Self-healing concrete composites for sustainable infrastructures: a review

Wei Zhang[1,†], Qiaofeng Zheng[2,‡], Ashraf Ashour[3,*], Baoguo Han [1,*]
[1] School of Civil Engineering, Dalian University of Technology, Dalian 116024, China
[2] Department of Engineering, University of Cambridge, Cambridge, CB2 1PZ, UK
[3] Faculty of Engineering & Informatics, University of Bradford, Bradford, BD7 1DP, UK

[†, ‡] Wei Zhang and Qiaofeng Zheng contributed equally, and they are alphabetically ordered.
* Corresponding author: hithanbaoguo@163.com, hanbaoguo@dlut.edu.cn, A.F.Ashour@bradford.ac.uk

Abstract

Cracks in concrete composites, whether autogenous or loading-initiated, are almost inevitable and often difficult to detect and repair, posing a threat to safety and durability of concrete infrastructures, especially for those with strict sealing requirements. The sustainable development of infrastructures calls for the birth of self-healing concrete composites, which has the built-in ability to autonomously repair narrow cracks. This paper reviews the fabrication, characterization, mechanisms and performances of autogenous and autonomous healing concretes. Autogenous healing materials such as mineral admixtures, fibers, nanofillers and curing agents, as well as autonomous healing methods such as electrodeposition, shape memory alloys, capsules, vascular and microbial technologies, have been proven to be effective to partially or even fully repair small cracks. As a result, the mechanical properties and durability of concrete infrastructure can be restored to some extent. However, autonomous healing techniques have shown a better performance in healing cracks than most of autogenous healing methods that are limited to healing of cracks having a narrower width than 150 μm. Self-healing concrete with biomimetic features, such as self-healing concrete based on shape memory alloys, capsules, vascular networks or bacteria, is a frontier subject in the field of material science. Self-healing technology provides concrete infrastructures with the ability to adapt and respond to the environment, exhibiting a great potential to facilitate the creation of a wide variety of smart materials and intelligent structures.

Keywords: self-healing concrete composites; autogenous; autonomous; crack; recovery

Contents

1. Introduction

In this paper, concrete composite is a collective term referring to concrete, cement mortar and cement paste as well as cementitious/cement-based materials/composites. As shown in Fig. 1 (a), concrete composite is the most widely used engineering material all around the world, mainly due to its excellent performance and low cost. Moreover, as can be seen from Fig. 1 (b), concrete has relatively low energy consumption compared with other engineering materials. Surprisingly, Fig. 1 (c) shows that concrete can reabsorb a large fraction of the cumulative CO_2 emission associated with the high-temperature calcination of carbonate minerals during cement production. In addition, in terms of resources, it is almost impossible to find an alternative construction material for concrete. This is because the main elements in concrete, including O, Si, Al, Fe and Ca, comprise 98% of the crustal composition, as shown in Fig. 1 (d). In the long run, on the basis of the increasing urbanization of developing countries and growing world's population, concrete will definitely continue to be the most produced and consumed construction material. Taking the two largest developing countries China and India for example, concrete consumption converted by the total amount of cement will nearly double in the coming several decades, as shown in Fig. 1 (e) [1–5].

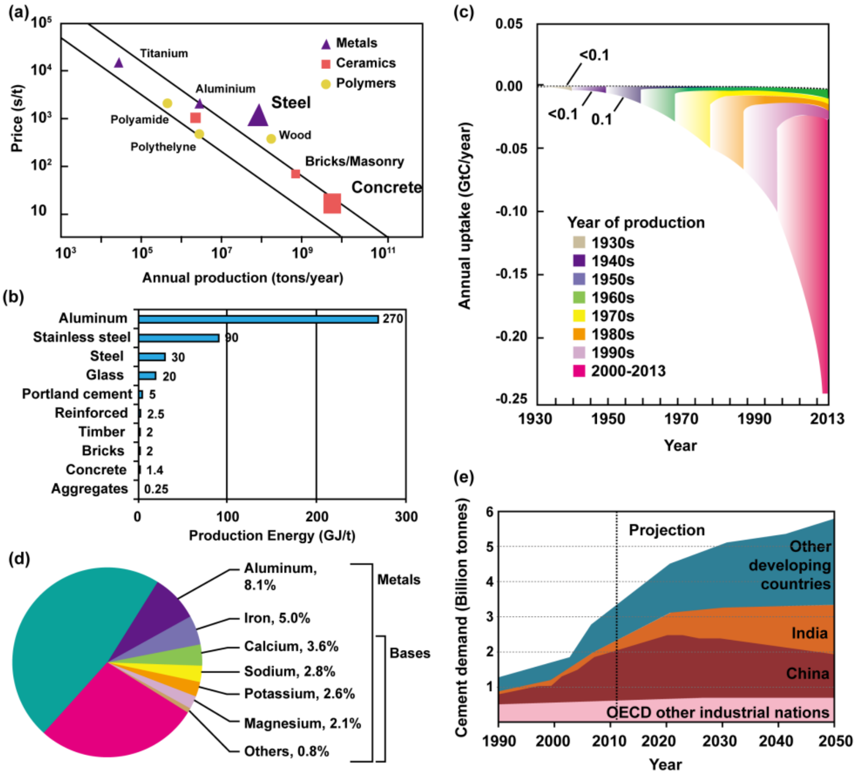


Fig. 1 a) Concrete price and usage; b) Energy consumption for concrete production; c) The cumulative carbon sequestration from 1930 to 2013; d) Elemental composition of the earth; e) Cement demand prediction [1–5].

As shown in Fig. 2, concrete has a multi-component, multi-phase and multi-scale nature but its production process is simple. Generally, concrete components include cement, water, aggregates, chemical additives and mineral additives, and the proportion can vary within a flexible range. Concrete is known for its brittleness, low tensile strength, poor deformation performance and multiple cracking behaviour. Particularly, the presence of cracks tends to weaken the integrity and the bearing capacity of structures, thus severely compromising their safety, serviceability and durability. These weaknesses have deeply concerned researchers and practitioners, especially with the current trend towards large-scale and complicated infrastructures built in extremely aggressive environments where multi-factor coupling effect makes the situation even trickier.

Conventional detection and maintenance are significant means to extend the service life of concrete structures, attracting widespread attention. However, the cost of manual maintenance can be prohibitively high for large infrastructures. In addition, it might be difficult or impossible to manually maintain cracked buildings, taking into account the crack locations, crack sizes and ongoing service requirements for infrastructures such as highways and tunnels. It is in these situations where self-healing concrete is likely to play a very useful role as it can repair cracks automatically and timely without any external intervention [6]. Since concrete is an open composite system, a lot of modifying materials such as fiber filler, powder filler, polymer, etc. can be easily integrated into concrete, and many of which have been proven effective to make concrete 'heal' or 'repair' itself [1–3].

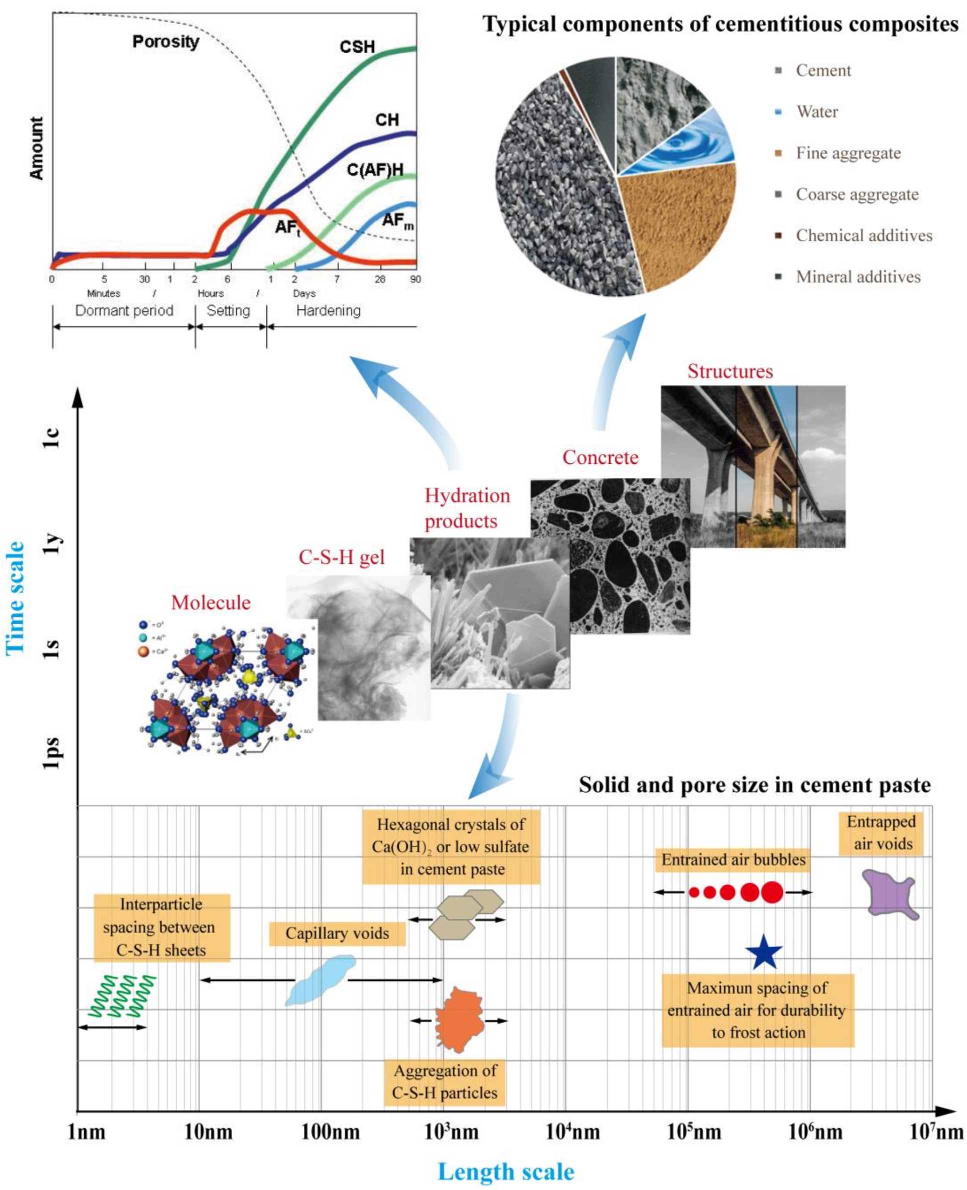


Fig. 2 Multi-component, multi-phase and multi-scale nature of concrete [1–3].

Self-healing or autogenous healing of cracks in concrete was first noticed by the French Academy of Science in 1836. This ability is results from further hydration of unhydrated cement particles and the carbonation of dissolved calcium hydroxide [7]. In 1974, Ivanov and Polyakov [8] observed the self-healing performance in hydraulic concrete. In 1984, Gray [9] found that under the condition of continuous water curing, the autogenous healing degree of the interfacial zone between steel fibers and cement mortar matrix was higher than that of fractured plain mortar or concrete. In 1995, silica fume was added to non-air entrained concrete by Jacobsen et al. [10] to fabricate self-healing concrete. The feasibility of using hollow fibers carrying healing agents [5-7], electrodeposition method [14] and microbial technology [15] to realize self-healing behavior of concrete were investigated in the late 20th century. Since then, tremendous amounts of researches on self-healing concrete have emerged in the 21st century. Self-healing techniques for concrete proposed in the literature can be classified in two different ways, namely materials mixing (mineral admixtures, fibers, nanofillers and curing agents) or self-healing technologies (electrodeposition, shape memory alloy, capsule, vascular and bacteria). The definition and classification, fabrication, characterization, mechanisms and properties (mainly self-healing efficiency) of the self-healing concrete based on the above methods are introduced systematically in this paper.

2. Definition and classification of self-healing concrete

Self-healing concrete, also known as self-repairing concrete, mainly refers to the concrete composite with the ability to repair small cracks automatically, without any external diagnosis or human intervention. Self-healing approaches in concrete can be divided into autogenous healing and autonomous healing. Autogenous healing is originated naturally from the cementitious material, i.e., further hydration of unhydrated cement in concrete, while autonomous healing requires a trigger to activate the process [16,17]. The mechanisms of autogenous healing are summarized in Fig. 3 [7] and identified as: 1) carbonation of calcium hydroxide; 2) cracks blockage caused by impurities in water and loose concrete particles due to crack shedding; 3) expansion of the hydrated concrete matrix in crack flanks; 4) continuing hydration of cement grains [18,19]. The autogenous healing efficiency can be enhanced by incorporating mineral admixtures, fibers, nanofillers and curing agents.

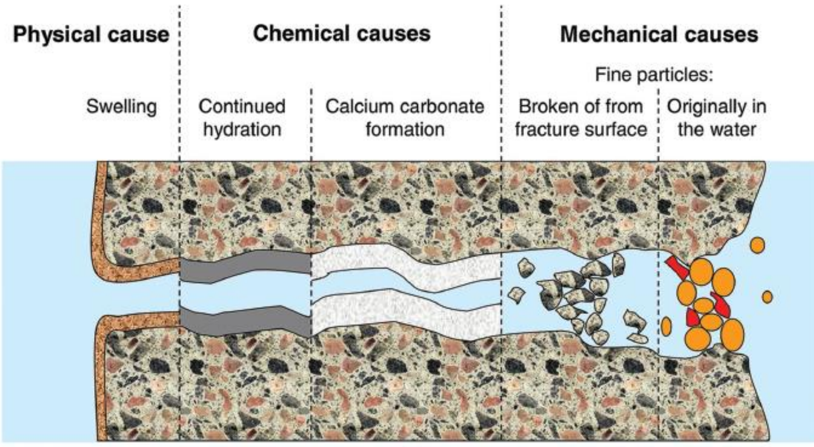


Fig. 3 The mechanisms of autogenous healing concrete [7].

Unlike autogenous healing, the autonomous healing relies on embedded unconventional engineered additions rather than unhydrated cement and has the potential to repair larger cracks. So far, numerous autonomous healing methods have been proposed and studied, including electrodeposition technology and embedding shape memory alloy (SMA), capsule, vascular or bacteria in concrete. Among them, electrodeposition technology is especially suitable for repairing marine concrete structures since it requires conductors (conductive concrete), electricity and electrolytes. Self-healing behavior of concrete with SMA needs thermal stimulation, while that with capsules or vascular is generally triggered by crack occurrence. However, both autogenous healing and autonomous healing methods are believed to be only capable of repairing cracks within a few hundreds of micrometers, meaning structural damage cannot be repaired.

3. Fabrication of self-healing concrete

3.1 Materials and mixing proportion

As stated, self-healing capability of concrete can be achieved and enhanced by incorporating healing materials and adopting self-healing technologies. Tables 1 and 2 summarize some popular healing materials for autogenous and autonomous healing concrete.

Table 1 Healing materials applied in autogenous healing concrete

Healing methods	Healing materials	Additives	References
Incorporating mineral admixtures	Fly ash (FA)	SP	[20]
		-	[6,21]
		PVA fiber, HRWRA/SP	[22–25]
	FA + Hydrated lime	PVA fiber, HRWRA	[25]
	Blast furnace slag + Limestone powder	PVA fiber, SP	[26]
	Blast furnace slag	-	[21,27]
		PVA fiber, HRWRA	[22,24,25]
	Expansive agent, Geo-materials, Chemical additives (single or hybrid)	SP	[28]
	Silica-based, Chemical expansive, Swelling and Crystalline additives (single or hybrid)	-	[29]
	Carbonated steel slag	-	[30]
	Reactive magnesium oxide (MgO)	-	[31]
Incorporating fibers	Polyethylene (PE) fiber, Steel cord fiber (single or hybrid)	SP, (SF)	[32,33]
	Polyvinylalcohol (PVA) fiber	FA, HRWRA/SP	[34–38]
		SF, SP	[33]
	Polypropylene (PP) fiber	SP	[39]
	Steel fibers	FA, SF, SP	[40]
	Steel macrofibers	-	[23]
	Steel macrofibers + Crystalline admixture		
	Carbon fiber	PVA fiber, FA,	[41]

		HRWRA,	
Incorporating nanofillers	Nano-SiO_2	FA, SF, SP	[42]
	Nano-TiO_2		
	Nano-ZrO_2		
	Carbon nanotubes	PVA fiber, FA, HRWRA	[41]
Incorporating curing agents	Lightweight aggregate (LWA)	Water reducing admixture	[43]
	LWA	(HRWRA)	[44,45]
	Eclipse Floor shrinkage reducing admixture (SRA)	-	[46]
	PVA fiber, Superabsorbent polymer (SAP) (hybrid)	SP, FA	[47]
	SAP	SF, SP	[48]
		SF, SP, Steel fiber, Defoamer	
	Polyethylene glycol (PEG)	-	[49–51]
	SAP	SP, SF	[52]
		SP	[53]

Note: SP, SF and HRWRA represent superplasticizer, silica fume and high range water reducing admixture, respectively.

Table 2 Healing materials applied in autonomous self-healing concrete

Healing technologies	Healing materials and conditions	Concentrate or size	Cargo	References
Electrodeposition technology	Electrolyte solutions + Direct current	0.1 mol/L	$MgCl_2$	[54–56]
		0.05, 0.1, 0.25, 0.50 mol/L	$ZnSO_4$	[50,55–58]
		0.01 mol/L	$AgNO_3$	[49,56,57]
		0.01 mol/L	$CuCl_2$	
		0.05, 0.1 mol/L	$Mg(NO_3)_2$	
		0.01 mol/L	$CuSO_4$	
		0.1 mol/L	$Ca(OH)_2$	
		0.1 mol/L	$NaHCO_3$	
		0.05, 0.1, 0.25, 0.50 mol/L	$MgSO_4$	
	Electrolyte solutions + Constant voltage	0.05, 0.10, 0.20, 0.50 mol/L	Sodium silicate	[59]
	Electrolyte solutions + Pluse current	0.25 mol/L	$ZnSO_4$	[60]
		0.25 mol/L	$MgSO_4$	[60]
Shape memory alloy embedded technology	Nitinol (NiTi) SMA strands + Electric actuation	-	-	[61]
	Seven-wire NiTi SMA bundle + Electric actuation	Φ15.3 mm	-	[62]
	NiTi SMA fibers + Heat treatment	Φ0.67/0.93/0.96/1 $L$50, Φ1 L 44-49 mm	-	[63–66]
	NiTiNb SMA fibers + Heat treatment	Φ0.67/1.08 $L$50, Φ1 $L$29-35 mm	-	[63,64,66]
	NiTi SMA wires/fibers + Electric actuation	Φ2, Φ0.965 $L$30 mm	-	[67,68]
Capsule technology	Silica microcapsules	Φ4.15 μm	Methylmethacrylate (healing agent), Triethylborane (catalyst), Sulfonated polystyrene particles	[69]
		Φ5-180 μm	Epoxy compound	[70]

	Polyurethane microcapsules	Φ40-800 μm	Sodium silicate solution	[71]
	Poly styrene-divinylbenzene microcapsules	Φ100-150 μm	Epoxy resins	[72]
	Microcapsules	-	Dicyclopentadiene/ Sodium silicate	[73]
	Melamine microcapsule	Φ5 μm	*Bacillus sphaericus* LMG 22557	[74]
	Urea-formaldehyde microcapsule	Φ73-309 μm	Epoxy resin E-51 (healing agent), Butyl glycidyl ether (thinner agent), MC120D (harden agent)	[75]
		Φ132, 180, 230 μm		[76,77]
	Polymeric microcapsules	Φ75, 150, 300, 500 μm	Dicyclopentadiene	[78]
	Phenol-formaldehyde resin microcapsules	Φ290, 98-632 μm	Sodium silicate solution	[79]
	Gelatin/acacia gum microcapsules	Φ300-700 μm	Sodium silicate solution	[80]
	Clay capsules	Φ2-4 mm	Calcium lactate + Nutrients	[81]
	Ag-alginate capsules	Φ2.4, 2.5 mm	Methyl methacrylate (oil core) + sodium dodecyl benzene sulfonate (urfactant)	[82]
	Glass tubes/fiber	Φ_i2 Φ_o2.2 L41.3/82.6, Φ_i3 Φ_o3.35 L18.4/36.7 mm	MEYCO MP 355 1K	[83]
		Φ4 $L$200/400 mm	Ethyl cyanoacrylate	[84]
		Φ_i4 Φ_o6 $L$250, Φ_i5 Φ_o7 $L$310 mm	Isocyanate prepolymer	[85]
		Φ_i3 $L$60/400 mm	Polyurethane	[86]
		Φ_i3 Φ_o3.35 $L$50 mm	Polymer precursors	[87]
	Ceramic tubes	Φ_i2.57 Φ_o2.99 $L$50, Φ_i3.34 Φ_o3.86 $L$15 mm	MEYCO MP 355 1K	[83]
		Φ_i3 $L$100 mm		[88]
		Φ_i3 $L$60 mm	Polyurethane	[86]
	Borosilicate glass tubes	Φ_i3 Φ_o3.35 $L$50 mm	Polyurethane	[89]
	Polymeric tubes	Φ_i3 Φ_o5 $L$50/100 mm	Epoxy resin	[90]
	Soda glass tubes	Φ_i6.15 $L$50 mm	Minerals	[91]
	Thin-walled concentric glass tubes	Φ_i6.15 Φ_o11.4 $L$50 mm	Expansive powder minerals (MgO, CaO, Bentonite)	[92]
	LWA	Φ4-8 mm	Sodium silicate solution	[93]
	Polymethylmethacrylate tube	Φ_i5 Φ_o7 $L$75 mm	MEYCO MP 355 1K	[94]
	Starch tube	Φ_i2.5 Φ_o8 $L$33 mm		
	Inorganic phosphate cement	Φ_i5 Φ_o7 $L$50 mm		
	Alumina ceramic	Φ_i2 Φ_o3 $L$50 mm		
Vascular technology	Glass fibers	-	Methyl methacrylate	[11]
	Glass capillary tubes	Φ_i3 Φ_o4 mm	Cyanoacrylate	[95]
	Glass tubes	Φ_i4 Φ_o5 mm	Saturated $Ca(OH)_2$ solution	[96]
	Porous concrete core	Φ35 mm	Epoxy (inject to core)	[97]
	Heat shrinkable tube	Φ3.2 mm	Cyanoacrylate, Sodium silicate	[98]
	Polyurethane tube	Φ4 mm		
	Polypropylene tubes	Φ4 mm	Sodium silicate	[99]
	Inorganic phosphate cement	Φ_i5 Φ_o7 mm	MEYCO MP355 1K	[94]
	Alumina	Φ_i2 Φ_o3 mm		
	Inorganic phosphate cement,	Φ_i3 Φ_o10 mm	Polyurethane based injection resin	[100]
	Clay			

Microbial technology	*Bacillus pasteurii* + Urea-$CaCl_2$ medium incubation	5×10^7, 5×10^8, 5×10^9 cells crack^{-1}	-	[101]
	Bacillus megaterium BSKAU	10^5 cells/mL	-	[102]
	Bacillus licheniformis BSKNAU			
	Bacillus flexus BSKNAU			
	Alkaliphilic spore-forming bacteria of the genus *Bacillus*	10^9 cm^{-3}	-	[103]
		1-10×10^8 spores cm^{-3}	-	[104]
	Bacillus sphaericus + Calcium sources	-	Calcium sources: calcium nitrate, calcium acetate	[105]
	Bacterial spores + Calcium lactate	1.7×10^5 spores g^{-1} light weight aggregate (LWA) particles.	-	[106]
	Bacillus sphaericus	5×10^6, 5×10^7, 5×10^8 cells/mL	-	[107,108]
	Bacillus sphaericus + Deposition medium	10^9 cells/mL	Deposition medium: urea, $Ca(NO_3)_2\cdot4H_2O$	[109]
	Sporoscarcina pasteurii + Grown culture	10^3, 10^5, 10^7 cells/mL	Grown culture: urea, $NaHCO_3$, NH_4Cl, nutrient broth, $CaCl_2\cdot2H_2O$	[110,111]
	Proteus mirabilis and *Proteus vulgaris* + Medium culture	-	Medium culture: urea, calcium carbonate, ammonium chloride, calcium chloride, nutrients	[112]
	Non-ureolytic bacteria + Nutrients	1×10^7 cells/cm^3, 10^9 cells/g microcapsules	Nutrients: calcium lactate, calcium glutamate, yeast extract	[113]
	*Bacillus sphaericu*s + Nutrients	10^9 cells/mL	Nutrients: yeast extract, urea, $Ca(NO_3)_2\cdot4H_2O$	[74,114,115]
		10^9 spores per hydrogel sheet	Bio-reagents: yeast extract, urea, calcium-nitrate	[116]
		2.25g	Nutrients: urea, yeast extract	[117]
	Alkaliphilic spore-forming bacteria + Substrate	10^9 cells/mL	-	[118]
	Diaphorobacter nitroreducens + Nutrients	2.25g	Nutrients: $Ca(NO_3)_2$, $Ca(HCOO)_2$	[117,119,120]
	Bacillus mucilaginous + Nutrient	10^9 cells/mL	Nutrient: $Ca(NO_3)_2$	[121]
	Pseudomonas aeruginosa + Nutrients	2.25g	Nutrients: $Ca(NO_3)_2$, $Ca(HCOO)_2$	[119,120]
	Bacillus Mucilaginous and *Brewers yeast* + Nutrients	10^8~10^9 cells/mL	Nutrients: sucrose, yeast extract and calcium nitrate	[122]
	Bacillus cohnii + Nutrient	5.2×10^8 cell/cm^3	Nutrient: Calcium lactate	[123]
	Bacillus Subtilis + Nutrients from curing solution	2.2×106 cells/mL	Nutrients: urea, $CaCl_2$	[124]
	Bacillus sphaericus and *Bacillus licheniformis* + Nutrients	250 μg/mL	Nutrients: $CaCl_2$, urea, yeast extract	[125]

Note: Φ_i, Φ_o and L represent inner diameter, outer diameter and length, respectively.

