals, Design Strategies, and Applications. Weinheim: Wiley-vch; 2009. pp. 141-198

[3] Qureshi TS, Al-Tabbaa A. Self-healing of drying shrinkage cracks in cement-based materials incorporating reactive MgO. Smart Materials and Structures. 2016;**25**:084004

[4] Li V, Yang E. Self-healing in concrete materials, self heal. mater. An Altern. Approach to 20 centuries. Materials Science. 2007;**100**:161

[5] ter Heide N, Schlangen E. Self-healing of early age cracks in concrete. In: First International Conference on Self Healing Materials. Noordwijk, The Netherlands; 2007. pp. 1-12

[6] Yang Y, Lepech MD, Yang E-H, Li VC. Autogenous healing of engineered cementitious composites under wet–dry cycles. Cement and Concrete Research. 2009;**39**:382-390

[7] Teall O, Pilegis M, Davies R, Sweeney J, Jefferson T, Lark R, et al. A shape memory polymer concrete crack closure system activated by electrical current. Smart Materials and Structures. 2018;**27** (7):075016

[8] Ahn T-H, Kishi T. Crack self-healing behavior of cementitious composites incorporating various mineral admixtures. Journal of Advanced Concrete Technology. 2010;**8**:171-186

[9] Sisomphon K, Copuroglu O, Koenders EAB. Self-healing of surface cracks in mortars with expansive additive and crystalline additive. Cement and Concrete Composites. 2012; **34**:566-574

[10] Huang H, Ye G, Shui Z. Feasibility of self-healing in cementitious materials—By using capsules or a vascular system? Construction and Building Materials. 2014;**63**:108-118

[11] Jiang Z, Li W, Yuan Z. Influence of mineral additives and environmental conditions on the self-healing capabilities of cementitious materials. Cement and Concrete Composites. 2015;**57**:116-127

[12] Van Tittelboom K, Gruyaert E, Rahier H, de Belie N. Influence of mix composition on the extent of autogenous crack healing by continued hydration or calcium carbonate formation. Construction and Building Materials. 2012;**37**:349-359

[13] Qian S, Zhou J, de Rooij MR, Schlangen E, Ye G, van Breugel K. Self-healing behavior of strain hardening cementitious composites incorporating local waste materials. Cement and Concrete Composites. 2009;**31**:613-621

[14] Antiohos SK, Papageorgiou A, Papadakis VG, Tsimas S. Influence of quicklime addition on the mechanical properties and hydration degree of blended cements containing different fly ashes. Construction and Building Materials. 2008;**22**:1191-1200

[15] Kanellopoulos A, Qureshi T, Al-Tabbaa A. Encapsulated mineral precursors for self-healing cement based composites. In: 5th International Conference on Self-Healing Materials; 2015

[16] Qureshi TS, Kanellopoulos A, Al-Tabbaa A. Encapsulation of

expansive powder minerals within a concentric glass capsule system for self-healing concrete. Construction and Building Materials. 2016;**121**:629-643

[17] Qureshi T, Kanellopoulos A, Al-Tabbaa A. Autogenous self-healing of cement with expansive minerals-I: Impact in early age crack healing. Construction and Building Materials. 2018;**192**:768-784

[18] Qureshi T, Kanellopoulos A, Al-Tabbaa A. Autogenous self-healing of cement with expansive minerals-II: Impact of age and the role of optimised expansive minerals in healing performance. Construction and Building Materials. 2019;**194**:266-275

[19] Qureshi TS. The Role of Expansive Minerals in the Autogenous and Autonomic Self-Healing of Cement Based Materials. Cambridge, UK: University of Cambridge; 2016

[20] Qureshi T, Al-Tabbaa A. The effect of magnesia on the self-healing performance of Portland cement with increased curing time. In: 1st International Conference on Ageing of Materials & Structures; Delft, The Netherlands; 2014. pp. 635-642

[21] Qureshi T, Al-Tabbaa A. Influence of expansive minerals on the self-healing of cement paste and mortar systems. In: Fifth International Conference on Self-Healing Materials; 2015

[22] Kanellopoulos A, Qureshi TS, Al-Tabbaa A. Glass encapsulated minerals for self-healing in cement based composites. Construction and Building Materials. 2015;**98**:780-791

[23] Li VC, Lim YM, Chan Y-W. Feasibility study of a passive smart self-healing cementitious composite. Composites. Part B, Engineering. 1998; **29**:819-827