The mixing proportion of self-healing concrete is usually determined according to the mix design method of conventional concrete. However, the incorporation of geo-materials with swelling characteristics or other materials with small particle size (such as nano materials) will reduce the rheological performance and workability of fresh concrete due to their water adsorption [126]. Generally, mineral admixtures are added as a partial replacement of cement, leading to a slight decrease in the amount of cement. However, the mechanical properties of concrete not always improve with the introduction of mineral admixtures [26,29,127]. The addition of capsules sometimes also has a negative impact on strengths to a certain extent [79]. Therefore, a suitable mixing proportion regarding each healing material should be determined via scientific experimental design methods such as uniform design [50] and orthogonal design [75] in combination with mix design [95] and dispersion methods described in the following section.

3.2 Mixing and dispersion process

Previous researches [128,129] indicate that mixing method, mixing speed and mixing time/duration prominently affect the properties of fresh and the hardened cementitious composites. In general, higher mixing speed and longer mixing duration decrease the fluidity and strength of cementitious composites but increase pores in the matrix [129]. Therefore, it is of great importance to adopt suitable mixing and dispersion methods. The most common mixing method is to put raw materials in a mechanical mixer in several steps and mix them until the desired homogeneity is achieved [20–22,26]. According to the mixing conditions of healing agent, the mixing process for healing concrete can be divided into dry mixing, wet mixing and latter mixing, as diagrammed in Fig. 4. For brittle self-healing materials, they should be embedded inside cementitious composites at the final step of mixing in order to protect them from breakage during fabrication [83,88]. Additionally, reinforcing steel bars, metallic wires or fibers are sometimes added to avoid premature failure of brittle self-healing materials during crack formation, as well as to control the crack width [76,79,91,114,130]. Hilloulin et al. [130] designed hollow tubular polymeric capsules which can remain intact during concrete mixing and break when cracks appear. Three steps were reported to produce the polymeric capsules [130]. Firstly, three different polymers with a low glass transition temperature were extruded. Then, the preheated capsules were mixed with other components. The capsules shifted from a brittle state to a rubbery state at this stage, so more capsules were able to survive. Finally, the capsules became brittle at room temperature [130]. Van Tittelboom et al. [86] proposed and evaluated two different methods to ensure the survival of brittle encapsulation materials during casting and possibly concrete mixing. In the first method, the glass and ceramic capsules containing the healing agent were protected by winding them with a cord and then coating a tiny mortar layer onto them. The second protection was to embed these capsules in a cement paste bar. Experimental results indicate that the first approach seemed to be more effective [86]. Similarly, Thao also tested and proved that two-layer protection method (the inner layer is a wrapped spiral wire and the outer layer is a wrapped thin mortar layer) is more favorable to protecting the glass tube in cement matrix, compared with monolayer protections such as mortar strip, steel mesh and spiral wires [85].

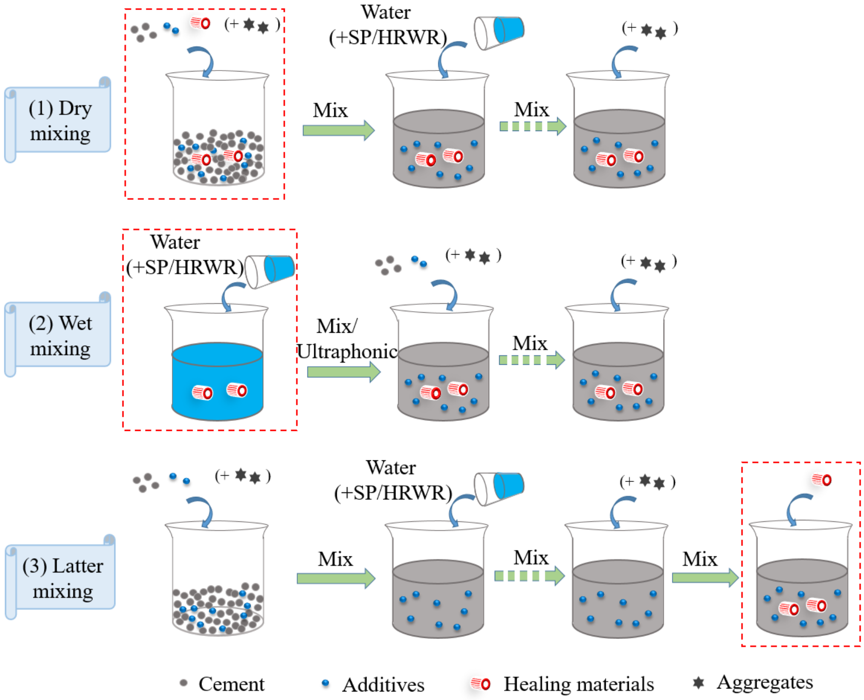


Fig. 4 Three mixing processes for healing concrete.

Uniform dispersion of healing materials is a prerequisite for obtaining excellent self-healing capacity, especial for micro and nano materials with large surface area and fibrous fillers with high aspect ratio. Besides mechanical mixing, additional physical methods like ultrasonic treatment [70] and chemical methods such as adding superplasticizer [20,26,42] or high-range water-reducing admixture (HRWR) [22,37,131] are used to further improve the dispersion and the fluidity of materials during fabrication process.

3.3 Molding and curing

The molding process of self-healing is basically the same as that of ordinary concrete. Generally, fresh concrete is poured into molds in several layers and each layer is subjected to mechanical vibration to achieve good compaction of structural elements [21,91]. Plenty of curing conditions at two stages, namely initial stage and self-healing stage, have been investigated [19–22,25–27,29,30,37–39,74,105,108,114,115,118]. Fig. 5 exhibits a summary of different curing systems at the two stages. Different curing conditions at self-healing stage are designed to simulate different environmental exposures and to explore their effects on self-healing. Water is confirmed as a crucial element to enhance self-healing performance for both autogenous and autonomous healing concrete, and even high humidity alone is inadequate to ensure self-healing [22,25,72,91]. Still water instead of flowing water curing results in a faster reduction in permeability coefficient and a greater decline in crack width for pre-cracked mortars with mineral admixtures. This is probably because flowing water drains away the hydroxide ions and calcium ions, decreasing the pH value and the concentration of calcium ions that are essential to the formation of healing products [29]. The research of Yıldırım et al. [25] indicates that CO_2-water curing (50 ± 5 °C, 50 ± 5% RH, 3% CO_2 and in water) was the best in comparison to the other three curing conditions (50 ± 5 °C, 50 ± 5% RH, without 3% CO_2 in air/water or with 3% CO_2 in air), followed by water curing. Sisomphon et al. [127] found the curing method of water/air cycles contributed to a better self-healing performance of strain hardening cementitious composites, followed by regularly refreshed tap water, tap water and air exposure orderly, in terms of the mechanical recovery. They believed that one of the possible reasons for the good effect of wet/dry cycles (i.e. water/air cycles) curing was that the evaporation of excess water during the drying phase led to an increase in the ions concentration in cracks, which promoted chemical reactions, precipitation and further hydration. Another reason was believed to be the penetration of CO_2 into cracks during the drying period, which facilitates the formation of carbonates [127]. However, water curing usually helps microbial concrete achieve a higher crack healing ratio, superior to wet/dry cycles curing or wet curing [118]. Deposition medium as a healing condition seems to be better than water for microbial concrete in terms of cracks repair and water absorption [114].

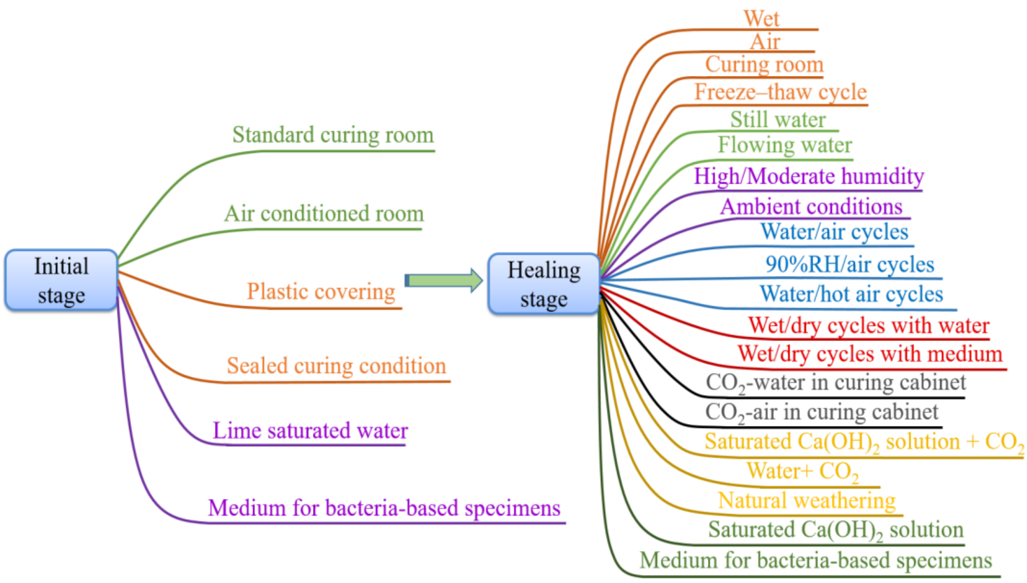


Fig. 5 Curing conditions at initial and self-healing stages.

4. Techniques for evaluating self-healing efficiency

The recovered microstructure (especially repaired cracks), regained durability and restored mechanical properties are generally obtained when cracks are filled with self-healing products. Visualization and determination techniques, durability tests and mechanical properties tests have been extensively applied to characterize the self-healing efficiency of self-healing concrete, as summarized in Table 3.

Table 3 Summary of techniques for evaluating self-healing efficiency

Techniques		Evaluations	References
Visualization and determination	Camera or optical microscope + image analysis	Crack characterization + healing rate	[21,24,25,29,31,40, 41,47,127]
	X-ray computed tomography (XCT)	3D visualization of crack healing	[39,40,83,97,108]
	Scanning electron microscope (SEM)	Microstructure; surface morphologies of healing products	[25,32,38,41,59,60, 127]
	Environmental scanning electron microscopy (ESEM)		[29]
	Backscattered electron image analysis		[32]
	Field emission scanning electron microscope		[69]
	Transmission electron microscopy	Morphology of healing products	[131]
	Energy dispersive spectrometer	Element analysis of healing products	[59,76,119,131]
	Energy dispersive x-ray spectroscopy	Chemical composition of healing products	[23,38]
	Raman spectroscopy		[32]
	X-ray diffraction (XRD)		[25,30,60,131]
	Fourier transform infrared spectroscopy		[91,93,120,131]
	Thermo gravimetric-	Hydration degree	[25,39,47,105]

	differential thermal analysis		
	Isothermal calorimetry	Hydration process	[21,30]
	Ethylene Diamine Tetra-acetic Acid titration method	Release behavior of healing agent from microcapsule	[132]
Improved durability	Accelerated carbonation test	Resistance against carbonation	[55]
	Rapid chloride permeability test	Resistance against chloride ingress	[20,22,24,25,76,110]
	Chloride diffusion test		[89]
	Corrosion test		[89]
	Water permeability test	Water tightness	[21,29,37,39,47,58,83,86,133]
	Capillary water absorption test/Sorptivity test	Water tightness	[20,36,91,93,105,114]
	Gas permeability	Gas tightness	[31,69,91]
	Electrical impedance test	Microstructural properties	[25]
	Mercury intrusion testing	Porosity	[19,56,59]
	Measurements of chloride ion concentration	Chloride removal by electrodeposition	[58]
	Electrochemical measurements	Re-passivity of steel bar by electrodeposition	[58]
	Electrochemical impedance spectroscopy measurement	Corrosion of steel bar	[134]
	Ultrasonic pulse velocity test	Degree of damage	[20,36,76,96,113]
	Acoustic emission location analysis	Degree of damage	[86,88,94]
Recovery in mechanical properties	Compression test	Recovery in strength, toughness, stiffness, modulus and/or fracture energy when reloading healed specimen; Formation of new cracks versus reopening of old cracks; Capsule breakage with crack appearance	[19,20,41,71,76]
	Tensile test		[32,35–38,40,101,133,134]
	Three-point bending test		[21,68,71,84,88,93,97,109,130,135,136]
	Four-point bending test		[26,41,47,113]
	Cyclic of three-point bending test		[95]
	Cyclic four-point bending test		[137,138]
	Fatigue test		[69,139,140]
	Dynamic mechanical analysis		[130]
	Impact loading test		[85]
	Nanoscale mechanical measurements		[113]
	Bond strength test	Bond strength between capsules and matrix	[130]
	Adhesion test	Adhesion strength between electrodeposits and mortar	[56]
	Resonant frequency test	Degree of damage	[23,24,35,37,38,131,141,142]

4.1 Crack healing

The crack characteristics, including crack length, crack depth, crack number and especially crack width, are key parameters for evaluating the self-healing efficiency, and can be measured by a camera or an optical microscope. However, these two techniques are limited to the detection of surface cracks. X-ray computed tomography (XCT) scan, a nondestructive method, is capable of observing both the external and internal features of specimens. Therefore, XCT observation has been widely utilized to quantify the crack healing efficiency inside self-healing concrete, and to monitor the status and rupture behavior of healing materials such as capsules [78,82,83,97,115,143].

Before crack healing measurement, cracks are mainly generated by either loading [56], thin copper plate introduction [102] or corrosion solution treatment [58]. Experimental results show that the healing products of continuous hydration or $CaCO_3$ precipitation are reasons for the crack closure of some healing concrete [39,74,91,106,121], while the crack-sealing mechanisms of self-healing concrete containing capsules or vascular system may differ from each other and depend on the healing agents contained. Fully sealed cracks in some self-healing concrete have also been reported [25,91,102,105,123,144].

4.2 Recovery in durability and mechanical properties

Cracks in concrete allow penetration of water and aggressive chemicals, causing steel rebars corrosion and concrete deterioration. In this sense, the significance of healing or sealing cracks lies in enhancing the water and gas tightness of concrete composite, thereby increasing its durability [20,83,86,120], even if water is not completely prevented from entering the cracks [86,120]. Van Tittelboom et al. noted [83] that the water permeability of preloaded concrete containing tubular capsules filled with healing agent obviously decreased after a period of healing, although it was still slightly higher than that of undamaged control samples. The rapid chloride permeability of concrete with high volume of fly ash and the gas tightness of concrete with glass encapsulated minerals showed the similar results [20,91]. Moreover, it is reported that SAP is able to directly block cracks after absorbing incoming water and swelling, which, however, is strongly influenced by the alkalinity and ionic content of the solution. Nevertheless, SAP will release the absorbed liquid and shrink during dry period, consequently leaving many voids in cement paste [145]. In addition, SAP can no longer form a barrier once it is not swollen.

In addition to improving or recovering the durability of self-healing concrete, many researchers [31,75,84,93,113,136] are pursuing the possibility of regaining mechanical properties (mainly static) after crack healing. In general, the mechanical properties of damaged self-healing concrete after healing are inferior to that of original specimens, although some researches indicate by using organic microcapsules (urea formoldehyde as the shell material and epoxy resin as the encapsulating healing agent), the recovery rate can reach more than 100% in terms of impermeability and strength [75,136].

5. Performance of autogenous healing concrete

5.1 Self-healing concrete containing mineral admixtures

The incorporation of some mineral admixtures (usually with high content) such as fly ash, blast furnace slag, carbonated steel slag, expansive materials, geo-materials, crystals and chemical additives also contributes to the self-healing of concrete [20,21,26,28–30]. The schematic illustration of self-healing approach based on mineral admixtures is demonstrated in Fig. 6. Huang et al. [27] developed a reactive transport model to simulate self-healing in Portland cement paste. According to thermodynamic modeling, the carbonation of newly formed reaction products first leads to an increase in the filling fraction of crack and then a decrease.

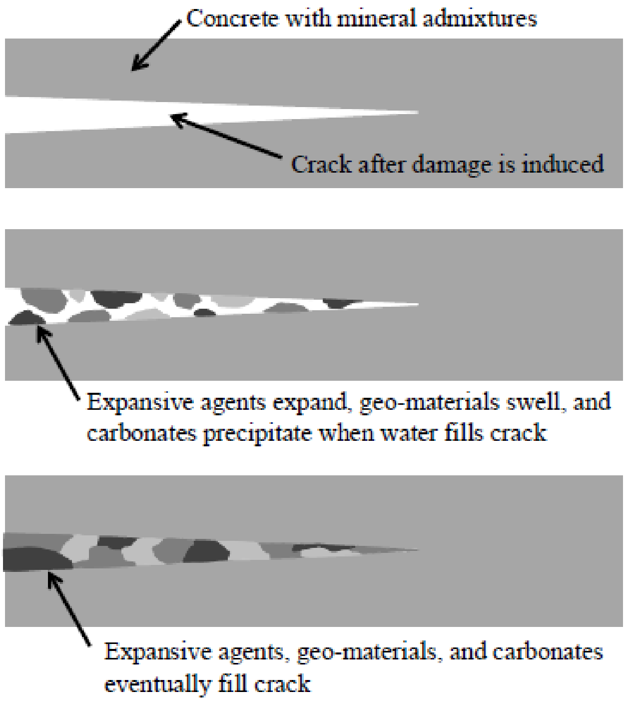


Fig. 6 Schematic illustration of self-healing approach by incorporating mineral admixtures [146].

Previous researches on the self-healing concrete with mineral admixtures are summarized in Table 4. Components and proportion of materials, crack feature and curing conditions are dominating factors affecting self-healing efficiency. Specifically, Class-C Fly ash is more recommended compared with Class-F fly ash, because the latter can exacerbate the deterioration of unloaded concrete or self-healing concrete under freeze-thaw cycles [22]. Compared with fly ash, blast furnace slag performs better in improving the self-healing performance of concrete, which is probably due to the higher pH value of the pore solution and higher CaO content of slag that will favor the precipitation of calcite [21,22]. Compared with single fly ash, blended ground-granulated blast furnace slag and fly ash contribute to a higher self-healing property of strain-hardening cementitious composites [147] Nonetheless, some other researchers have obtained opposite results [24,25]. Additionally, adding chemical expansive additives is a better choice than using silica-based, swelling or crystalline components alone. This is because chemical expansive additives can quickly increase their volume to seal cracks while crystallization takes time to generate healing products. For silica-based minerals, the formation of C-S-H gel is a time-consuming process and can be affected by environment. For multiple mineral materials, the combination of silica-based, swelling and crystalline components is optimal [29,127]. Nevertheless, for modified sulfur composites, a higher ratio of calcium sulfoaluminate expansive agent to Portland cement generally results in a lower compressive strength [148]. Low water to cementitious material ratio and high content of cementitious material seem to be more beneficial to promote self-healing performance as more unhydrated gelling material will be available in the system for further hydration [19–21,26,149]. For similar reasons, high amount of fly ash improves the recovered resonant frequency and strain capacity, that is, higher self-healing efficiency [23]. Besides, adding hydrated lime contributes to more repeatable and pervasive self-healing of cementitious composites with high volume of fly ash [150]. Moreover, microcracks with smaller width are preferable because less healing materials or products are required to fill the crack and connect the sides of the crack [26,27]. However, self-healing via adding mineral is limited, and cracks with width exceeding a certain critical value cannot be sealed appropriately. For example, Yang et al. [37] suggested for engineered cementitious composites (ECC) , crack width must be controlled within 150 μm, preferably below 50 μm, in order to achieve prominent self-healing performance. In addition to the above self-healing concrete of short age, ECC with a high volume fraction of fly ash continues moderate medium-term self-healing beyond the age of 270 d [23]. Furthermore, one-year-old specimens still show outstanding self-healing performance after 30 d of healed curing [25]. Estefanía Cuenca et al. [151] observed that the crystalline admixture (Penetron Admix ®) contributes to crack closure under repeated cracking-healing cycles lasting for one year.

Curing condition can also greatly affect the self-healing behavior. In comparison to curing conditions of continuous air and freeze-thaw cycles, continuous water curing has greater effect on improving the chloride ion permeability, especially for the preloaded specimens [22]. Lower pre-strain and higher RH are more favourable for self-healing performance. Hung et al. observed higher stiffness retention factors of strain-hardening cementitious composites in the water condition (>90%) than that in the dry condition

(<30%) [147]. Sisomphon et al. [127] pointed out that the curing condition of water/air cycles could lead to the optimum mechanical recovery in comparison to water curing or air exposure. Furthermore, it turns out that the early cracks are more easily healed when cured in still rather than flowing water. High pH values, high temperatures and high calcium ion contents also benefit self-healing process [29].

Table 4 Summary of self-healing concrete with mineral admixtures

Types of matrix	Mineral admixtures	Results	Healing products	References
Self-consolidating concrete	Fly ash (35%, 55%)	(1) For 90% of preloading, compressive strength loss decreases from 27% to 7%; (2) Lower increase in permeation properties	-	[20]
	-	For 90% of preloading, compressive strength loss decreases from 19% to 13%		
Pre-cracked fiber reinforced strain hardening cementitious composites	Blast furnace slag (ratio:1.2) + Limestone powder (ratios: 1.5, 2, 3)	(1) Deflection recovery of 65-105%; (2) Healing 10-60 μm cracks	Calcium carbonate ($CaCO_3$)	[26]
Cement paste	Fly ash (15%, 25%, 50%)	(1) Higher increase in compressive strength; (2) Higher decrease in total capillary pores; (3) Lower effective chloride diffusion coefficient	-	[19]
	Expansive agent, Geo-materials, Chemical additives (total of 10%)	Healing 0.2 mm crack	Hydrogarnet, Calcite, Fibrous phases from chemical additives	[28]
	Reactive magnesium oxide (MgO) (4%, 8%, 12%)	(1) Healing cracks up to 500 μm; (2) Crack area reduction of about 74%-99%	Calcite, Portlandite, Calcium silicate hydrates (C-S-H), Ettringite	[31]
	Blast furnace slag (66%)	10 μm wide artificial gap is filled about 60%	C-S-H, Ettringite, Hydrogarnet, OH^- hydrotalcite	[27]
Concrete	Expansive agent, self-healing agent (total of 7%)	(1) Lower water permeability; (2) Healing 0.27 mm crack	$CaCO_3$	[28]
Cement paste/Concrete	Blast furnace slag (50%, 70%, 85%)/ Fly ash (30%, 50%)	Healing cracks up to 200 μm	$CaCO_3$	[21]
Engineered cementitious composites	Class-F fly ash (rato: 2.2)/ (Class-C fly ash) (ratio: 2.2)	Healing cracks up to 30 / (50) μm	C-S-H, Calcite	[22]
	Ground granulated blast furnace slag (ratio: 2.2)	Healing cracks up to 100 μm	Calcite	
	Calcium-sulfoaluminate based expansive additive,	A combination of admixtures obtains the optimum mechanical recovery	$CaCO_3$, C-S-H, Ettringite	[127]

	Crystalline additive			
	Fly ash (ratio: 1.2)/ (Ground granulated blast furnace slag) (ratio: 1.2)	(1) Recovering 85% / (74%) of initial resonant frequency after six repetitive preload applications; (2) Crack width limited to 130 / (190 μm)	-	[24]
	Class-F fly ash (ratios: 1.2, 1.6, 2)	(1) Tensile strength / stiffness retention ratios: (>70%)/ (>60%); (2) Healing cracks up to 110μm	$CaCO_3$, C-S-H	[23]
	Fly ash (ratio: 1.2)	(1) Healing cracks up to 458 μm; (2) Crack healing rate of 100%	$CaCO_3$, Slight C-S-H and Calcium aluminium silicate hydrates (C-A-S-H)	[25]
	Fly ash (ratio: 1.2) + Hydrated lime (5%)	(1) Healing cracks up to 356 μm; (2) Crack healing rate of 91%	$CaCO_3$, slight C-S-H and C-A-S-H	
	Ground granulated blast furnace slag (ratio: 1.2)	(1) Healing cracks up to 386 μm; (2) Crack healing rate of 68%	$CaCO_3$	
Cement mortar	Silica-based materials	CEA provides the greatest crack self-healing rate	$CaCO_3$, Small amount of C-S-H	[29]
	Chemical expansive agents (CEA)			
	Swelling minerals			
	Crystalline components			
Concrete	Carbonated steel slag	(1) Maximum healing crack width/length: 20 μm/5 mm; (2) Generating new narrow cracks	$CaCO_3$, C-S-H, $Ca(OH)_2$, Calcium-aluminat-ferrite hydrate, Amorphous silica	[30]

Note: The percentage or ratio of mineral admixtures is relative to the amount of cement or binder.

5.2 Self-healing concrete containing fibers

Incorporating fibers is also an effective means of developing self-healing concrete, and the most commonly utilized fibers are PVA, PE, PP, steel and carbon fibers. Natural fibers, glass fiber and other synthetic fibers [152,153] can also be employed as healing materials. Two mechanisms of self-healing in fiber reinforced concrete are shown in Fig. 7. On one hand, crack width can be limited by fibers, thus the self-healing efficiency is enhanced as less healing product will be needed to fill the cracks [24]. On the other hand, fibers can play an important role in bridging cracks by attaching crystallization products, which helps self-healing [32,34,131].

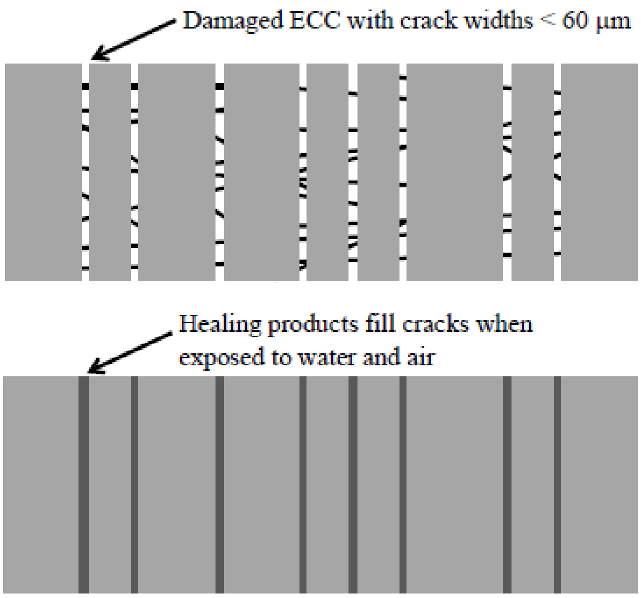


Fig. 7 Schematic illustration of the self-healing approach by autonomously tight crack width [146].

The self-healing property of concrete with fibers, especially ECC, has been widely studied. According to the research of Yang et al. [37], self-healing behavior of ECC with 4.5% of PVA fibers could take place in cracks with width less than 150 μm, although crack width below 50 μm was preferred. The resonant frequency of cracked ECC was recovered by 76% to 100% after self-healing and its stiffness also showed a distinct rebound. Even for pre-damaged specimens that are deliberately subjected to tensile strain of up to 3%, the tensile strain capacity after self-healing was almost fully recovered [37]. Hung et al. [38] reported that when the cracked specimens were submerged in water or exposed to natural weathering with high humidity, they could regain the multiple cracking behavior and even show a higher reloading strength than the preloading strength. The self-healing ability of ECC can also be improved by adding carbon fiber, and the recovery of flexural strength, deflection and electrical resistivity can be accelerated with the increasing fiber content within certain range [41]. The self-healing phenomenon of ECC is due to further hydration and carbonation. Kan et al. [131] observed that the main self-healing products of ECC are C-S-H and $CaCO_3$ [131].

Desmettre et al. [133] found that, the water tightness of fiber reinforced concrete was significantly better than that of reinforced normal-strength concrete at a same stress level in the reinforcement, either under constant loading or cyclic loading. For fiber reinforced concrete, cyclic loading did not impact the self-healing behavior, but even promoted it. With the addition of synthetic fibers such as PVA, PE and PP fibers, the cracks with width larger than 0.1 mm in concrete could been healed [39]. Moreover, researchers have found that the use of hybrid fibers is usually better than a single type of fiber [32,33]. Homma et al. [32] compared the self-healing capability of fiber reinforced cementitious composites containing 1) PE fiber; 2) steel cord fiber; and 3) both of PE and steel cord fibers. In their study, the strength recovery rate (c) was defined as follows:

$$c = \frac{\sigma_2 - \sigma_0}{\sigma_1 - \sigma_0} \times 100 \quad (1)$$

where σ_0 is the stress at the unloading in the first tension test, σ_1 is the tensile strength in the first tension test, and σ_2 is the tensile strength after the self-healing.

Fig. 8 shows that the self-healing concrete with a combination of PE and steel cord fibers can restore tensile strength over 100% when the residual elongation is smaller than even 2 mm, indicating that tensile strength after self-healing can reach the first unloading stress even the tensile strength in the first tension test [32]. The addition of PE and steel cord as hybrid fibers also makes concrete composites exhibit relatively high recovery rates of water tightness and mechanical properties even for cracks about 0.7 mm wide [33].

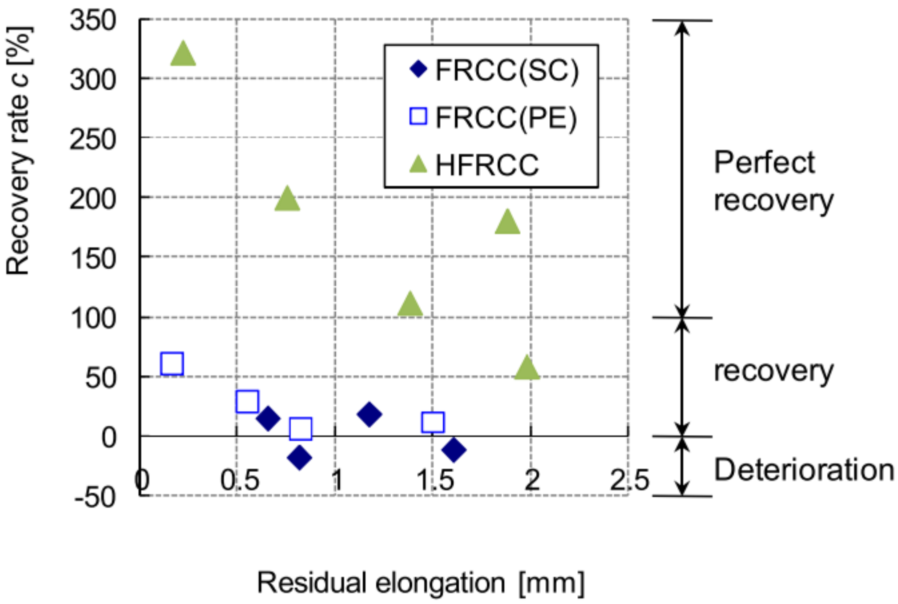


Fig. 8 Relationship between recovery rate and residual elongation. (FRCC(SC), FRCC(PE) and HFRCC represent concrete containing steel cord fiber, PE fiber and both of steel cord and PE fibers, respectively) [32].

The widely used steel fiber in concrete exhibited the ability to stimulate self-healing of concrete. The research of Kim et al. [40] shows that after being healed in water for 14 d, the first cracking strength of steel-fiber reinforced cement composites recovered by up to 36% and the post cracking strength recovery was almost 100%. Escoffres et al. [144] reported that under monotonic loading, high-performance fiber reinforced concrete (HPFRC) and HPFRC with crystalline admixture (HPFRC-CA) showed maximal crack widths 39% lower and water permeability 3.1 times inferior than high-performance concrete. Under a 7-day constant loading and a continuous water flow, cracks of HPFRC and HPFRC-CA were completely healed, whereas the sealed cracks in high-performance concrete accounted for only 60%. The healing products were identified as calcite and ettringite in HPFRC, while the products were aragonite in HPFRC-CA [144]. Although steel fiber can greatly enhance the self-healing behavior and mechanical performance of concrete, there are concerns that water or high moisture content, which is necessary for healing process as aforementioned, is very likely to cause the corrosion of steel fiber. Therefore, waterproof treatment is suggested in this case.

Influencing factors on self-healing performance are also investigated, including crack characteristics, fiber type, fiber amount, curing age and exposure conditions. Rougher and thinner cracks are confirmed to facilitate self-healing [32,34,133]. Fiber reinforced cementitious composite with cracks narrower than 0.1 mm has good self-healing property in terms of its water tightness [33]. Twisted steel fibers produce smaller crack width than hooked steel fibers, and the use of fine silica sand causes a slight increase in post cracking strength and a decrease in crack width [40]. Choi et al. [39] found that PVA fiber with polarity was superior to PE and PP fibers because it was able to restore water tightness of cement mortar and promote the precipitation of self-healing substances. The amount of fiber per volume has a significant effect on self-healing as it affects the quantity of the attached products [32]. Researchers have found that mature specimens have better recovery than early-age specimens due to the formation of more cracks with smaller width [34,35,131]. However, the self-healing of early-age specimens has high robustness when the preloading strain is limited to less than 0.3%, which is 30 times greater than the failure strain of normal concrete materials (0.01%) [35]. In terms of curing conditions, a higher temperature favors the self-healing of fiber reinforced concrete because it accelerates the early hydration, similar to self-healing concrete with mineral admixtures. Yang et al. [37] found that for cyclic curing conditions, such as water/air cycles and water/hot air cycles, autogenous healing developed rapidly in the first few cycles but greatly slowed down after 4-5 cycles and eventually remained stable beyond 10 cycles. The study of Kan et al. [131] showed that after 10 water/air cycles of curing, the resonant frequency of ECC with PVA fiber recovered more than 90%, even at a 2.0% imposed strain. Compared with exposure condition of de-icing salt freeze/thaw cycles, water freeze/thaw cycles result in a higher self-healing degree of concrete [36]. It is believed that the healing in water ensures the best self-healing capability, followed by natural weathering with high humidity. Besides, the recovery of resonant frequency and the tensile stiffness of damaged concrete also increase with the rise of humidity [38].

5.3 Self-healing concrete containing nanofillers

Numerous studies [154–157] show that nanotechnology has great potential to modify concrete materials from many different aspects owing to their special structure and excellent properties. In the field of self-healing concrete, however, research on nanofillers as self-healing materials is still limited [158–160]. In summary, three mechanisms have been proposed to explain how nanofillers improve the self-healing of concrete. Firstly, nanofillers act as nucleation sites in pore solution for hydration products, thus promoting further hydration. A model explaining the nucleating effect of nanomaterials is shown in Fig. 9, where figures (a), (b) and (c) separately describe the hydration of pure cement, the cementitious composites with inert nanofillers and the cementitious composites with active nanofillers. It can also be seen from Fig. 9 (b) and (c) that hydration products can form not only around the cement particles, but also around nanofillers because of their nucleating effect. As a result, the hydration process of unhydrated cement particles is accelerated [161]. Secondly, the incorporation of nanofillers improves the three-dimensional network structure of cement matrix, produces more fine cracks and disperses the propagation direction of cracks [161–163]. Fig. 9 (b) and (c) also show that the cementitious composites with nanofillers have a denser matrix than pure cement. Thirdly, active nanofillers, such as nano-SiO_2 and nano-SiO_2 coated nano-TiO_2 with pozzolanic reactivity, can react with $Ca(OH)_2$ to produce additional calcium silicate hydration, thereby improving the compactness of specimens [42,164,165].

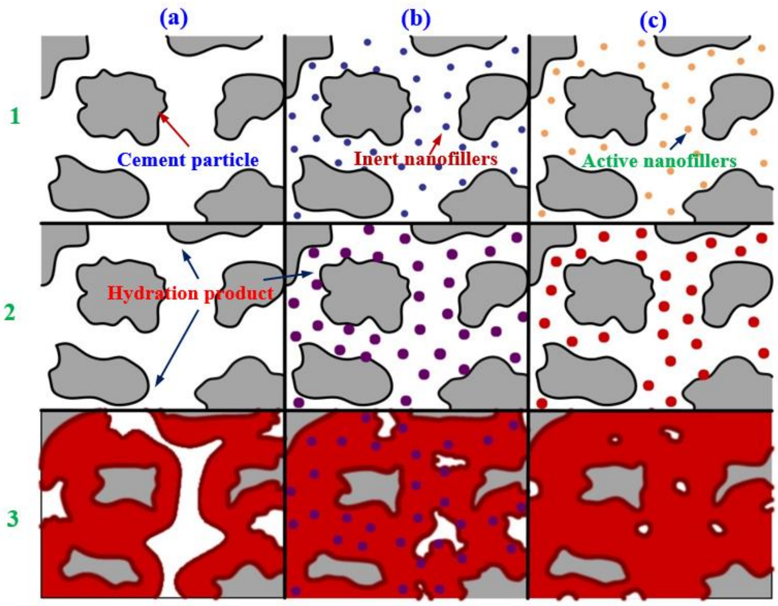


Fig. 9 Hydration of (a) pure cement, (b) cementitious composites with inert nanofillers and (c) cementitious composites with active nanofillers [161].

There are some studies [166–171] about the effects of nanofillers on the mechanical performance and durability of concrete. In most cases, nanofillers exhibit good enhancing effect, indicating the promising application of nanofillers in self-healing concrete. According to the study of Siad et al. [41], the maximum crack width in ECC incorporating 0.25% and 0.5% carbon nanotubes (CNTs) was 50 μm under a four-point loading test, which was lower than that of control sample (70 μm). Besides, increased CNTs content led to accelerated and enhanced recovery of flexural strength and deflection, greater recovery of electrical resistivity and more cracks but with decreased crack width. Wang et al. [42] reported that the incorporation of either nano-SiO_2, nano-TiO_2 or nano-ZrO_2 was able to enhance the self-healing capability of reactive powder concrete (RPC). The nanofillers weakened and even eliminated the Kaiser effect of RPC under secondary loadings, indicating that the internal cracks were healed to some extent. The self-healing coefficients of compressive (Cs) and flexural strength (Fs) of nanofillers modified RPC are calculated according to equations (2) and (3), and the results are exhibited in Fig. 10.

$$C_s = C_1/C_2 \quad (2)$$

$$F_s = F_1/F_2 \quad (3)$$

where C_1 is the 90-d compressive strength of RPC after self-healing, C_2 is the 90-d compressive strength of RPC without preloading, F_1 is the 90-d flexural strength of RPC after self-healing, F_2 is the 90-d flexural strength of RPC without preloading.

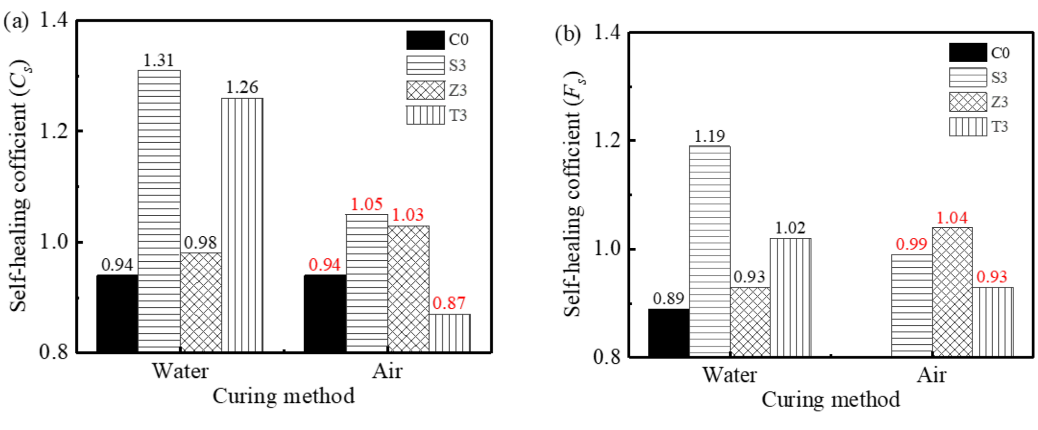


Fig. 10 The self-healing coefficient of RPC under (a) compressive load and (b) flexural load (Note: C0 represents RPC without nanofillers, and S3, Z3 and T3 represents RPC with 3% nano-SiO_2, nano-ZrO_2 and nano-TiO_2, respectively) [42].

Among these three nanofillers, nano-SiO_2 is the most effective one in terms of the self-healing performance of RPC. Besides, water curing is also identified as a key factor for self-healing concrete with nanofillers. When healed in water, the self-healing coefficients of compressive and flexural strengths of RPC containing 3% of nano-SiO_2 were 39.4% and 33.7% higher than that of control sample, respectively [42].

5.4 Self-healing concrete containing curing agents

Internal curing enabled by curing agents is another method to help concrete achieve self-healing property. Curing agents act as internal water reservoirs that absorb and store water when there is sufficient water, and as the humidity gradient occurs, they will gradually release the contained water to unhydrated cement to support continuous hydration. Therefore, the autogenous shrinkage and plastic shrinkage due to low water to binder ratio (W/B) can be significantly reduced. Common curing agents include LWA such as ceramsite and pumice, and chemical admixtures such as SAP and SRA. The swelling of SAP during water ingress may seal cracks, prevent the liquid from intruding, and help regain the overall water tightness, as illustrated in Fig. 11 [172]. The water storage capacity of LWA is generally 5% -25% by weight of LWA, while SAP and SRA have ultra-high water adsorption property and can absorb water more than 1,000 times their own weight [173].

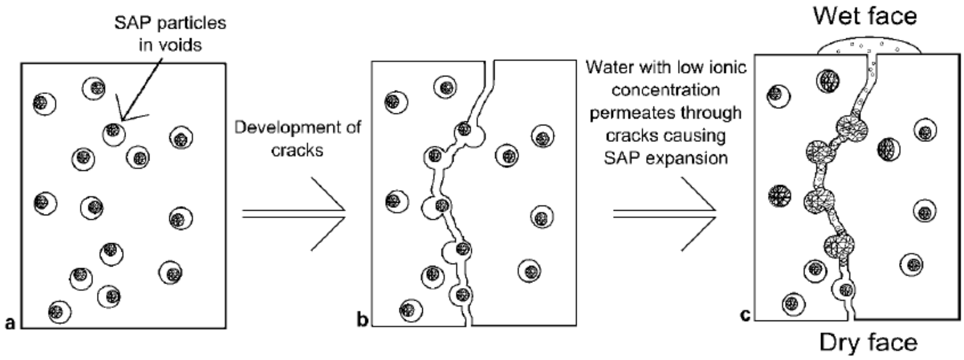


Fig. 11 Schematic showing potential mechanism of self-sealing cracks using SAP [145].