[24] Dry CM. Design of self-growing, self-sensing, and self-repairing materials for engineering applications. In: Smart Materials. International Society for Optics and Photonics. 2001; **4234**:23-29

[25] Yang Z, Hollar J, He X, Shi X. A self-healing cementitious composite using oil core/silica gel shell microcapsules. Cement and Concrete Composites. 2011; **33**:506-512

[26] Wang JY, Soens H, Verstraete W, de Belie N. Self-healing concrete by use of microencapsulated bacterial spores. Cement and Concrete Research. 2014; **56**:139-152

[27] Joseph C, Jefferson AD, Isaacs B, Lark RJ, Gardner DR. Experimental investigation of adhesive-based self-healing of cementitious materials. Magazine of Concrete Research. 2010; **62**:831-843

[28] Mihashi H, Kaneko Y, Nishiwaki T, Otsuka K. Fundamental study on development of intelligent concrete characterized by self-healing capability for strength. Trans. Japan Concrete Institute. 2001;**22**:441-450

[29] Alghamri R, Kanellopoulos A, Litina C, Al-Tabbaa A. Preparation and polymeric encapsulation of powder mineral pellets for self-healing cement based materials. Construction and Building Materials. 2018;**186**:247-262

[30] de Belie N, Gruyaert E, Al-Tabbaa A, Antonaci P, Baera C, Bajare D, et al. A review of self-healing concrete for damage management of structures. Advanced Materials Interfaces. 2018;**5**: 1800074

[31] Jonkers HM, Thijssen A, Muyzer G, Copuroglu O, Schlangen E. Application of bacteria as self-healing agent for the development of sustainable concrete. Ecological Engineering. 2010;**36**:230-235

[32] Reeksting BJ, Hoffmann TD, Tan L, Paine K, Gebhard S. In-depth profiling of calcite precipitation by environmental bacteria reveals fundamental mechanistic differences with relevance to application. bioRxiv. 2019:850883

[33] Siddique R, Chahal NK. Effect of ureolytic bacteria on concrete properties. Construction and Building Materials. 2011;**25**:3791-3801

[34] Lauer K, Slate F. Autogenous healing of cement paste. ACI Journal Proceedings. 1956;**52**:1083-1098

[35] Edvardsen C. Water permeability and autogeneous healing of cracks in concrete. ACI Materials Journal. 1999; **96**:448-454

[36] Reinhardt H-W, Jooss M. Permeability and self-healing of cracked concrete as a function of temperature and crack width. Cement and Concrete Research. 2003;**33**:981-985

[37] Li VC. On engineered cementitious composites (ECC). Journal of Advanced Concrete Technology. 2003;**1**(3): 215-230

[38] Hosoda A, Komatsu S, Ahn T, Kishi T, Ikeno S, Kobayashi K. Self healing properties with various crack widths under continuous water leakage. Concrete Repair, Rehabilitation and Retrofitting II. 2009:221-227

[39] Jaroenratanapirom D, Sahamitmongkol R. Effects of different mineral additives and cracking ages on self-healing performance of mortar. In: Proceedings of the 6th Annual Concrete Conference; Petchaburi, Thailand; 2010

[40] Termkhajornkit P, Nawa T, Yamashiro Y, Saito T. Self-healing ability of fly ash-cement systems. Cement and Concrete Composites. 2009;**31**:195-203

[41] Watanabe T, Fujiwara Y, Hashimoto C, Ishimaru K. Evaluation of self healing effect in fly-ash concrete by ultrasonic test method. International Journal of Modern Physics B. 2011;**25**: 4307-4310

[42] Olivier K. Experimental studies of self-healing cementitious materials incorporating mineral admixtures. Proceedings of the Fourth International Conference on Self-Healing Materials. 2013:21-24

[43] Zhou ZH, Li ZQ, Xu DY, Yu JH. Influence of slag and fly ash on the self-healing ability of concrete. Advances in Materials Research. 2011;**306-307**: 1020-1023

[44] Huang H, Ye G, Damidot D. Effect of blast furnace slag on self-healing of microcracks in cementitious materials. Cement and Concrete Research. 2014; **60**:68-82

[45] Valcke S, de Rooij M, Nijland TG, Fisher H, Mendoza S. Carriers of Self-Healing Agents in Concrete and Their Effect on the Microstructure. TNO report No. TNO-034-DTM-2009-04262 for IOP project of healing built-in building materials. 2009