According to Powers' model [174], binder is fully hydrated when W/B is equal to or higher than 0.36, and only partial binder hydration is achieved when W/B is below 0.36. Based on Powers' model, the sealed curing cement paste with a W/B of 0.30 can only reach the hydration degree of 0.73 due to the lack of water, as shown in Fig. 12 (a). Fig. 12 (b) and (c) show that when the system is supplemented with an extra internal curing water of 3.20% and 7.36% by total water volume, the hydration degree proceeds to 0.77 and 0.83, respectively. The chemical shrinkage is reduced and even completely eliminated. Fig. 12 (d) indicates that maximum theoretical hydration degree enhances as the volume of internal curing water increases, but it remains at 0.83 when the internal curing water reaches the limit value of 7.36%, due to the absence of pore space [44]. Therefore, the content of internal curing water is of great significance for the self-healing of concrete.

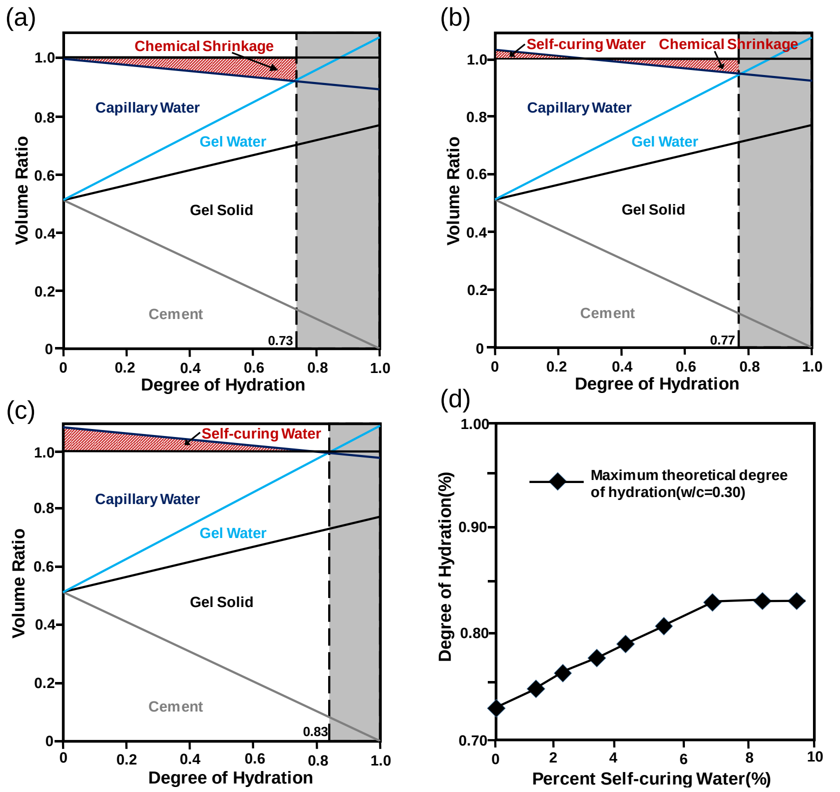


Fig. 12 Powers' model showing phase distributions for (a) W/B=0.30 paste (b) 3.20% internal curing water and (c) 7.36% internal curing water. (d) Maximum theoretical degree of hydration as a function of internal curing water [44].

The effects of curing agents on self-healing performance of concrete are summarized in Table 5. The incorporation of curing agents containing extra curing water can improve workability, later hydration degree of cement and freeze/thaw resistance, and reduce but not completely eliminate autogenous shrinkage caused by macro pores formation [50,52,56,172,174,175]. Fine LWA with larger specific surface area is more conducive to internal curing than coarse LWA because it provides a more uniform distribution of additional curing water [176]. The swollen SAP can not only physically block cracks, but may also promote the autogenous healing of cracks by reducing the flowrate. Lee et al. [145] pointed out that the swelling ratios SAP in tap water, 0.12 wt.% NaCl solution or synthetic shallow groundwater were far larger than that in synthetic pore solution. In addition, the flowrate of the first three solutions through a 340 mm wide model crack (i.e., a slit made with two parallel glass slides) substantially decreased with the application of SAP below 1% (in volume). However, the swelling of SAP in synthetic seawater was limited, so it was not suitable for marine structures. SAP A (a cross-linked copolymer of acrylamide and sodium acrylate) is a preferable curing agent than SAP B (a cross-linked potassium salt polyacrylate), considering the more effective mitigation of autogenous shrinkage [53]. Some experimental results suggest that the compressive strength of concrete with curing agents is improved compared with control samples, while others show a downward trend [43,46,48,52,177,178]. This is because that a proper amount of internal curing water can result in a higher degree of binder hydration, but excessive curing water may cause some spherical capillary pores [179]. Although the presence of SAP led to a reduction in compressive strength, cracks with initial effective crack width up to 0.4mm in SAP modified sulfur composites were completely sealed [148]. Moreover, there are still some challenges for SAP-enabled self-healing concrete to overcome, such as the need of additional water to compensate for the swelling of SAP, the formation of SAP clusters and the negative effect of macropore formation [172].

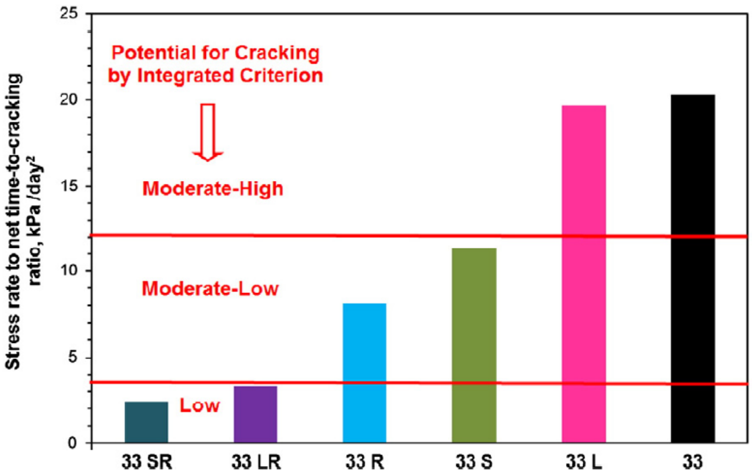


Fig. 13 Estimation of cracking potential by integrated criterion (Note: 33SR, 33LR, 33R, 33S, 33L and 33 represent concrete with a combination of SAP and SRA, a combination of LWA and SRA, SRA, SPA, LWA and control concrete, and the water/cement (W/C) of all samples is 0.33) [46].

Table 5 Summary of self-healing concrete with curing agents

Matrix type	Curing agents	Results	References
High-performance blended cement mortar	Fine LWA	(1) Higher compressive strength; (2) Lower autogenous deformation	[43]
Concrete	LWA (3.8%,6%,7.3%, 10%,11%,14.3%, 16%,18.3%,25.3%, 29.3%,33%)	(1) Reducing even eliminating autogenous shrinkage; (2) Reducing plastic shrinkage cracking; (3) Higher hydration degree; (4) Less susceptible to early age thermal cracking	[45]
	Shrinkage reducing admixture polyethylene glycol (PEG400) (0.5%, 1%, 1.5%, 2%)	(1) Higher compressive strength (≤7.23%), split tensile strength (≤11.60%) and modulus of rupture (≤8.57%) for M20; (4) Nearly no change for M25 and M40	[51,180]
	PEG400 (0.5%, 1%, 1.5%)	Higher compressive strength (≤22.28%), split tensile strength (≤ 36.79%) and durability (≤18.64%) at 28 d	[177]
High-performance concrete	SAP	(1) Lower autogenous shrinkage (≤57%) after 144 h; (2) Lower compressive strength (≤27.6%), tensile strength (≤33.2%) and modulus of elasticity (≤24.9%)	[52]
Ultra-high	SAP (0.206%,	(1) Reducing autogenous shrinkage (from >600 to 120	[48]

performance concrete	0.313%, 0.5%)	μm/m) at 30 d; (2) Reducing self-desiccation and mechanical properties; (3) Promoting hydration	
High-performance concrete	Eclipse Floor SRA, LWA, SAP (single and hybrid)	(1) Lower free shrinkage (especially SRA); (2) Lower early strength (LWA, SRA); (3) Higher weight loss upon drying (LWA, SAP); (4) Reduction in creep/relaxation capacity	[46]
Microfiber-reinforced cementitious material	SAP (1%)	(1) Higher healing degree; (2) The cracks ranging in depth from 0 to 800-1000 μm was fully healed in case of wet/dry cycles	[181]

6. Performances of autonomous healing concrete

6.1 Self-healing concrete based on electrodeposition technology

The mechanism of self-healing behavior in reinforced concrete based on electrodeposition technology is illustrated in Fig. 14, benefiting from the characteristics of reinforced concrete and water environment condition. By applying a weak direct current between rebar in reinforced concrete structures and an external electrode (an anode), electrodeposits will occur around rebar and a barrier coating of inorganic insoluble compounds such as ZnO, $Mg(OH)_2$ and $CaCO_3$, etc. will form in cracks and on concrete surfaces [49]. Therefore, cracks in concrete can be filled and the surface of concrete is sealed, preventing further corrosion. As mentioned above, this electrochemical technology requires conditions of conductive concrete, electric current and electrolyte solution.

Electrodeposition technology is usually adopted to repair cracks in reinforced concrete. In 1999, Otsuki et al. [14] applied this electrodeposition method to repair cracked reinforced concrete and found that the formed electrodeposits could provide protection from detrimental materials. In 2001, Ryu [55] observed that the drying shrinkage cracks with width of 0.05-0.10 mm were almost fully closed after 14 d of testing. The electrodeposits are ZnO, $Mg(OH)_2$, $CaCO_3$, CuO, Ag and $CuSO_4$ when the immersion solutions contain $ZnSO_4$, $MgCl_2/Mg(NO_3)_2$, Ca^{2+}, $CuCl_2$, $AgNO_3$ and $Cu_4SO_4(OH)_6$, respectively. These layers of inorganic compounds provided a physical barrier, as a result, the flux of gas or solution inside the concrete was reduced [55,56]. For example, in a research conducted by Ryu [50], cracks up to 1 mm were completely healed after 30 d when immersed in solution of $ZnSO_4$. Crack filling depth showed an increasing trend with the growth of crack width, contrary to the change of closing speed [50,58]. In addition, the rate of crack closure initially increased rapidly and then slowed down, but eventually reached a high value, even up to 100% [55,57,58]. Ryu and Otsuki [58] found that when $ZnSO_4$ was selected as the immersion solution, the thickness of the electrodeposit layer on the concrete surface was about 0.5-2 mm and electrodeposits penetration reached about 2 mm and 8 mm deep for 0.2 mm and 0.6 mm wide cracks respectively. Chu et al. [57] reported that the crack filling depth was between 4.5 and 13.2 mm for reinforced concrete immersed in $ZnSO_4$ solution. As a result, the mechanical strength, water tightness, carbonation resistance, permeability resistance, corrosion resistance and resistivity of reinforced concrete were all enhanced by electrodeposition technology [54,55,58].

Significant influencing parameters such as healing time, electrolyte solution, water/cement ratio, current density and applied voltage have also been investigated. Among $MgCl_2$, $ZnSO_4$, $AgNO_3$, $CuCl_2$, $Mg(NO3)_2$, $CuSO_4$, $Ca(OH)_2$, $NaHCO_3$ solutions, $MgCl_2$ and $ZnSO_4$ are the most suitable solutions for the precipitation of deposition products inside and outside cracks in mortars [56]. Jiang et al. [49] evaluated the effect of electrodeposition method on the self-healing efficiency of cracks by simulating cracked concrete with porous concrete. They found that the total void ratio of porous concrete had little effect on healing effectiveness of electrodeposition at early age. Larger current density, higher concentration of electrolyte solution, higher solution temperature and greater W/C can promote the precipitation of electrodeposits or crack closure. The increase in W/C also benefits crack closure because it leads to increased porosity and reduced resistivity of concrete, which ultimately causes a higher electric current. It is determined that pulse current results in a better healing effect than direct current, since it contributes to higher ratios of weight gain, surface coating, crack closure and larger crack filling depth. Microstructure analysis indicates that pulse current transforms the structure of sediments from porous honeycomb-like one to a uniform and dense layered one without changing the composition [60]. With suitable technological parameters, the strength and the durability of reinforced concrete can be improved to some extent [49,50,54,57].

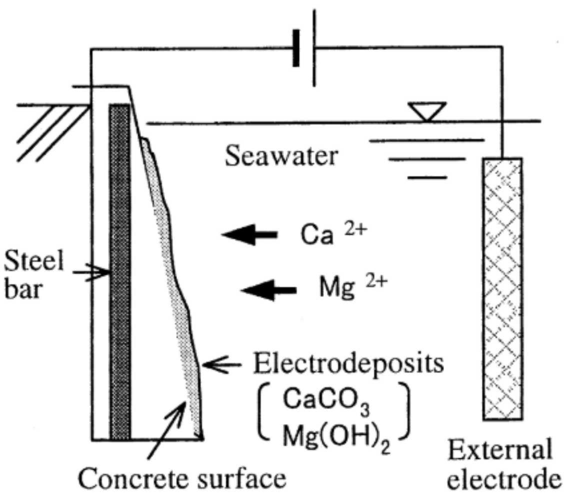


Fig. 14 Application of electrodeposition in marine structure [58].

6.2 Self-healing concrete based on shape memory alloy technology

SMA has a nature of shape memory, transforming from martensite phase to austenite phase when heated. That means the shape (length and diameter) of prestrained SMA in concrete can be recovered under the actuation of thermal energy (usually electrical currents), thereby repairing cracks, i.e., exhibiting self-healing capacity [61]. SMA has different composite systems, among which the most commonly used system in concrete is NiTi SMA.

Both experimental and simulation results indicate that SMA simulation helps crack repair, as summarized in Table 6. The heated SMA wires could rapidly close cracks after unloading, showing the potential to repair emergency damage in concrete structures [67,182]. Compared with SMA wires, the combination of SMA wires and brittle fibers containing adhesives can better repair the smart beam [182]. In addition to providing crack recovering capability, SMA also enhances the deflection recovery, bond strength, flexural strength, Young's modulus and ductility of cementitious composites because of its shape memory effect [66–68,138]. For example, Li et al. [67] observed that the mid-span deflection of a concrete beam was reduced by 74.3% with a least deflection of 1.27 mm when temperature rose to about 110 °C. Li et al. [62] found that the recovering force exerted by the shape memory effect of SMA bundles in smart concrete beams can be controlled, which was almost proportional to the temperature of SMA bundles. The deflection generated by SMA bundles at the middle span of the beam was approximately 0.44 mm and the average overload resistance of each beam was about 2.98 kN. However, the environmental impact was remarkable. The mid-span displacement of the concrete beam caused by environment temperature was about 12 times that induced by the restoring force of SMA bundles. Choi et al. [68] evaluated crack-closing capability of cement mortar beams with four types of NiTi SMA fibers based on the degree of crack recovery and deflection-recovery factor. The results are listed in Table 6 and Fig. 15, respectively. Straight-paper fiber and dog-bone-paper fiber have deflection recovery factors greater than 1.0, which means that their upward deflections exceed the downward deflections. However, the fibers without paper have values below 1.0, manifesting that the downward deflections are not fully recovered. Li et al. [141] conducted a comparative research on the self-healing behavior of reinforced concrete, SMA reinforced concrete and SMA reinforced ECC. They observed that SMA reinforced ECC beams showed distributed microcracking damage feature (multiple crack with width less than 40 μm), minimal residual deformation and complete self-recovery under cyclic flexural loading, as plotted in Fig.

16.

Table 6 Cracks of beams before and after heating

SMA	Temperature	Cracks (mm)		Degree of crack recovery $(w_0-w_1)/w_0$	References
		Before heating w_0	After heating w_1		
NiTi (number: 4)	110 °C	3.98	0.65	83.7%	[67]
SMA wires (2mm)	110 °C	0.2769	0.2656	4.1%	[183]
SMA wires (3mm)	110 °C	0.2769	0.2534	8.5%	
SMA wires (4mm)	110 °C	0.2769	0.2312	16.5%	
Straight NiTi fiber (number: 5)	-	0.58	0.29	50.0%	[68]
Dog-bone NiTi fiber (number: 5)		0.38	0.15	60.5%	
Straight-paper NiTi fiber (number: 5)		0.28	0.09	67.8%	
Dog-bone-paper NiTi fiber (number: 5)		0.56	0.05	91.0%	
Straight NiTi fiber (number: 2)	125 °C	0.56	0.15	73.2%	[63]
Straight NiTi fiber (number: 3)		0.53	0.04	92.4%	
Straight NiTi fiber (number: 4)		0.57	0.00	100%	
Dog-bone NiTi fiber (number: 2)		0.49	0.27	44.9%	
Dog-bone NiTi fiber (number: 3)		0.53	0.28	47.2%	
Dog-bone NiTi fiber (number: 4)		0.56	0.22	62.5%	
Straight NiTiNb fiber (number: 2)		0.53	0.3	43.4%	
Straight NiTiNb fiber (number: 3)		0.54	0.29	46.2%	
Straight NiTiNb fiber (number: 4)		0.56	0.14	76.8%	

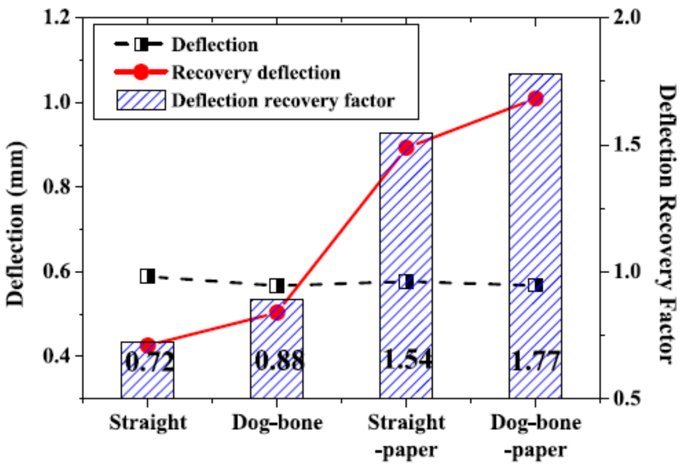


Fig. 15 Deflection recovery factor [68].

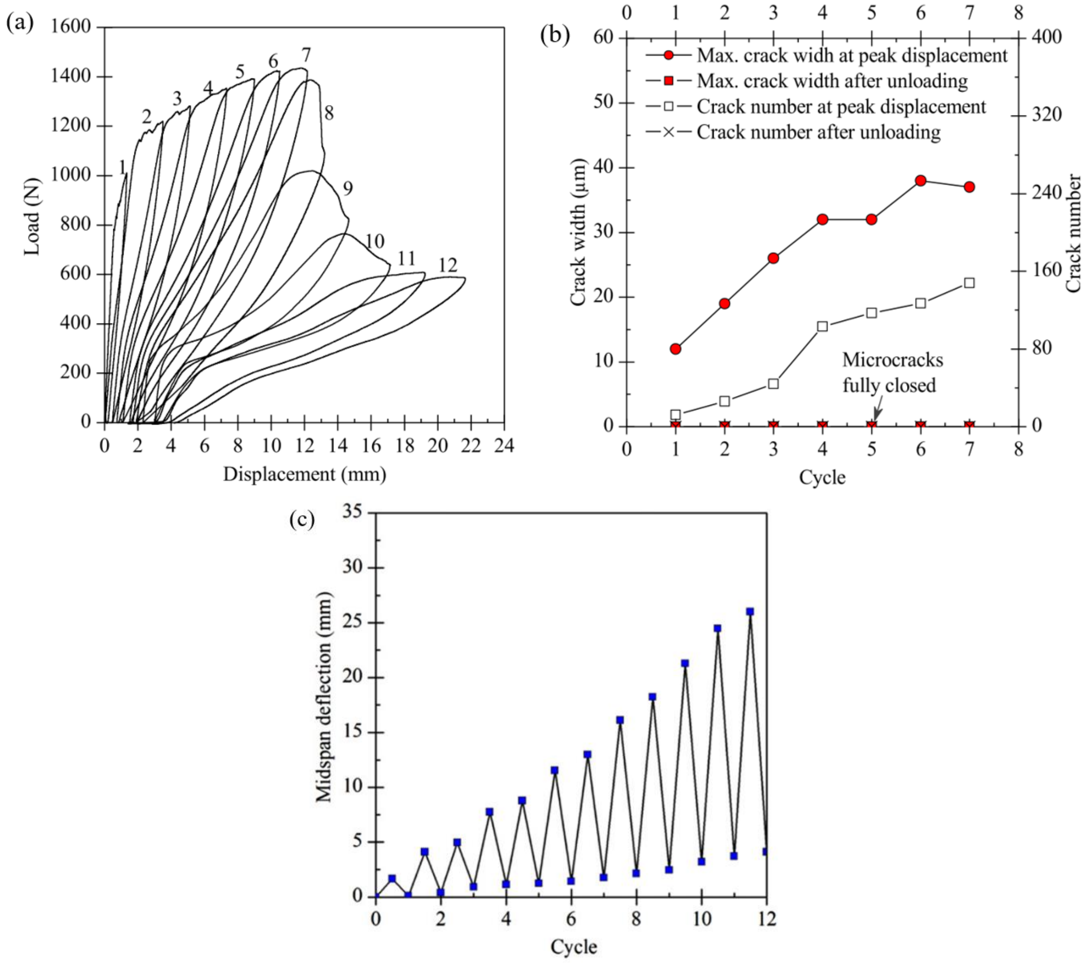


Fig. 16 SMA-ECC beam behavior under cyclic loading: (a) load (at roller) versus displacement response; (b) crack number and maximum crack width at peak displacement and after unloading for each cycle; and (c) midspan deflection at peak displacement and after unloading for each cycle [137].

The shape change of SMA before and after heat treatment enhances its pull-out resistance, and some factors affecting the pull-out resistance and crack closure such as shape, type and size of SMA have been explored. It was verified [65,66] that a short period of heat treatment shortened the length of cold-drawn SMA fibers but expanded their diameter. The former could generate pre-stressing effects and increase the Young's modulus of cementitious composites, while the latter can enhance the pull-out resistance, thus resulting in a greater crack closing potential. Moreover, the pull-out resistance of deformed SMA fibers, especially dog bone-shaped fibers, was generally higher than that of smooth SMA fibers [64,68]. However, Lee et al. came to a different conclusion, that is, the straight fibers showed greater post-cracking residual strength and crack-closing ratio than the dog-bone fibers. This may be because that the pre-activation of the shape memory effect at both ends of the fibers caused a reduction in the total length of the dog-bone fibers, which means the lower adhesion length [63] In contrast to end-deformed and crimped SMA fibers, dog bone-shaped SMA fibers exhibited the best improvement in bond strength after heat treatment. The deformed NiTiNb SMA fibers showed higher pull-out resistance and crack recovery than deformed NiTi SMA fibers, but the relationship is reversed for smooth fibers [64,68]. According to finite element analysis, larger diameter of SMA and smaller reinforcement ratio is beneficial for improving repair ability [183]. The experimental results of Sherif et al. [138] indicate that cement mortar with 30-mm-long SMA fibers exhibited better crack recovery performance than that with 20-mm-long SMA fibers because shorter fibers might produce permanent deformation at high deformation levels. Adding 1.0% of SMA fibers allowed cement mortar to achieve the minimum crack propagation and maximum crack recovery rate.

6.3 Self-healing concrete based on capsule technology

Incorporating capsules (containing healing agent) and catalytic chemical triggers (optional) into concrete is another method to realize self-healing. Capsules can be classified into microcapsules and macrocapsules according to their size. The autonomous healing process is illustrated in Fig. 17 [184]. First of all, crack ruptures the embedded capsules on its developing path, causing the healing agent to flow into cracks under capillary force or gravity. Then, chemical reactions take place between the healing agent and matrix material to bond the crack planes together and change the shape of the crack tip.

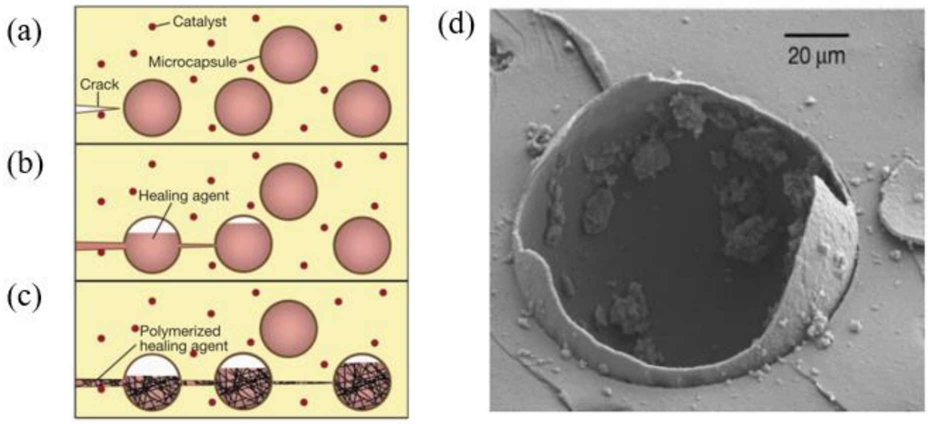


Fig. 17 Healing concept of the capsule technology: (a) cracks form in the matrix; (b) the capsules rupture, releasing the healing agent into the crack plane; (c) the healing agent contacts the catalyst, triggering chemical reaction that bonds the crack faces closed; (d) ESEM image showing a ruptured microcapsule [184].

The research about self-healing concrete based on capsule technology has been booming since White et al. [184] studied the self-healing of polymer composites in 2001. Preparation of suitable capsules, appropriate capsule content and self-healing efficiency are the hotspots of most recent research investigations. Ideally, capsules should possess the appropriate size, shell thickness, healing agent, surviving ability during mixing, good interfacial adhesion and compatibility with concrete matrix, chemical and mechanical stability, and favorable sensitivity to cracks. In order to achieve satisfactory self-healing performance, the probability of capsules being hit should be increased as much as possible. Zemskov et al. [81] proposed two two-dimensional analytical models to calculate the probability of a crack hitting encapsulated particles. The presented functions can estimate the combination of crack lengths, capsule size, and mean inter-capsule distance in order to analyze the efficiency of a self-healing material. Lv and Chen [185,186] also put forward a probability model based on the targeted healing level to determine the theoretical dosage of capsules required in the matrix. They pointed out that the hitting probability may increase as the crack grows, but improve as the capsule size increases. Besides, the shape of capsules also affects the hitting probability.

6.3.1 Microcapsule

Zhu et al. [90] summarized several microencapsulation techniques, including in situ polymerization, interfacial polymerization, pickering emulsion templating, mini-emulsion polymerization, solvent evaporation/solvent extraction, sol-gel reaction and miscellaneous. Other methods of fabricating microcapsules such as interfacial self-assembly process [69], extrusion spheronization or extrusion hollow tube [130,132] and complex coacervation [113] have also been reported. The mean diameter and size distribution of microcapsules can be controlled through adjusting the agitation rate during the synthesis [78]. Stirring rate, pH value, core-wall ratio and reaction temperature all have influences on the preparation of microcapsules [73,136]. For example, stirring rate and pH value are the most significant factors affecting the size distribution of melamine urea-formaldehyde microcapsules. For melamine urea-formaldehyde microcapsules, increasing shell material and temperature or lowering pH can promote their mechanical properties. Specifically, an optimal synthesis method of urea-formaldehyde microcapsules has been proposed by Li et al. [136], which is to produce microcapsules at a core-wall ratio of 1:1, a temperature of 60 °C, a stirring rate of 300–400 r/min, and the pH value of 2~3.

The shell materials and internal materials of microcapsules are summarized in Table 2. The self-healing mechanisms of microcapsules are basically determined by the self-healing agent. The self-healing mechanisms of methylmethacrylate monomer is polymerization triggered by the catalyst, which bonds the crack faces together [69]. For dicyclopentadiene, it repairs cracks through ring opening metathesis polymerization [73]. When epoxy resin is released from microcapsules, it will react with the thinner agent and harden agent premixed in matrix material to form healing products, and then fill the cracks [76]. When sodium silicate is used as a healing agent, it will react with the calcium hydroxide in cement and produces C-S-H gels to repair cracks [71]. The precipitation of portlandite accompanied with the further hydration of unhydrated cement are the main mechanisms of self-healing induced by $Ca(OH)_2$ solution [96]. The healing agent, MEYCO MP355 1K, is a two-component polyurethane pre-polymer, having the ability to seal cracks by an expanding foaming reaction that occurs in humid environment [94].

The self-healing efficiency of microcapsule method has been widely investigated, and it can vary with different healing agent. Yang et al. [69] designed microcapsules with oil core (healing agent or catalyst) and silica gel shell and used these microcapsules with an average diameter of 4.15 μm to prepare self-healing mortar. Due to the self-healing effect of microcapsules, the gas permeability of carbon microfiber-reinforced mortar was reduced by 66.8% at 30 d by adding a small dosage of microcapsule, and the crack resistance and the toughness under fatigue load were both enhanced. For polyurethane microcapsules containing sodium silicate, concrete with 2% volume of microcapsules gained 20%-26% recovery in flexural strength [71]. According to the experimental study of Gilford et al. [73], a low dosage (0.25%) of dicyclopentadiene microcapsule at pH level of 3.1 resulted in 30% increase in the modulus of elasticity of concrete after cracking, while the modulus of elasticity only improved by 11% when 5% of sodium silicate microcapsules at the same pH level were added. Lv et al. [78] developed the polymeric microcapsule with henol-formaldehyde resin as shell and dicyclopentadiene as healing agent. It was reported that the microcapsules were chemically stable in both simulated pore solution and actual cement environment. The 3D images obtained from X-ray computed tomography (XCT) in Fig. 18 indicates that the microcapsules were well dispersed and sensitive to cracks triggering. Minnebo et al. [94] studied the feasibility of polymethylmethacrylate, starch, inorganic phosphate cement and alumina to develop encapsulation system, and the latter two materials were successful. Numerical simulation results showed that the self-healing efficiency of cracks provided by saturated $Ca(OH)_2$ solution carried in capsules was very low because the solution was quickly absorbed by the bulk material. Moreover, the amount of healing agent used for crack repair increased linearly with the capsule dosage and diameter, thus contributing to higher self-healing efficiency [96]. Perez et al. [70,187] synthesized epoxy-containing silica microcapsules and amine-functionalized silica nanoparticles and used them to build cement pastes with innovative self-healing system. The silica shell of the microcapsule could react with the portlandite in cement matrix so as to improve the bond with the cement matrix. This means that silica microcapsules could have good compatibility with the cement matrix. Pozzolanic reaction also occurred between amine-functionalized silica nanoparticles and portlandite, and the amine-functionalized cement matrix was generated during this process. Once the epoxy compound encounters the amine functional groups that were tethered in the silicate chains of the matrix, they will react and then cracks will be sealed by hardened epoxy. The stability of microcapsules during the preparation and hydration was confirmed, and 150 μm wide cracks were sealed [70] .

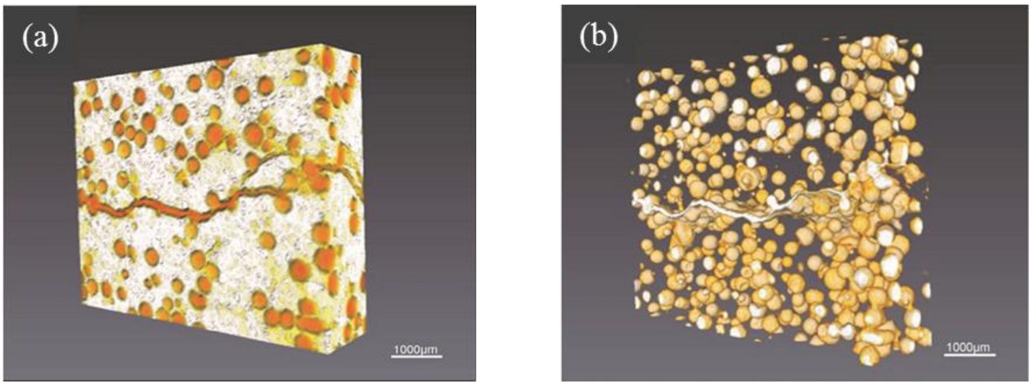


Fig. 18 3D reconstructed tomographic images of the segmented raw data (a) a selected section of fractured cement paste (b) a 3D rendering of the spatial dispersion of microcapsules [78].

Several factors, including microcapsule size [188], microcapsules content [76,77], crack width [77], preload level [72], healing age and curing temperature [77], significantly affect the self-healing efficiency. The researches of Dong et al. [76,77] indicate that the self-healing efficiency improved with the increase of microcapsules content (2%, 4%, 6%, 8%) and size (132 μm, 180 μm, 230 μm). Cracks healed by 20.71%-45.59%, and compressive strength and impermeability recovered up to about 13% and 19.8%, respectively [76]. Kanellopoulos and Giannaros [79] observed that as the volume fraction of microcapsules increased from 4% to 32% (i.e., 0.79%-6% in mass), the crack mouth healing rate of mortar gradually improved. The areal crack mouth healing reached almost 100% when 32% volume fraction microcapsules were incorporated, and the healing products were mainly ettringite and C-S-H. Besides, larger crack size caused lower crack mouth healing rate. According to the rapid chloride migration test conducted by Dong et al. [77], the self-healing efficiency is positively correlated to preloading strength on concrete. This is because more microcracks form at higher loading strength, which eventually triggers more microcapsules to fill the cracks. Wang et al. [75] drew a different conclusion that the average strength recovery rate of cementitious composites was almost proportional to the amount of organic microcapsules, and preloading and W/C had no substantial influence, as shown in Fig. 19. Li et al [72] studied the effects of microcapsule content (1%, 2%), curing condition (in water or air) and pre-damage level (30%, 60%, 100%) on the self-healing efficiency of cement paste containing microcapsules enclosing epoxy resin. The specimens with 1% microcapsules and subjected to 30% pre-damage had the best strength recovery when aged in air, while the specimens aged in water showed the best mechanical recovery when 2% of microcapsules were added and 60% pre-damage was applied [72]. It has been confirmed that longer healing time is beneficial for a higher self-healing efficiency. Besides, if the increase in temperature favors curing reaction of healing agents such as epoxy resin E-51, it will help to achieve a better healing effect [77].

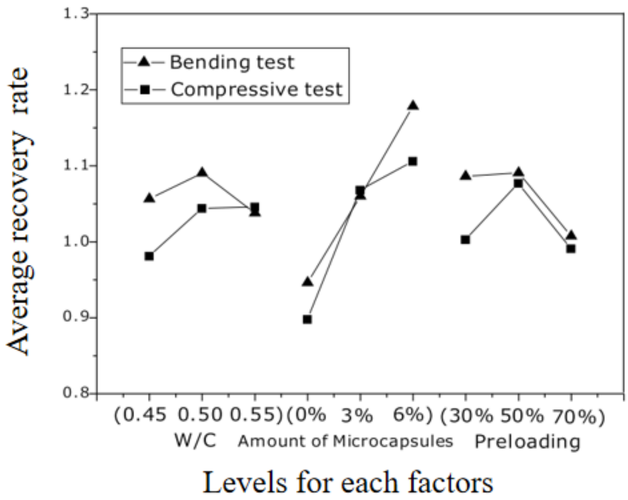


Fig. 19 Relationship between the factors and strength recovery rate [75].

Ideal microcapsules should not only provide outstanding self-healing efficiency, but also have no negative impact on other properties of concrete such as mechanical properties and durability. Therefore, the influence of microcapsules on the initial performances of concrete matrix has also been investigated. Dong et al. [76,77] found that the urea-formaldehyde/epoxy resin microcapsules could survive the mixing and exhibit good compatibility with cementitious materials due to their excellent surface texture, suitable size and remarkable thermal stability. The fractions of large pores (size of >200 nm), capillary porosity, continuous pore diameter and pore connectivity were decreased dramatically [77]. The research of Pelletier et al. [71] showed that when polyurethane microcapsules containing sodium silicate was added, the compressive strength of concrete was not affected while the improved toughness and the attenuation of corrosion were obtained. Strong inhibition of chloride-induced corrosion for steel bars could also be realized by polystyrene resin/sodium monofluorophosphate microcapsule, according to the experiment by Dong et al. [137]. Kanellopoulos et al. [79] reported that the addition of polymeric microcapsules containing sodium silicate did not affect hydration and setting time but improved viscosity. Nevertheless, deterioration of mechanical properties of self-healing concrete with microcapsules has also been reported. Kanellopoulos et al. [79] found that the compressive strength showed a consistent decrease (~27%) with increasing concentration of microcapsules, but the enhancement in self-healing potential offset the decline in compressive strength and elastic modulus. Decline in compressive strength was also reported by Perez et al. [72], who believed it was due to the presence of a minor content of macropores and the low strength of capsules. Dong et al. [77] observed a 5%-25% decrease in compressive strength with increasing microcapsules content from 2% to 8%. When 1%-5% microcapsules containing bacterial spores were incorporated, the compressive strength was reduced by 15%-34% [74].

The keys to achieving self-healing performance based on capsule technology are how to ensure the viability of capsules during mixing, how to release the healing agent and how to activate the healing mechanism (as described in Section 6.3.2). Kanellopoulos et al. [80] produced gelatin/acacia gum microcapsules that can change their mechanical behavior under hydrated and dried conditions, from a rubbery soft state to a glassy stiff state. This transition in properties helps microcapsules survive the wet mixing process with cement and rupture successfully when cracks form in the dry composite, and then the encapsulated sodium silicate solution is released. The microcapsules are also stable at high temperatures up to 190°C or in strong alkaline solutions that simulates the pH environment of concrete. Dong et al. [132] studied the releasing behavior of microcapsules in simulated concrete pore solution. The experimental results indicate that the release of the corrosion inhibitor covered with polystyrene resin increased with time and declined with decreasing pH value, and it was effectively controlled by the wall thickness of the microcapsules, as shown in Fig. 20. Therefore, such microcapsules are good candidates for achieving intelligent release control in an alkaline cementitious environment. As the average size of phenol-formaldehyde microcapsules increases and the shell thickness decreases, the mechanical force required to trigger the microcapsules increases correspondingly. Smaller synthetic microcapsules are generally more susceptible to mechanical triggering caused by cracks [143].

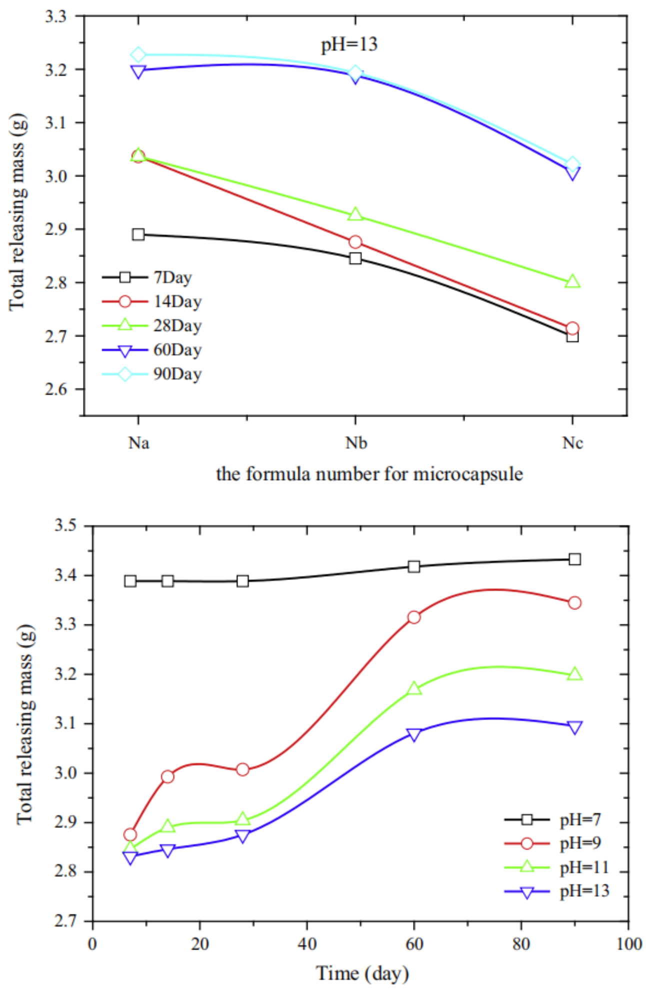


Fig. 20 Total released mass of (a) microcapsules with different formulae and (b) sample Nb as a function of time at different pH values (Note: Na, Nb and Nc are capsules with the mean diameters of 694.9 µm, 720.1µm and 772.0µm, respectively.) [132].

6.3.2 Macrocapsule

The most commonly employed macrocapsule containers are spherical macrocapsules, hollow tubes (glass tubes, ceramic tubes, polymeric tubes, etc.) and porous carriers such as LWA. The diameter of macrocapsules is usually a few millimeters. When expansive powder minerals such as CaO, MgO and bentonite are utilized as healing agents, unhydrated minerals present on the crack surface and that released from capsules will participate in the rehydration reaction to achieve self-healing ability. Hydration products such as $Ca(OH)_2$, $Mg(OH)_2$, C-S-H and alumino-silicate hydrates will bridge the crack. Then the carbonization of reactive hydrating products will further repair cracks [92]. The key issue is to activate the healing ability of capsules to achieve the self-healing of concrete. Generally, the self-healing agent is released from capsules by a mechanical trigger, such as the puncture of cracks. Xiong et al. [82] developed a novel capsule-based self-recovery system that utilizes chloride ions as a trigger.

These capsules are made of a silver alginate hydrogel using orifice solid bath method, and they will disintegrate when exposed to chloride ions, thus releasing the activated core materials, as shown in Fig. 21. This process occurs even at a very low concentration of chloride ions (0.1 wt. %). This capsule-based self-recovery system is believed to have the potential for self-healing or corrosion-inhibiting applications, especially in marine environment.

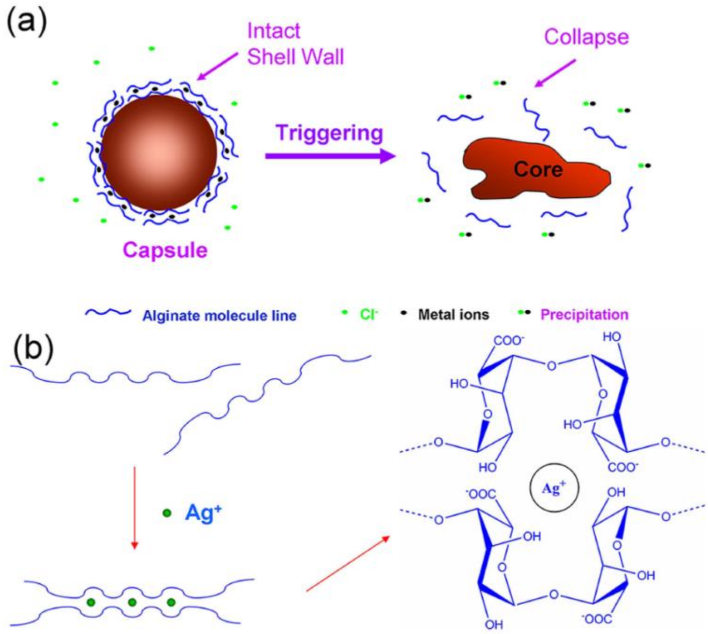
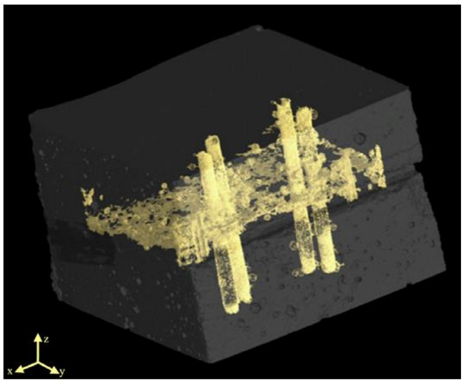
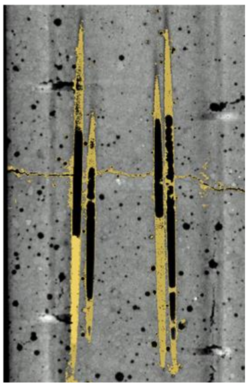


Fig. 21 (a) Schematic of capsules triggered by chloride ions, (b) The structure of alginate chelated with Ag^+ [82].