[46] Qian SZ, Zhou J, Schlangen E. Influence of curing condition and precracking time on the self-healing behavior of engineered cementitious composites. Cement and Concrete Composites. 2010;**32**:686-693

[47] Sisomphon K, Copuroglu O, Fraaij A. Application of encapsulated lightweight aggregate impregnated with sodium monofluorophosphate as a self-healing agent in blast furnace slag mortar. Heron. 2011;**56**:17-36

[48] Lee Y-S, Ryou J-S. Self healing behavior for crack closing of expansive agent via granulation/film coating method. Construction and Building Materials. 2014;**71**:188-193

[49] Ferrara L, Krelani V, Moretti F. On the use of crystalline admixtures in cement based construction materials: From porosity reducers to promoters of self healing. Smart Materials and Structures. 2016;**25**:084002

[50] Sahmaran M, Yildirim G, Erdem TK. Self-healing capability of cementitious composites incorporating different supplementary cementitious materials. Cement and Concrete Composites. 2013;**35**:89-101

[51] Ferrara L, Krelani V, Carsana M. A "fracture testing" based approach to assess crack healing of concrete with and without crystalline admixtures. Construction and Building Materials. 2014;**68**:535-551

[52] Sherir MAA, Hossain KMA, Lachemi M. The influence of MgO-type expansive agent incorporated in self-healing system of engineered cementitious composites. Construction and Building Materials. 2017;**149**: 164-185

[53] van Tittelboom K, de Belie N. Self-healing in cementitious materials—A review. Materials. 2013;**6**:2182-2217

[54] van Tittelboom K, de Belie N, van Loo D, Jacobs P. Self-healing efficiency of cementitious materials containing tubular capsules filled with healing agent. Cement and Concrete Composites. 2011;**33**(4):497-505

[55] Thao T, Johnson T, Tong QS, Dai PS. Implementation of self-healing in concrete—Proof of concept. IES Journal Part A: Civil & Structural Engineering. 2009;**2**:116-125

[56] Davies R, Pilegis M, Kanellopoulos A, Sharma T, Teall O, Gardner D, et al. Multi-scale cementitious self-healing systems and their application in concrete structures. In: 9th International Concrete Conference. Dundee; 2016

[57] Kanellopoulos A, Giannaros P, Al-Tabbaa A. The effect of varying volume fraction of microcapsules on fresh, mechanical and self-healing properties of mortars. Construction and Building Materials. 2016;**122**:577-593

[58] Pelletier MM, Brown R, Shukla A, Bose A. Self-healing Concrete with a Microencapsulated Healing Agent. Kingston: University of Rhode Island; 2011

[59] Mostavi E, Asadi S, Hassan MM, Alansari M. Evaluation of self-healing mechanisms in concrete with double-walled sodium silicate microcapsules. Journal of Materials in Civil Engineering. 2015;**27**:04015035

[60] Kanellopoulos A, Giannaros P, Palmer D, Kerr A, Al-Tabbaa A. Polymeric microcapsules with switchable mechanical properties for self-healing concrete: Synthesis, characterisation and proof of concept. Smart Materials and Structures. 2017;**26**: 045025

[61] Al-Tabbaa A, Litina C, Giannaros P, Kanellopoulos A, Souza L. First UK field application and performance of microcapsule-based self-healing concrete. Construction and Building Materials. 2019;**208**:669-685

[62] Litina C. Development and Performance of Self-Healing Blended Cement Grouts with Microencapsulated Mineral Agents. Cambridge, UK: University of Cambridge; 2015

[63] Souza LR, Kanellopoulos A, Al-Tabbaa A. Synthesis and characterization of acrylate microcapsules using microfluidics for self-healing in cementitious materials. In: Fifth International Conference on Self-Healing Materials. Durham, USA; 2015. pp. 1-4

[64] Kishi T. Development of crack self-healing concrete by cost beneficial

semi-capsulation technique. In: Third International Conference on Sustainable Construction Materials and Technologies. Kyoto, Japan; 2013. pp. 1-9

[65] Wiktor V, Jonkers HM. Quantification of crack-healing in novel bacteria-based self-healing concrete. Cement and Concrete Composites. 1 August 2011;**33**(7):763-770

[66] van Tittelboom K, de Belie N, de Muynck W, Verstraete W. Use of bacteria to repair cracks in concrete. Cement and Concrete Research. 2010; **40**:157-166