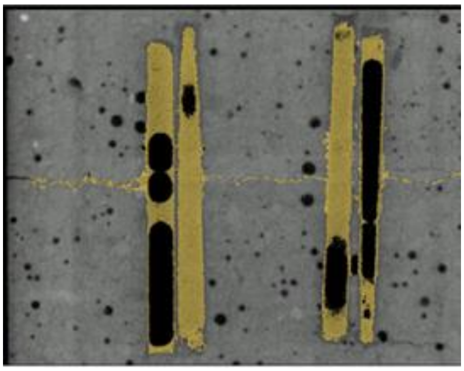
Van Tittelboom et al. [83] embedded two couples of tubular capsules separately containing healing agent and a combination of accelerator and water into cement mortar, and tested the recovery of strength and stiffness of specimens under multiple loading cycles. More than 50% of the original strength recovery and stiffness recovery were achieved during the first loading cycle. During the second reloading, however, the recovery dropped to a maximum of 23% and 34%, respectively. Additionally, the water permeability reduced by 10^2 to 10^4 times. High resolution X-ray computed tomography (HRXCT) image in Fig. 22 manifests that cracks are filled with healing agents. According to water permeability tests and HRXCT-scans, ceramic tubes seem to perform better as encapsulation materials than glass tubes. Thao [85] observed that the reinforced beam embedded with glass tubes containing isocyanate prepolymer achieved 88% and 85% of normalized stiffness recovery in the first and the second healing cycle, respectively. For columns and slabs, stiffness is restored up to 70% and 99%, respectively. Sun et al. [84] pointed out that the self-healing system could also be formed by embedding hollow glass fiber containing healing agent into concrete. Simulation results manifeste that the strength recovery rate exceeded 50% when the crack width was controlled below 0.3 mm. Van Tittelboom et al. [88] fabricated concrete beams embedded with ceramic tubes, each of which were protected by means of mortar bars and contained either prepolymer of polyurethane or a mixture of accelerator and water. As a result of autonomous self-healing, strength and stiffness recovered by more than 80% of the original values. Additionally, the strength and stiffness regain of the self-healing cracks with polyurethane was the same as that of the cracks manually repaired by high strength epoxy resin. The means of adding glass tubes-encapsulated polyurethane to cement mortar was able to seal cracks and prevent chloride penetration. This autonomous healing method was able to seal crack widths of 100 μm and 300 μm for chloride penetration in 67% and 33% of the cases, respectively, although the proportion was slightly lower than the manual crack healing [89]. Feiteira et al. [87] explored the feasibility of encapsulated polymer precursors for healing moving cracks in concrete. The precursors were identified to have good crack-filling potential, but the recovery of mechanical stiffness was limited to a maximum of 30% due to the low stiffness of the cured polymers and was only effective for crack mouth displacements up to 20 μm.



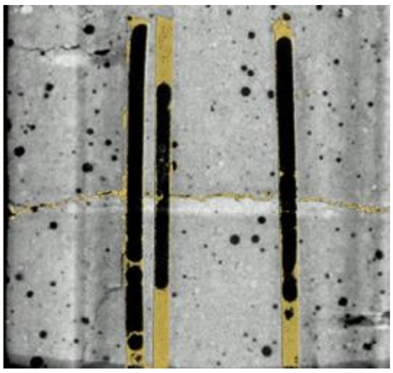
(a) 3D visualization of the region of the mortar sample which contained the tubes and the crack



(b) Y-direction CT cross section through the sample with 2mm diameter glass tubes



(c) Y-direction CT cross section through the sample with 3mm diameter glass tubes



(d) Y-direction CT cross section through the sample with ceramic tubes

Fig. 22 Images of self-healing concrete by HRXCT [83].

Encapsulated healing agent brings some improvement in water tightness of concrete due to self-healing, but the self-healing efficiency greatly depends on the number of cracks, the width of crack, and especially the number of cracks that pass through capsules and cause the healing agent to seep [86]. Kanellopoulos et al. [91] investigated the influences of four glass encapsulated minerals (sodium silicate, colloidal silica, tetraethyl orthosilicate and magnesium oxide) and three curing methods on the self-healing property of cement mortar. All mineral compounds resulted inappropriate load recovery, crack area closure, reduced sorptivity and decreased intrinsic gas permeability. Sodium silicate and colloidal silica turned out to be the optimal healing minerals, which was supported by the results of load and durability recovery. Qureshi et al. [92] developed a kind of concentric glass macrocapsules containing the expansive minerals (outer capsule) and water (inner capsule), which could close large cracks (about 400 μm) in cement mortar. The crack sealing and the strength recovery of cement mortar immersed in water regained by about 95% and 25% at 28 d, respectively, and continued to rise with healing age. In terms of capillary absorption of cracked cement mortar after healing, the improvement in self-healing efficiency was also significant. The release of healing agents is also influenced by the aspect ratio of capsules and the viscosity of encapsulated healing agents. Compared with long tubes, short tubes are preferable for achieving self-healing, probably due to the high attractive forces inside long tubes [86]. The low viscosity of the precursor is the key to effective sealing of cracks. The polymer precursor with super low viscosity as the healing agent has a global strain capacity between 50% and 100%, after which the sealing effect is disrupted. The failure mode occurs when the polymer debonds from the crack walls as the crack gradually opens. For foaming precursors, the failure mode is the rupture of closed foam cells [87].

Porous carriers can also be employed as containers of healing agents. Alghamri et al. [93] observed that concrete containing LWA impregnated with a sodium silicate solution obtained a pre-cracking strength recovery of about 80%, which was more than five times the recovery of control specimens. The sorptivity index was reduced by 50%. Furthermore, the incorporation of impregnated LWA did not lose the expected mechanical properties of the concrete specimens.

6.4 Self-healing concrete based on vascular technology

The vascular technology applied to self-healing concrete is a biomimetic method. Similar to the human cardiovascular system and the plant vascular tissue system, liquid healing agents can be timely transported to the injury site through the vascular network in concrete, and the healing agent can even be continuously supplied from an external source of the structure. The vascular networks in concrete include 1D channel, 2D and 3D channel networks. For 1D channels, the healing agent can be input from one or both ends of the concrete surface [96,98]. The transport of adhesives in other complex transport paths can be realized through multi-flow junction nodes within the network [98]. Cracking of concrete causes the brittle tubes to rupture, and then the healing agent is released into cracks for repairing under the action of capillary force, gravity, surface tension and negative pressure force, as shown in Fig. 23 [95,189].

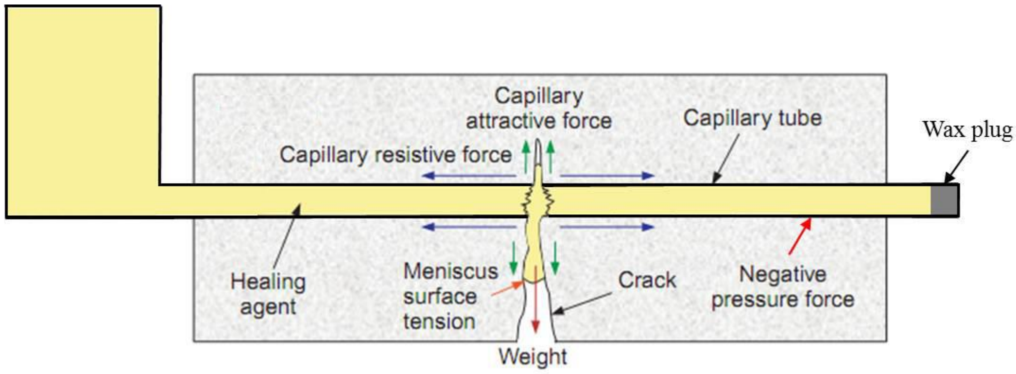


Fig. 23 Schematic illustration of the main forces acting on an internally encapsulated healing agent [95].

In 1994, Dry et al. [11] firstly proposed the vascular method to heal the cracks in concrete. They embedded hollow glass fibers containing liquid methyl methacrylate within concrete and found no loss of strength but improvement of permeability and flexural toughness. Joseph et al. [95] used cyanoacrylate-filled glass tubes as 1D vascular channel in reinforced mortar beams. Primary and secondary healing response occurred during the first and second loading cycles, respectively. Besides, the increase of reinforcement percentage and the decreasing loading rate were found to cause a higher stiffness of the primary healing response. Sun et al. [84] found that the method of embedding glass tube carrying cyanoacrylate (i.e., superglue) enabled concrete to obtain a strength recovery rate of 39.5%-63.5% for different crack width. Huang et al. [96] conducted a comparative study on the self-healing efficiency of cementitious composites using capsules or a vascular system. Owing to the continuous supply of healing agents, they deemed that the vascular method was superior to the capsule approach. After continuous supply of saturated $Ca(OH)_2$ solution for 250 h, the ultrasonic pulse velocity through the reinforced concrete beam regained by about 80%. Davies et al. [98] developed a novel 2 D vascular network that left no extra material in situ in concrete. The results of three-point flexural bending test indicate that applying pressure to the network promoted the flow of the healing agent, allowing it to penetrate the majority of cracks up to a width of 0.2 mm. The combination of this pressurized vascular network and externally supplied healing agent (cyanoacrylate and sodium silicate) significantly enhanced strength recovery. Minnebo et al. [94] designed a vascular system to provide multiple self-healing. The concrete beams carrying inorganic phosphate cement and alumina network showed greater strength and stiffness recovery than control samples. The stiffness of some samples even achieved more than 100% of original values. Another developed vascular system with inorganic phosphate cement tubes or clay tubes also exhibited excellent self-healing efficiency, and inorganic phosphate cement tubes had a higher self-healing efficiency, reaching 106 % and 73 % at second loading and third loading, respectively [100].

Several means to create vascular network inside concrete have been proposed. The most common approach is to embed brittle tubes in concrete. These tubes should be strong enough to survive the concrete mixing and casting process, but they will break when cracks occur, releasing the healing agent inside tubes to fill cracks [11,84,95,96]. Sangadji and Schlangen [97] developed a different way to provide multiple flow paths by introducing porous concrete in concrete structures. The healing agent was injected manually through the topside injection channel. Experimental results demonstrate that this novel approach of imitating bone self-healing could seal macro-cracks (as shown in Fig. 24) and restore strength. Davies et al. [98] put forward a novel method for fabricating 1D and 2 D vascular networks in concrete. The network was created by embedding heat shrinkable tubes or polyurethane tubes during casting process and then removing the tubes after casting to leave permanent channels. A bespoke 3D polylactic acid connection could maximize the flow area between the perpendicular channels. Minnebo et al. [94] fabricated a vascular system, consisting of tubes connected a 3D printed distribution piece. The distribution piece has four outlets that are connected to the tubes and one inlet accessible from outside. This vascular system is capable of carrying healing agent and providing self-healing and multiple-self-healing.

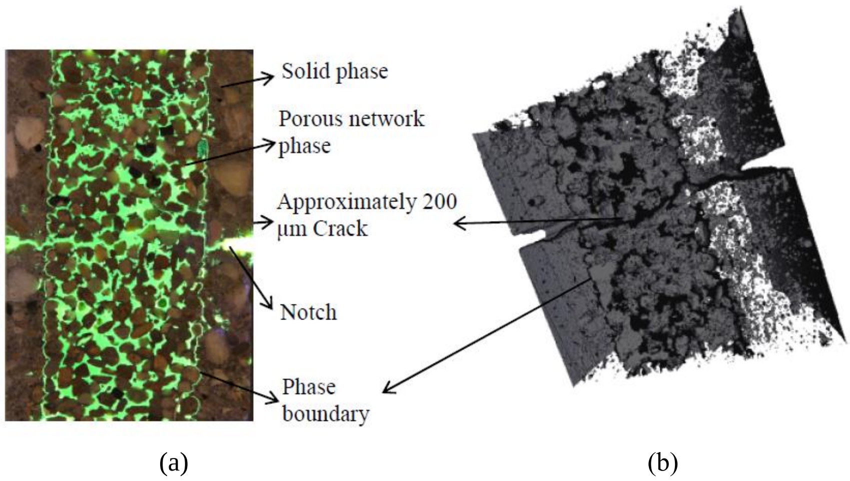


Fig. 24 (a) Longitudinal cross section showing the crack which has been filled by epoxy, (b) 3D reconstruction of the vascular concrete after crack propagation [97].

6.5 Self-healing concrete based on microbial technology

6.5.1 Mechanisms

$CaCO_3$ precipitation is a common natural phenomenon that can be found in marine water, freshwater and soils, and numerous bacterial species are associated with this phenomenon [175,190]. A variety of metabolic pathways of bacteria can lead to the formation of $CaCO_3$, mainly including hydrolysis of urea (equations (4) and (5)) [191], oxidation of organic compounds [104] and nitrate (NO_3^-) reduction [120].

$$CO(NH_2)_2 + 2H_2O \rightarrow 2NH_4^+ + CO_3^{2-} \quad (4)$$

$$CO_3^{2-} + Ca^{2+} \leftrightarrow CaCO_3 \quad (5)$$

The process of bacterial oxidation of calcium lactate is shown in equation (6). The metabolically active bacteria consume oxygen, which may help the steel reinforcement resist corrosion. The produced CO_2 molecules further react with $Ca(OH)_2$, thus increasing calcium carbonate-based minerals (equation (7)) [104].

$$CaC_6H_{10}O_6 + 6O_2 \rightarrow CaCO_3 + 5CO_2 + 5H_2O \quad (6)$$

$$5CO_2 + Ca(OH)_2 \rightarrow 5CaCO_3 + 5H_2O \quad (7)$$

Nitrate (NO_3^-) reduction mainly occurs under O_2 limited condition and can not only induce $CaCO_3$ precipitation (Equation (8)), but also produce NO_2^- (Equation (9)), which is known as corrosion inhibitor [120].

$$Ca(HCOO)_2 + 0.4Ca(NO_3)_2 \rightarrow 1.4CaCO_3 + 0.4N_2 + 0.6CO_2 + H_2O \quad (8)$$

$$2HCOO^- + 2NO_3^- + 2H^+ \rightarrow 2CO_2 + 2H_2O + 2NO_2^- \quad (9)$$

The benefits and drawbacks of different metabolic pathways of $CaCO_3$ precipitation are listed in Table 7. Fig. 25 shows a schematic diagram of the ureolytic carbonate precipitation occurring on the bacterial cell walls [191]. Firstly, the calcium ions in the solution can be attracted to the negatively charged bacterial cell walls. Urea is dissolved into inorganic carbon and ammonium by urease inside bacteria. When the local calcium ions are oversaturated, $CaCO_3$ precipitates on the cell wall of the bacteria, and eventually the entire cell is encapsulated.

Table 7 The metabolic pathways of $CaCO_3$ precipitation

Metabolic pathways	Benefits	Drawbacks
Hydrolysis of urea	1) A large amount of carbonate is produced	Excessive ammonium

	quickly 2) Catalyzed by urease	production
Oxidation of organic compounds	1) Less environmental impact 2) CO_2 is produced, which can react with portlandite	Carbonate production takes more time
Nitrate (NO_3^-) reduction	1) Occurs when O_2 is limited 2) Less environmental impact	Lower $CaCO_3$ precipitation than hydrolysis of urea

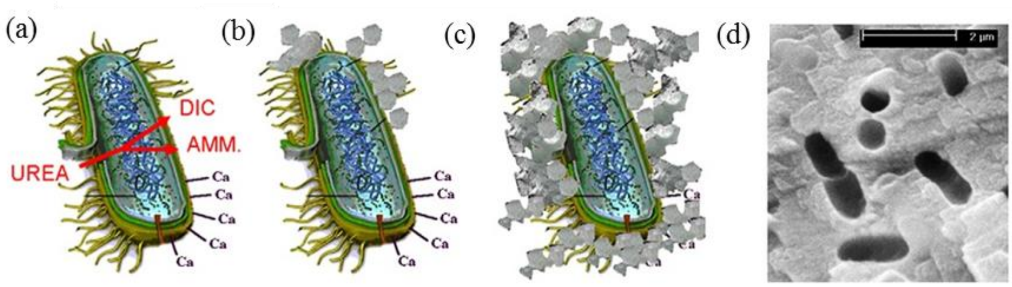


Fig. 25 Simplified representation of the events occurring during the ureolytic induced carbonate precipitation: (a) bacteria attract calcium ions, and dissolves urea into dissolved inorganic carbon and ammonium; (b) precipitation of $CaCO_3$ on the bacterial cell wall; (c) the whole cell becomes encapsulated; (d) the imprints of bacterial cells involved in carbonate precipitation [191].

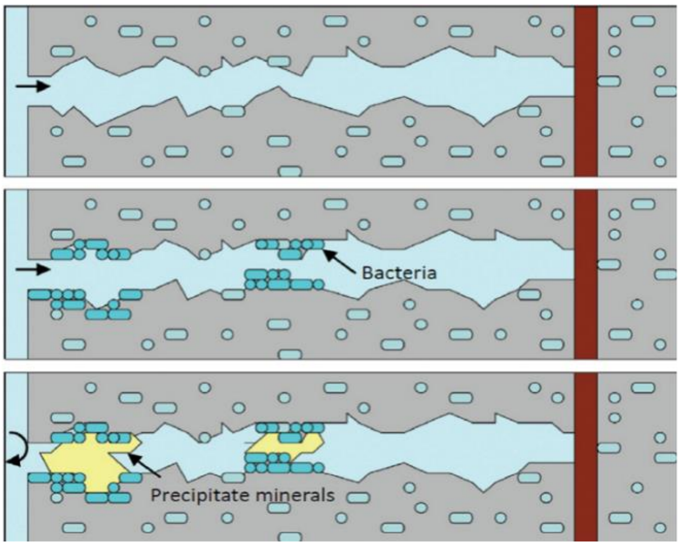


Fig. 26 Schematic scenario of crack-healing by concrete-immobilized bacteria [192].

Based on the above mechanism, bacteria can be utilized to repair cracks in concrete by precipitating minerals (mainly $CaCO_3$), as shown in Fig. 26 [192]. Firstly, dormant but viable bacteria are added to the concrete matrix. The nutrients are incorporated into concrete at the same time [104,105] or supplied by nutrient solution during curing process [107]. The dormant bacteria will be activated by water entering newly formed cracks and then seal these cracks through the process of $CaCO_3$ precipitation caused by metabolism.

6.5.2 Different types of bacteria

In order to achieve self-healing of concrete based on microbial technology, both bacteria, nutrients and carbon or nitrogen sources are required. Furthermore, it is of great significance to select suitable bacteria and calcium/nitrogen sources to survive dry, barren and alkaline concrete.

Many kinds of urea bacteria, such as *Bacillus sphaericus, Sporosarcina pasteurii (*also named *Bacillus pasteurii)*, *Sporosarcina ureae, Bacillus megaterium*, *Proteus mirabilis*, *Proteus vulgaris* and *Bacillus Subtilis*, have been investigated to develop self-healing concrete. The positive effects of bacteria on strength and durability of concrete are widely reported. The microbial technology for repairing cracks dates back to 1995, when Gollapudi et al. [15] firstly used bacteria (*Bacillus pasteurii*) to induce $CaCO_3$ precipitation to plug highly permeable channels. Achal et al. [107] found that the compressive strength of cement mortar containing bacteria increased by 36% and the water absorption was six times less than that of control specimens, when the bacterial culture or water-to-cement ratio was 0.47. Achal et al. [108] also found that this biogenic treatment could heal simulated cracks with depth of 27.2 mm in cement mortar, resulting in increased compressive strength (40%) and improved durability. Chahal et al. [110] investigated the influence of different concentrations of *Sporoscarcina pasteurii* bacteria (10^3, 10^5 and 10^7 cells/mL) on the compressive strength, water absorption and rapid chloride permeability of concrete with and without fly ash. It turned out that concrete with a bacterial content of 10^5 cells/mL performed best among all specimens. Similar results were obtained in bacterial concrete with fly ash and silica fume [111]. *Proteus mirabilis* and *Proteus vulgaris* are also able to produce urease enzymes and generate $CaCO_3$ to fill cracked concrete. However, they are unsuitable to be added into fresh concrete because the internal pH is higher than the optimum pH for both bacteria. *Proteus vulgaris* is an opportunistic pathogen of humans that can cause urinary tract infections and wound infections, therefore it should be used with caution [112]. Kalhori and Bagherpour [124] applied *Bacillus Subtilis*, a gram-positive bacterium with high spore formation capability, for improving properties of shotcrete cured in urea-$CaCl_2$ solution and repairing cracks. Bacteria-exposed shotcrete specimens obtained a 30% increase in compressive strength in comparison to control specimens, and the compressive strength was 10% higher than that of conventional cast concrete specimens with the same mix design. The presence of bacteria in both the mix design step and the curing solution was found to enhance the tensile strength of shotcrete and decrease its water absorption, permeability and porosity.

Aerobic heterotrophic bacteria such as *Bacillus cohnii*, *Bacillus pseudofirmus* and phylogenetically related facultative aerobic strains are also suitable bacteria to enhance the self-healing properties of concrete. Jonkers and Schlangen [103] incorporated alkaliphilic spore-forming bacteria of the genus *Bacillus* into concrete as self-healing agent. They found that high content of bacteria (10^9 cells/mL) and some suitable organic growth substrates (amino acids aspartate and glutamate) did affect the compressive and flexural tensile strength of concrete. The survival time of *Bacillus* bacteria in cement paste has been confirmed to be up to 4 months, although the life span is probably limited when the pore diameter in cement paste drops below 1 μm, the typical size of *Bacillus* spores [104].

Denitrifying bacteria, such as *Diaphorobacter nitroreducens* and *Pseudomonas aeruginosa,* induces $CaCO_3$ precipitation through nitrate reduction, thereby enhancing the self-healing properties of concrete. Erşan et al. [120] found the maximum crack width healed in mortar specimens separately containing the above two protected denitrifying bacteria was 370 ± 20 μm at 28 d and 480 ± 16 μm at 56 d. There was no significant difference in effective crack closure between samples with the above two bacteria at 28 d, and the water tightness of cracks with width of 465 ± 21 μm after 56 d reached 85%. At alkaline pH conditions, NO_2^- tends to accumulate in both axenic culture and non-axenic culture (i.e., activated compact denitrifying core culture), which inhibits steel corrosion to a certain extent in corrosive electrolyte solution (0.05 M Cl^-, pH 9) and the control parameter is $[NO_2^-]$: $[Cl^-]$ ratio. When the ratio is less than 1, pitting corrosion occurs at around -100 mV [119].

Unlike ureolytic bacteria, aerobic heterotrophic bacteria and denitrifying bacteria, *Bacillus mucilaginous* produces carbonic anhydrase to promote the inter-conversion between CO_2 from atmosphere and $CaCO_3$. The bacteria exhibit excellent repairing capability for early-age cracks. It was found [121] that cracks narrower than 0.4 mm could be almost completely filled after 30 d of water curing, although the area repair rate dropped significantly along with cracking age. Self-healing effect did not even occur when the cracking age exceeded 60 d. Moreover, the increasing crack width led to a decrease in the depth of precipitated $CaCO_3$. In addition to crack width and cracking age, curing method also greatly affects the self-healing property of microbial concrete, and water curing seems to have the best promoting effect (as shown in Fig. 27) [118].

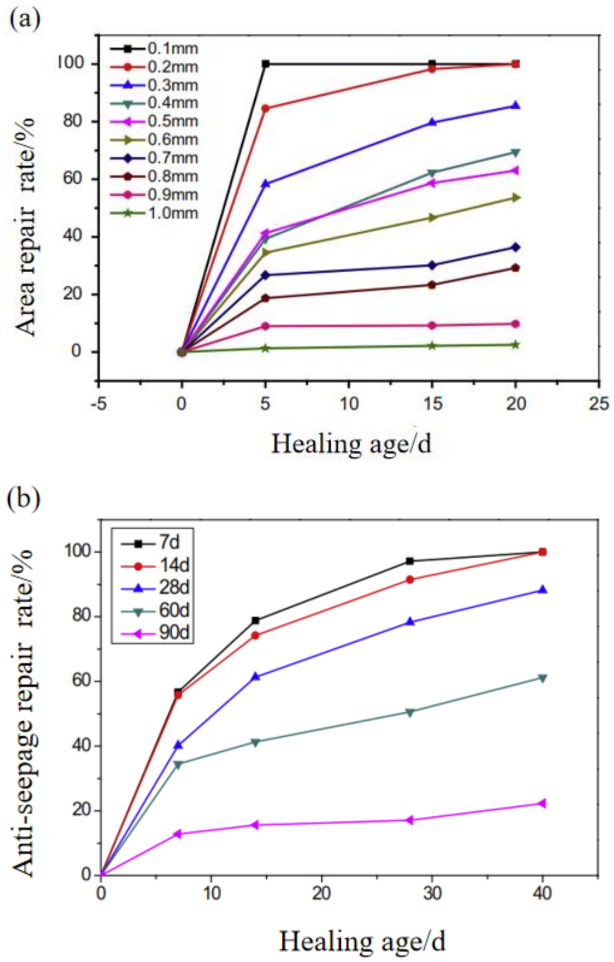


Fig. 27 The repair rate of specimens (a) with different crack width and (b) in different cracking age after different repair time [118].

Luo and Qian [193] investigated the effects of three types of bacteria-based self-healing agents on hydration kinetics and compressive strength of cementitious materials. These self-healing agents were combinations of spore-forming alkali-resistant bacteria spores' powder and one type of calcium source (calcium lactate, calcium formate or calcium nitrate). Significant improvement in rheology was observed with the addition of all types of bacteria-based self-healing agents. The bacteria-based self-healing agent consisting of bacteria spores' powder and calcium lactate delayed the hydration of cement, while bacteria spores' powder in combination with calcium formate or calcium nitrate accelerated the hydration. However, the incorporation of bacteria spores combined with calcium lactate or calcium formate resulted in an enhancement in compressive strength, but the other type of self-healing agent caused a decline. Calcium lactate and calcium acetate has been proved to be suitable nutrients by oxygen consumption investigation and compressive strength test, while sodium gluconate is not an appropriate source of nutrient for alkaliphilic spore-forming bacteria of the genus *Bacillus* [194].

6.5.3 Protection of bacteria

Appropriate treatment to protect encapsulated bacteria from the high-pH environment of concrete and adverse environmental changes is important for repairing concrete and maintaining the high metabolic activity of bacteria. Commonly used protective materials are silica gel, expanded clay particles, granular activated carbon particles, diatomaceous earth, polyurethane, hydrogel, granular activated carbon and porous materials such as expanded shale aggregates, expanded perlite and ceramsite.

While pure bacteria cultures were incapable of bridging the cracks and improving compressive strength of pre-cracked concrete [105,195], the application of protection techniques can bring more satisfactory self-healing performance [195]. For instance, 10 mm deep cracks could even be fully filled with precipitated $CaCO_3$ crystals when silica gel was selected as protective material [105]. A variety of protection materials carrying bacteria have been widely investigated. Wiktor and Jonkers [106] utilized porous expanded clay particles to protect bio-chemical two-component self-healing agent, which consisted of a mixture of bacterial spores and calcium lactate. After 100 d of healing, the maximum healed crack width in bacteria-based mortar specimens was more than twice the size (0.46 mm) of healed crack in control specimens (0.18 mm). Bacterial spores embedded in expanded clay particles remained viable and functional several months after concrete casting. Similarly, granular activated carbon particles can also be employed as an effective protective carrier for bacteria [120]. Wang et al. [114] selected diatomaceous earth as the material to immobilize bacteria, which resulted in a much higher ureolytic activity compared with un-immobilized bacteria in cement matrix. The amount of decomposed urea increased as the concentration of diatomaceous earth increased, and the optimum concentration was 60% of the bacterial suspension (weight/volume). Thanks to the aid of immobilized bacteria at the concentration of 10^9 cells/mL, cracks with width of 0.15-0.17 mm in mortar specimens were partly or even completely filled by precipitated calcium carbonate, when the specimens were immersed in water and the deposition medium, respectively. Bacteria-based cracked specimens healed in the deposition medium had the lowest water absorption, which was 30% of that of the control group. Polyurethane was first selected as the immobilized material for *Bacillus pasteurii* in 2001 [101]. The results show that the bacteria still retain ureolytic activity and carbonatogenesis activity after being immobilized into silica gel and polyurethane. Furthermore, Wang et al. [109] believed that although polyurethane immobilized bacteria exhibited a lower activity than silica gel immobilized bacteria, it was more beneficial to protect the bacteria with polyurethane as the carrier, considering the higher strength regain (60%) and more pronounced decrease in water permeability. In another investigation, Wang et al. [115] fabricated self-healing concrete containing hydrogel encapsulated bacteria and found their healing rate ranged from 70% to 100% for the cracks smaller than 0.3 mm, which was more than 50% higher than that of non-bacteria series. The maximum bridging crack width was about 0.5 mm in the specimens with bio-hydrogels within 7 d [115,116]. Healing products with a total volume ratio of 2.2% were obtained in specimens with bio-hydrogel, which was about 60% higher than that of specimens with pure hydrogel. The 3D HRXCT images in Fig. 28 manifest that the healing products are mostly distributed in the surface layer and drops sharply in the subsurface layer and deep inside the sample [115].

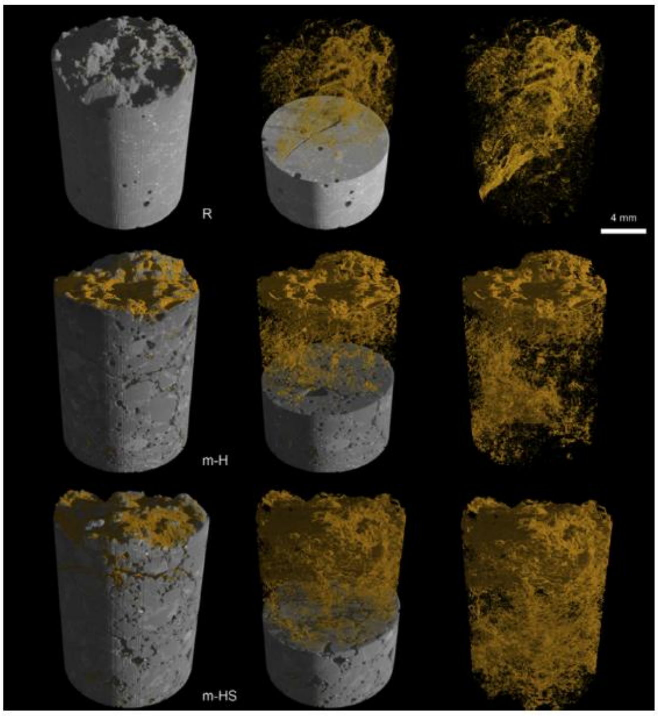


Fig. 28 3D rendered view of the spatial distribution of healing products (in yellow) in the control sample (R), sample with pure hydrogels (m-H) and sample with bio-hydrogels (m-HS) after treatment (left: outlook of samples plus the precipitation; middle: distribution of precipitates inside; right: the whole precipitates in the sample) [115].

Nitrate reducing $CaCO_3$ precipitating bacteria, namely *Pseudomonas aeruginosa* and *Diaphorobacter nitroreducens*, can survive in the mortar environment if protected by diatomaceous earth, expanded clay or granular activated carbon. Besides, the self-immobilized non-axenic culture called "activated compact denitrifying core" does not require additional protection when applied in mortar, and it performs better than the protected axenic cultures in all tests [119]. According to the experiment carried out by Chen et al. [122], the area repair rate of section surface of the samples with bacteria and nutrients immobilized into ceramsite reached 87.5% and the flexural strength of repaired specimens increased from 56% to 72%

compared with microbiological methods. Zhang et al. [123] investigated the feasibility of expanded perlite or expanded clay as a novel bacterial carrier in self-healing concrete. The experimental results shown in Fig. 29 demonstrate that immobilizing bacteria with expanded perlite is more beneficial because it helps heal larger cracks (0.79 mm) after 28 d of healing than specimens with expanded clay-immobilized bacteria.

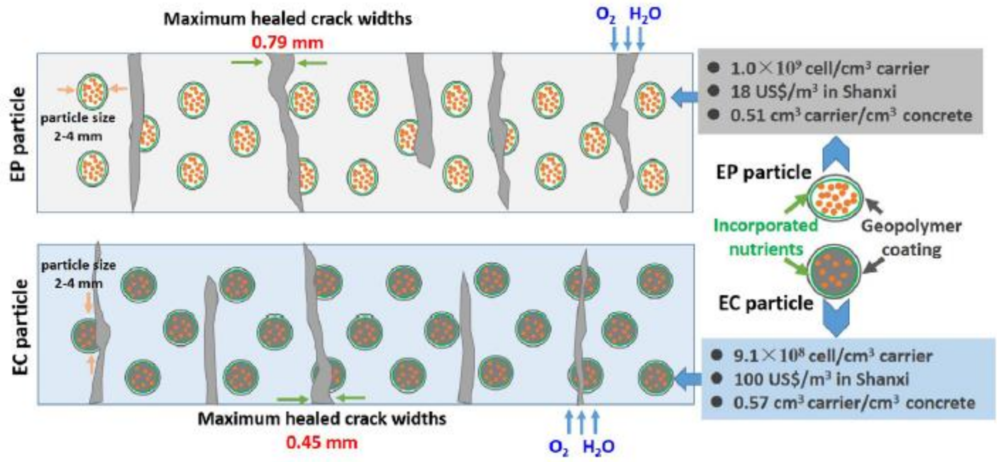


Fig. 29 Schematic diagram of the two types of healing processes (expanded perlite (EP) and expanded clay (EC)) [123].

Unlike the above means for ensuring the metabolic activity of bacteria, Bundur et al. [124] used pre-wetted lightweight fine expanded shale aggregates as internal nutrient reservoirs to improve cell viability of *Sporosarcina pasteurii* in mortar, and this method did not bring any substantial loss in strength. In addition to the aforementioned traditional protective materials, nano materials such as graphite nanoplatelets and magnetic iron oxide nanoparticle have also been applied as novel carriers for *Bacillus* cells in bacteria-based self-healing concrete due to the high adsorption capacity of nanoparticles. The investigation by Khaliq et al. indicated that in terms of crack healing efficiency, graphite nanoplatelets were good carrier compounds for concrete pre-cracked at 3 d and 7 d, while LWA was more effective for specimens pre-cracked at 14 d and 28 d [195]. Seifan et al. [125] synthesized magnetic iron oxide nanoparticles and immobilized *Bacillus* cells with these nanoparticles using electrostatic attraction force. The bio-concrete specimen showed strong crack sealing ability and pore sealing performance. In terms of water penetration resistance, the initial and the secondary water absorption rates of bio-concrete specimens were 26% and 22% lower than those of control samples, respectively.

7. Summary and prospects

Cracking and degradation are unavoidable processes during the service of concrete structures, resulting in huge annual maintenance costs. Self-healing concrete with the ability to automatically repair small cracks helps to address this issue. The potential benefits of self-healing concrete include improved reliability, enhanced structural performance, extended service life, reduced life cycle costs, and reduced burdens on resources, energy as well as environment.

In general, the self-healing concrete is divided into autogenous and autonomous healing concretes. Autogenous healing can be realized by introducing fibers, minerals, nanofillers and internal curing agents, while the autonomous healing technologies mainly include electrodeposition technology, SMA technology, capsule technology, vascular technology and microbial technology. Self-healing mechanisms in cementitious materials are a combination of complicated physical, chemical and mechanical processes. The four main mechanisms of autogenous healing are swelling/expansion effect of materials, continued hydration, calcium carbonation formation and filling effect of fine particles. The mechanisms of self-healing based on electrodeposition, SMA and microbial technologies are mainly electrodeposition coating, shape memory effect and $CaCO_3$ precipitation, respectively, while the mechanisms of capsules and vascular system are varied and primarily depend on the healing agent contained.

Due to crack healing, the mechanical properties and durability of concrete structures are restored to some extent in most cases. However, most autogenous healing methods currently are only possible to completely repair cracks no wider than 150 μm. In contrast, autonomous healing technologies have the potential to heal larger cracks, even up to 1 mm, and usually act faster. Even so, it is still hard to pick a perfect healing approach as they all have advantages and shortcomings.

At present, most researches on self-healing concrete are accomplished in the laboratory and mainly focus on static loading. Some key parameters such as compatibility of healing materials with cementitious materials, self-healing efficiency and repeatability are discussed in this review. Further study on the long-term reliability of self-healing behavior is needed considering the short shelf life of healing materials, especially polymeric healing agents. In the future, a new generation of self-healing concrete with high self-healing efficiency will develop towards multiple scales, multiple dimensions, integrated healing technologies, mass production and low cost. The integration of some new technology may promote the development of self-repairing concrete, such as nanotechnology, biotechnology and 3D printing technology.

Acknowledgments

The authors would like to thank the National Key Research and Development Program of China

(2018YFC0705601) for funding.

References

[1] B. Han, L. Zhang, J. Ou. Smart and multifunctional concrete toward sustainable infrastructures, Berlin: Springer, 2017.

[2] P.K. Mehta, P.J.M. Monteiro. Concrete microstructure, properties and materials. 2006.

[3] B. Han, X. Yu, J. Ou. Self-sensing concrete in smart structures, Amsterdam: Elsevier, 2014.

[4] P.C. AõÈtcin. Cements of yesterday and today: concrete of tomorrow. Cement and Concrete Research. 2000, 30 (9): 1349–1359.

[5] F. Xi, S.J. Davis, P. Ciais, D. Crawford-Brown, D. Guan, C. Pade, T. Shi, M. Syddall, J. Lv, L. Ji, L. Bing, J. Wang, W. Wei, K.H. Yang, B. Lagerblad, I. Galan, C. Andrade, Y. Zhang, Z. Liu. Substantial global carbon uptake by cement carbonation. Nature Geoscience. 2016, 9 (12): 880–883.

[6] M. Wu, B. Johannesson, M. Geiker. A review: Self-healing in cementitious materials and engineered cementitious composite as a self-healing material. Construction and Building Materials. 2012, 28 (1): 571–583.

[7] M. de Rooij, K. Van Tittelboom, N. De Belie, E. Schlangen. Self-healing phenomena in cement-based materials. Springer, Dordrecht, 2013.

[8] F.M. Ivanov, B.I. Polyakov. Self-healing and durability of hydraulic concrete. Hydrotechnical Construction. 1974, 8 (9): 844–849.

[9] R.J. Gray. Autogenous healing of fiber/materix interfacial bond in fiber-reinforced mortar. Cement and Concrete Research. 1984, 14 (3): 315–317.

[10] S. Jacobsen, J. Marchand, H. Hugues. Sem observations of the microstructure of frost deteriorated and self-healed concretes. Cement and Concrete Research. 1995, 25 (8): 1781–1790.

[11] D. Carolyn. Matrix cracking repair and filling using active and passive modes for smart timed release of chemicals from fibers into cement matrices. Smart Materials and Structures. 1994, 3 (2): 118–123.

[12] C.M. Dry. Improvement in reinforcing bond strength in reinforced concrete with self-repairing chemical adhesives. Smart Structures and Materials 1997: Smart Systems for Bridges, Structures, and Highways. International Society for Optics and Photonics. 1997, 3043: 44–50.

[13] V.C. Li, Y.M. Lim, Y.W. Chan. Feasibility study of a passive smart self-healing cementitious

composite. Composites Part B. 1998, 29 (6): 819–827.

[14] O. Otsuki, M. Hisada, J.S. Ryu, E. Banshoya. Rehabilitation of concrete cracks by electrodeposition. Concrete International. 1999, 21 (3): 58–63.

[15] U.K. Gollapudi, C.L. Knutson, S.S. Bang, M.R. Islam. A new method for controlling leaching through permeable channels. Chemosphere. 1995, 30 (4): 259–705.

[16] V. TittelboomKim, N. De Belie. Self-healing in cementitious materials-A review. Mateials. 2013, 6 (6): 2182–2217.

[17] W. Tang, O. Kardani, H. Cui. Robust evaluation of self-healing efficiency in cementitious materials - A review. Construction and Building Materials. 2015, 81: 233–247.

[18] N. Ter Heide. Crack healing in hydrating concrete, Delft University of Technology, 2005.

[19] P. Termkhajornkit, T. Nawa, Y. Yamashiro, T. Saito. Self-healing ability of fly ash – cement systems. Cement and Concrete Composites. 2009, 31 (3): 195–203.

[20] M. Şahmaran, S.B. Keskin, G. Ozerkan, I.O. Yaman. Self-healing of mechanically-loaded self consolidating concretes with high volumes of fly ash. Cement and Concrete Composites. 2008, 30 (10): 872–879.

[21] K. Van Tittelboom, E. Gruyaert, H. Rahier, N.D.B. Belie. 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.

[22] M. Sahmaran, G. Yildirim, T.K. Erdem. Self-healing capability of cementitious composites incorporating different supplementary cementitious materials. Cement and Concrete Composites. 2013, 35 (1): 89–101.

[23] C.C. Hung, Y.F. Su. Medium-term self-healing evaluation of Engineered Cementitious Composites with varying amounts of fly ash and exposure durations. Construction and Building Materials. 2016, 118: 194–203.

[24] M. Şahmaran, G. Yildirim, R. Noori, E. Ozbay, M. Lachemi. Repeatability and pervasiveness of self-healing in engineered cementitious composites. ACI Materials Journal. 2015, 112 (4): 513–522.

[25] G. Yıldırım, A.H. Khiavi, S. Yeşilmen, M. Şahmaran. Self-healing performance of aged cementitious composites. Cement and Concrete Composites. 2018, 87: 172–186.

[26] S. Qian, J. Zhou, M.R. De Rooij, E. Schlangen, G. Ye, K. Van Breugel. Self-healing behavior of

strain hardening cementitious composites incorporating local waste materials. Cement and Concrete Composites. 2009, 31 (9): 613–621.

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

[28] T. Ahn, T. Kishi. Crack self-healing behavior of cementitious composites incorporating various mineral admixtures. Journal of Advanced Concrete Technology. 2010, 8 (2): 171–186.

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

[30] B. Pang, Z. Zhou, P. Hou, P. Du, L. Zhang, H. Xu. Autogenous and engineered healing mechanisms of carbonated steel slag aggregate in concrete. Construction and Building Materials. 2016, 107: 191–202.

[31] T.S. Qureshi, A. Al-Tabbaa. Self-healing of drying shrinkage cracks in cement-based materials incorporating reactive MgO. Smart Materials and Structures. 2016, 25 (8): 084004.

[32] D. Homma, H. Mihashi, T. Nishiwaki. Self-healing capability of fibre reinforced cementitious composites. Journal of Advanced Concrete Technology. 2009, 7 (2): 217–228.

[33] T. Nishiwaki, S. Kwon, D. Homma, M. Yamada, H. Mihashi. Self-healing capability of fiber-reinforced cementitious composites for recovery of watertightness and mechanical properties. Materials. 2014, 7 (3): 2141–2154.

[34] L.L. Kan, H.S. Shi. Investigation of self-healing behavior of Engineered Cementitious Composites (ECC) materials. Construction and Building Materials. 2012, 29: 348–356.

[35] Y. Yang, E. Yang, V.C. Li. Autogenous healing of engineered cementitious composites at early age. Cement and Concrete Research. 2011, 41 (2): 176–183.

[36] Y. Zhu, Y. Yang, Y. Yao. Autogenous self-healing of engineered cementitious composites under freeze–thaw cycles. Construction and Building Materials. 2012, 34: 522–530.

[37] Y. Yang, M.D. Lepech, E. Yang, V.C. Li. Autogenous healing of engineered cementitious composites under wet – dry cycles. Cement and Concrete Research. 2009, 39 (5): 382–390.

[38] C. Hung, Y. Su, H. Hung. Impact of natural weathering on medium-term self-healing performance of fiber reinforced cementitious composites with intrinsic crack-width control capability. Cement and Concrete Composites. 2017, 80: 200–209.

[39] H. Choi, M. Inoue, S. Kwon, H. Choi, M. Lim. Effective crack control of concrete by self-healing of cementitious composites using synthetic fiber. Materials. 2016, 9 (4): 248.

[40] D.J. Kim, S.H. Kang, T.H. Ahn. Mechanical characterization of high-performance steel-fiber reinforced cement composites with self-healing effect. Materials. 2014, 7 (1): 508–526.

[41] H. Siad, M. Lachemi, M. Sahmaran, H.A. Mesbah, K.A. Hossain. Advanced engineered cementitious composites with combined self-sensing and self-healing functionalities. Construction and Building Materials. 2018, 176: 313–322.

[42] J. Wang, S. Ding, B. Han, Y. Ni, J. Ou. Self-healing properties of reactive powder concrete with nanofillers. Smart Materials and Structures. 2018, 27 (11): 115033.

[43] D.P. Bentz. Internal curing of high-performance blended cement mortars. ACI Materials Journal. 2007, 104 (4): 408–414.

[44] R. Henkensiefken, J. Castro, D. Bentz, T. Nantung, J. Weiss. Water absorption in internally cured mortar made with water-filled lightweight aggregate. Cement and Concrete Research. 2009, 39 (10): 883–892.

[45] J. Schlitter, R. Henkensiefken, J. Castro, K. Raoufi, J. Weiss. Development of internally cured concrete for increased service life-FHWA/IN/JTRP-2010/10, 2010.

[46] S. Zhutovsky, K. Kovler, A. Bentur. Effect of hybrid curing on cracking potential of high-performance concrete. Cement and Concrete Research. 2013, 54: 36–42.

[47] D. Snoeck, K. Van Tittelboom, S. Steuperaert, P. Dubruel, N. De Belie. Self-healing cementitious materials by the combination of microfibres and superabsorbent polymers. Journal of Intelligent Material Systems and Structures. 2014, 25 (1): 13–24.

[48] J. Justs, M. Wyrzykowski, D. Bajare, P. Lura. Internal curing by superabsorbent polymers in ultra-high performance concrete. Cement and Concrete Research. 2015, 76: 82–90.

[49] J. Zhengwu, X. Feng, S. Zhenping, W. Peiming. Healing effectiveness of cracks rehabilitation in reinforced concrete using electrodeposition method. Journal of Wuhan University of Technology-Materials Science Edition. 2008, 23 (6): 917–922.

[50] J.S. Ryu. Influence of crack width, cover depth, water – cement ratio and temperature on the formation of electrodeposits on the concrete surface. Magazine of Concrete Research. 2003, 55 (1): 35–40.

[51] S. Tyagi. An experimental investigation of self curing concrete incorporated with polyethylene

glycol as self curing agent. International Research Journal of Engineering and Technology. 2015, 2 (6): 129–132.

[52] B. Craeye, M. Geirnaert, G. De Schutter. Super absorbing polymers as an internal curing agent for mitigation of early-age cracking of high-performance concrete bridge decks. Construction and Building Materials. 2011, 25 (1): 1–13.

[53] D. Snoeck, L. Pel, N. De Belie. The water kinetics of superabsorbent polymers during cement hydration and internal curing visualized and studied by NMR. Scientific Reports. 2017, 7 (1): 1–14.

[54] J.S. Ryou, N. Otsuki. Experimental study on repair of concrete structural members by electrochemical method. Scripta Materialia. 2005, 52 (11): 1123–1127.

[55] J.S. Ryu. An experimental study on the repair of concrete crack by electrochemical technique. Materials and Structures. 2001, 34 (241): 433–437.

[56] N. Otsuki, J.S. Ryu. Use of electrodeposition for repair of concrete with shrinkage cracks. Journal of Materials in Civil Engineering. 2001, 13 (2): 136–142.

[57] C. Hongqiang, J. Linhua, X. Chuansheng, Y. Lushen, X. Ning. Use of electrochemical method for repair of concrete cracks. Construction and Building Materials. 2014, 73: 58–66.

[58] J.S. Ryu, N. Otsuki. Crack closure of reinforced concrete by electrodeposition technique. Cement and Concrete Research. 2002, 32: 159–164.

[59] J. Xu, H. Shan, C. Zhang, L. Jiang, L. Tang, Y. Xu, N. Xu. Surface coating treatment and densification of mortar by electrodeposition method. Magazine of Concrete Research. 2016, 68 (2): 69–79.

[60] H. Chu, L. Jiang, Z. Song, Y. Xu, S. Zhao, C. Xiong. Repair of concrete crack by pulse electro-deposition technique. Construction and Building Materials. 2017, 148: 241–248.

[61] A.K. Maji, I. Negree. Smart presteressing with shape-memory alloy. Journal of Engineering Mechanics. 1998, 124 (10): 1121–1128.

[62] L. Li, Q. Li, F. Zhang. Behavior of smart concrete beams with embedded shape memory alloy bundles. Journal of Intelligent Material Systems and Structures. 2007, 18 (10): 1003–1014.

[63] K.J. Lee, J.H. Lee, C.Y. Jung, E. Choi. Crack-closing performance of NiTi and NiTiNb fibers in cement mortar beams using shape memory effects. Composite Structures. 2018, 202: 710–718.

[64] D.J. Kim, H.A. Kim, Y.S. Chung, E. Choi. Pullout resistance of deformed shape memory alloy

fibers embedded in cement mortar. Journal of Intelligent Material Systems and Structures. 2016, 27 (2): 249–260.

[65] D.J. Kim, H.A. Kim, Y.S. Chung, E. Choi. Pullout resistance of straight NiTi shape memory alloy fibers in cement mortar after cold drawing and heat treatment. Composites Part B. 2014, 67: 588–594.

[66] M. Kyoung, D. Joo, Y. Chung, E. Choi. Direct tensile behavior of shape-memory-alloy fiber-reinforced cement composites. Construction and Building Materials. 2016, 102: 462–470.

[67] H. Li, Z.Q. Liu, J.P. Ou. Behavior of a simple concrete beam driven by shape memory alloy wires. Smart Materials and Structures. 2006, 15 (4): 1039–1046.

[68] E. Choi, D.J. Kim, Y.S. Chung, H.S. Kim, C. Jung. Crack-closing of cement mortar beams using NiTi cold-drawn SMA short fibers. Smart Materials and Structures. 2015, 24 (1): 015018.

[69] Z. Yang, J. Hollar, X. He, X. Shi. A self-healing cementitious composite using oil core / silica gel shell microcapsules. Cement and Concrete Composites. 2011, 33 (4): 506–512.

[70] G. Perez, J.J. Gaitero, E. Erkizia, I. Jimenez, A. Guerrero. Characterisation of cement pastes with innovative self-healing system based in epoxy-amine adhesive. Cement and Concrete Composites. 2015, 60: 55–64.

[71] M.M. Pelletier, R. Brown, A. Shukla, A. Bose. Self-healing concrete with a microencapsulated healing agent. Cement and Concrete Research. 2010,.

[72] W. Li, Z. Jiang, Z. Yang, N. Zhao, W. Yuan. Self-healing efficiency of cementitious materials containing microcapsules filled with healing adhesive: Mechanical restoration and healing process monitored by water absorption. PLoS One. 2013, 8 (11): e81616.

[73] J. Gilford, M.M. Hassan, T. Rupnow, M. Barbato, A. Okeil, S. Asadi. Dicyclopentadiene and sodium silicate microencapsulation for self-healing of concrete. Journal of Materials in Civil Engineering. 2014, 26 (5): 886–896.

[74] J.Y. Wang, H. Soens, W. Verstraete, N. De Belie. Self-healing concrete by use of microencapsulated bacterial spores. Cement and Concrete Research. 2014, 56: 139–152.

[75] X. Wang, F. Xing, M. Zhang, N. Han, Z. Qian. Experimental study on cementitious composites embedded with organic microcapsules. Materials. 2013, 6 (9): 4064–4081.

[76] B. Dong, G. Fang, W. Ding, Y. Liu, J. Zhang, N. Han, F. Xing. Self-healing features in cementitious material with urea–formaldehyde/epoxy microcapsules. Construction and Building

Materials. 2016, 106: 608–617.

[77] B. Dong, G. Fang, Y. Wang, Y. Liu, S. Hong, J. Zhang, S. Lin, F. Xing. Performance recovery concerning the permeability of concrete by means of a microcapsule based self-healing system. Cement and Concrete Composites. 2017, 78: 84–96.

[78] L. Lv, Z. Yang, G. Chen, G. Zhu, N. Han, E. Schlangen, F. Xing. Synthesis and characterization of a new polymeric microcapsule and feasibility investigation in self-healing cementitious materials. Construction and Building Materials. 2016, 105: 487–495.

[79] A. Kanellopoulos, P. Giannaros. 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.

[80] A. Kanellopoulos, P. Giannaros, D. Palmer, A. Kerr, A. Al-Tabbaa. Polymeric microcapsules with switchable mechanical properties for self-healing concrete: Synthesis, characterisation and proof of concept. Smart Materials and Structures. 2017, 26 (4): 045025.

[81] S. V. Zemskov, H.M. Jonkers, F.J. Vermolen. Two analytical models for the probability characteristics of a crack hitting encapsulated particles: Application to self-healing materials. Computational Materials Science. 2011, 50 (12): 3323–3333.

[82] W. Xiong, T. Jiaoning, G. Zhu, N. Han, E. Schlangen, B. Dong, X. Wang, F. Xing. A novel capsule-based self-recovery system with a chloride ion trigger. Scientific Reports. 2015, 5: 10866.

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

[84] L. Sun, W.Y. Yu, Q. Ge. Experimental research on the self-healing performance of micro-cracks in concrete bridge. Advanced Materials Research. 2011, (250-253): 28–32.

[85] T.D.P. Thao. Quast-brittle self-healing healing materials: numerical modelling and applications in civil engineering. Degree of Doctor of Philosophy Departent of Civil and Environmental Engineering National Univerity of Singapore. 2011,.

[86] K. Van Tittelboom, E. Tsangouri, D. Van Hemelrijck, N. De Belie. The efficiency of self-healing concrete using alternative manufacturing procedures and more realistic crack patterns. Cement and Concrete Composites. 2015, 57: 142–152.

[87] J. Feiteira, E. Gruyaert, N. De Belie. Self-healing of moving cracks in concrete by means of

encapsulated polymer precursors. Construction and Building Materials. 2016, 102: 671–678.

[88] K. Van Tittelboom, N. De Belie, F. Lehmann, C.U. Grosse. Acoustic emission analysis for the quantification of autonomous crack healing in concrete. Construction and Building Materials. 2012, 28 (1): 333–341.

[89] M. Maes, K. Van Tittelboom, N. De Belie. The efficiency of self-healing cementitious materials by means of encapsulated polyurethane in chloride containing environments. Construction and Building Materials. 2014, 71: 528–537.

[90] D.Y. Zhu, M.Z. Rong, M.Q. Zhang. Self-healing polymeric materials based on microencapsulated healing agents: From design to preparation. Progress in Polymer Science. 2015, (49-50): 175–220.

[91] A. Kanellopoulos, T.S. Qureshi, A. Al-Tabbaa. Glass encapsulated minerals for self-healing in cement based composites. Construction and Building Materials. 2015, 98: 780–791.

[92] T.S. Qureshi, A. Kanellopoulos, A. Al-Tabbaa. Encapsulation of expansive powder minerals within a concentric glass capsule system for self-healing concrete by in situ hybridization. Construction and Building Materials Journal. 2016, 121: 629–643.

[93] R. Alghamri, A. Kanellopoulos, A. Al-Tabbaa. Impregnation and encapsulation of lightweight aggregates for self-healing concrete. Construction and Building Materials. 2016, 124: 910–921.

[94] P. Minnebo, G. Thierens, G. De Valck, K. Van Tittelboom, N. De Belie, D. Van Hemelrijck, E. Tsangouri. A novel design of autonomously healed concrete: towards a vascular healing network. Materials. 2017, 10 (1): 49.

[95] C. Joseph, A.D. Jefferson, B. Isaacs, R. Lark, D. Gardner. Experimental investigation of adhesive-based self-healing of cementitious materials. Magazine of Concrete Research. 2010, 62 (11): 831–843.

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

[97] S. Sangadji, E. Schlangen. Self healing of concrete structures-novel approach using porous network concrete. Journal of Advanced Concrete Technology. 2012, 10 (5): 185–194.

[98] R. Davies, A. Jefferson, R. Lark, D. Gardner. A novel 2D vascular network in cementitious materials. Concrete - Innovation and Design: fib Symposium Proceedings. 2015: 249-250.

[99] U. Kingdom. Multil-scale cementitious self-healing systems and their application in concrete

structures, in: 9th Int. Concr. Conf., At Dundee, Scotland, 2016.

[100] P. Minnebo, K. Van Tittelboom, N. De Belie, D. Van Hemelrijck. Vascular self-healing of a reinforced concrete beam under 4-point bending. 14th International Conference on Durability of Building Materials and Components (XIV DBMC). 2017: 1–9.

[101] S. Bang, J. Galinat, V. Ramakrishnan. Calcite precipitation induced by polyurethane-immobilized Bacillus pasteurii. Enzyme and Microbial Technology. 2001, 28 (4–5): 404–409.

[102] S. Krishnapriya, D.L. Venkatesh Babu, P.A. G. Isolation and identification of bacteria to improve the strength of concrete. Microbiological Research. 2015, 174: 48–55.

[103] H.M. Jonkers, E. Schlangen. Crack repair by concrete-immobilized bacteria. Proceedings of the First International Conference on Self Healing Materials. 2007: 18–20.

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

[105] K. Van Tittelboom, N. De Belie, W. De Muynck, W. Verstraete. Use of bacteria to repair cracks in concrete. Cement and Concrete Research. 2010, 40 (1): 157–166.

[106] V. Wiktor, H.M. Jonkers. Quantification of crack-healing in novel bacteria-based self-healing concrete. Cement and Concrete Composites. 2011, 33 (7): 763–770.

[107] V. Achal, A. Mukherjee, M.S. Reddy. Microbial concrete: way to enhance the durability of building structures. Journal of Materials in Civil Engineering. 2011, 23 (6): 730–734.

[108] V. Achal, A. Mukerjee, M. Sudhakara Reddy. Biogenic treatment improves the durability and remediates the cracks of concrete structures. Construction and Building Materials. 2013, 48: 1–5.

[109] J. Wang, K. Van Tittelboom, N. De Belie, W. Verstraete. Use of silica gel or polyurethane immobilized bacteria for self-healing concrete. Construction and Building Materials. 2012, 26 (1): 532–540.

[110] N. Chahal, R. Siddique, A. Rajor. Influence of bacteria on the compressive strength, water absorption and rapid chloride permeability of fly ash concrete. Construction and Building Materials. 2012, 28 (1): 351–356.

[111] N. Chahal, R. Siddique. Permeation properties of concrete made with fly ash and silica fume: Influence of ureolytic bacteria. Construction and Building Materials. 2013, 49: 161–174.

[112] A. Talaiekhozani, A. Keyvanfar, R. Andalib, M. Samadi, A. Shafaghat, H. Kamyab, M.Z.A. Majid, R.M. Zin, M.A. Fulazzaky, C.T. Lee, M.W. Hussin. Application of Proteus mirabilis and Proteus vulgaris mixture to design self-healing concrete. Desalination and Water Treatment. 2014, 52 (19–21): 3623–3630.

[113] J. Xu, W. Yao. Multiscale mechanical quantification of self-healing concrete incorporating non-ureolytic bacteria-based healing agent. Cement and Concrete Research. 2014, 64: 1–10.

[114] J.Y. Wang, N. De Belie, W. Verstraete. Diatomaceous earth as a protective vehicle for bacteria applied for self-healing concrete. Journal of Industrial Microbiology and Biotechnology. 2012, 39: 567–577.

[115] J. Wang, J. Dewanckele, V. Cnudde, S. Van Vlierberghe, W. Verstraete, N. De Belie. X-ray computed tomography proof of bacterial-based self-healing in concrete. Cement and Concrete Composites. 2014, 53: 289–304.

[116] J.Y. Wang, D. Snoeck, S. Van Vlierberghe, W. Verstraete, N. De Belie. Application of hydrogel encapsulated carbonate precipitating bacteria for approaching a realistic self-healing in concrete. Construction and Building Materials. 2014, 68: 110–119.

[117] Y.Ç. Ersßan, F.B. Da Silva, N. Boon, W. Verstraete, N. De Belie. Screening of bacteria and concrete compatible protection materials. Construction and Building Materials Journal. 2015, 88: 196–203.

[118] M. Luo, C.X. Qian, R.Y. Li. Factors affecting crack repairing capacity of bacteria-based self-healing concrete. Construction and Building Materials. 2015, 87: 1–7.

[119] Y.Ç. Erşan, H. Verbruggen, I. De Graeve, W. Verstraete, N. De Belie, N. Boon. Nitrate reducing CaCO3 precipitating bacteria survive in mortar and inhibit steel corrosion. Cement and Concrete Research. 2016, 83: 19–30.

[120] Y.Ç. Erşan, E. Hernandez-Sanabria, N. Boon, N. De Belie. Enhanced crack closure performance of microbial mortar through nitrate reduction. Cement and Concrete Composites. 2016, 70: 159–170.

[121] C. Qian, H. Chen, L. Ren, M. Luo. Self-healing of early age cracks in cement-based materials by mineralization of carbonic anhydrase microorganism. Frontiers in Microbiology. 2015, 6: 1225.

[122] H. Chen, C. Qian, H. Huang. Self-healing cementitious materials based on bacteria and nutrients immobilized respectively. Construction and Building Materials. 2016, 126: 297–303.

[123] J. Zhang, Y. Liu, T. Feng, M. Zhou, L. Zhao, A. Zhou, Z. Li. Immobilizing bacteria in expanded perlite for the crack self-healing in concrete. Construction and Building Materials. 2017, 148: 610–617.

[124] H. Kalhori, R. Bagherpour. Application of carbonate precipitating bacteria for improving properties and repairing cracks of shotcrete. Construction and Building Materials. 2017, 148: 249–260.

[125] M. Seifan, A.K. Sarmah, A. Ebrahiminezhad, Y. Ghasemi, A.K. Samani, A. Berenjian. Bio-reinforced self-healing concrete using magnetic iron oxide nanoparticles. Applied Microbiology and Biotechnology. 2018, 102 (5): 2167–2178.

[126] S. Chuah, Z. Pan, J.G. Sanjayan, C.M. Wang, W.H. Duan. Nano reinforced cement and concrete composites and new perspective from graphene oxide. Construction and Building Materials. 2014, 73: 113–124.

[127] K. Sisomphon, O. Copuroglu, E.A.B. Koenders. Effect of exposure conditions on self healing behavior of strain hardening cementitious composites incorporating various cementitious materials. Construction and Building Materials. 2013, 42 217–224.

[128] J. Dils, G. De Schutter, V. Boel. Influence of mixing procedure and mixer type on fresh and hardened properties of concrete: A review. Materials and Structures/Materiaux et Constructions. 2012, 45 (11): 1673–1683.

[129] P.N. Hiremath, S.C. Yaragal. Influence of mixing method, speed and duration on the fresh and hardened properties of Reactive Powder Concrete. Construction and Building Materials. 2017, 141: 271–288.

[130] B. Hilloulin, K. Van Tittelboom, E. Gruyaert, N. De Belie, A. Loukili. Design of polymeric capsules for self-healing concrete. Cement and Concrete Composites. 2015, 55: 298–307.

[131] L. Kan, H. Shi, A.R. Sakulich, V.C. Li. Self-healing characterization of Engineered Cementitious Composites (ECC). ACI Materials Journal. 2010, 107 (6): 617–624.

[132] B. Dong, Y. Wang, G. Fang, N. Han, F. Xing, Y. Lu. Smart releasing behavior of a chemical self-healing microcapsule in the stimulated concrete pore solution. Cement and Concrete Composites. 2015, 56: 46–50.

[133] C. Desmettre, J.P. Charron. Water permeability of reinforced concrete subjected to cyclic tensile loading. ACI Materials Journal. 2013, 110 (1): 79–88.

[134] B. Dong, Y. Wang, W. Ding, S. Li, N. Han, F. Xing, Y. Lu. Electrochemical impedance study on steel corrosion in the simulated concrete system with a novel self-healing microcapsule. Construction and Building Materials. 2014, 56: 1–6.

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

[136] W. Li, X. Zhu, N. Zhao, Z. Jiang. Preparation and properties of melamine urea-formaldehyde microcapsules for self-healing of cementitious materials. Materials. 2016, 9 (3): 152.

[137] X. Li, M. Li, G. Song. Energy-dissipating and self-repairing SMA-ECC composite material system. Smart Materials and Structures. 2015, 24: 025024.

[138] M.M. Sherif, E.M. Khakimova, O.E. Ozbulut, D.K. Harris, H.C. Ozyildirim. Behavior of mortar beams with randomly distributed superelastic shape memory alloy fibers. Journal of Intelligent Material Systems and Structures. 2018, 29 (4): 684–695.

[139] D. Sun, J. Hu, X. Zhu. Size optimization and self-healing evaluation of microcapsules in asphalt binder. Colloid and Polymer Science. 2015, 293 (12): 3505–3516.

[140] Q. Liu, Á. García, E. Schlangen, M. Van De Ven. Induction healing of asphalt mastic and porous asphalt concrete. Construction and Building Materials. 2011, 25 (9): 3746–3752.

[141] L. Kan, H. Shi. Investigation of self-healing behavior of Engineered Cementitious Composites (ECC) materials. Construction and Building Materials. 2012, 29: 348–356.

[142] D. Snoeck, N. De Belie. From straw in bricks to modern use of microfibers in cementitious composites for improved autogenous healing – A review. Construction and Building Materials. 2015, 95: 774–787.

[143] L. Lv, E. Schlangen, Z. Yang, F. Xing. Micromechanical properties of a new polymeric microcapsule for self-healing cementitious materials. Materials. 2016, 9 (12): 1025.

[144] P. Escoffres, C. Desmettre, J.P. Charron. Effect of a crystalline admixture on the self-healing capability of high-performance fiber reinforced concretes in service conditions. Construction and Building Materials. 2018, 173: 763–774.

[145] H. Lee. Potential of superabsorbent polymer for self-sealing cracks in concrete. Advances in Applied Ceramics. 2010, 109 (5): 296–302.

[146] V.C. Li, E. Herbert. Robust self-healing concrete for sustainable infrastructure. Journal of

Advanced Concrete Technology. 2012, 10 (6): 207–218.

[147] C. Hung, Y. Su, Y. Su. Mechanical properties and self-healing evaluation of strain-hardening cementitious composites with high volumes of hybrid pozzolan materials. Composites Part B. 2018, 133: 15–25.

[148] S. Gwon, E. Ahn, M. Shin. Self-healing of modified sulfur composites with calcium sulfoaluminate cement and superabsorbent polymer. Composites Part B. 2019, 162: 469–483.

[149] H. Huang, G. Ye, D. Damidot. Characterization and quantification of self-healing behaviors of microcracks due to further hydration in cement paste. Cement and Concrete Research. 2013, 52: 71–81.

[150] G. Yildirim, M. Sahmaran, H. Ahmed. Influence of hydrated lime addition on the self-healing capability of high-volume fly ash incorporated cementitious composites. Journal of Materials in Civil Engineering. 2014, 27 (6): 4014187.

[151] E. Cuenca, A. Tejedor, L. Ferrara. A methodology to assess crack-sealing effectiveness of crystalline admixtures under repeated cracking-healing cycles. Construction and Building Materials. 2018, 179: 619–632.

[152] D. Snoeck, N. De Belie. From straw in bricks to modern use of microfibers in cementitious composites for improved autogenous healing - A review. Construction and Building Materials. 2015, 95: 774–787.

[153] D. Snoeck, P.A. Smetryns, N. De Belie. Improved multiple cracking and autogenous healing in cementitious materials by means of chemically-treated natural fibres. Biosystems Engineering. 2015, 139: 87–99.

[154] A.P. Singh, B.K. Gupta, M. Mishra, Govind, A. Chandra, R.B. Mathur, S.K. Dhawan. Multiwalled carbon nanotube/cement composites with exceptional electromagnetic interference shielding properties. Carbon. 2013, 56 86–96.

[155] B. Han, S. Sun, S. Ding, L. Zhang, X. Yu, J. Ou. Review of nanocarbon-engineered multifunctional cementitious composites. Composites Part A: Applied Science and Manufacturing. 2015, 70: 69–81.

[156] M.S.M. Norhasri, M.S. Hamidah, A.M. Fadzil. Applications of using nano material in concrete: A review. Construction and Building Materials. 2017, 133 91–97.

[157] Z. Li, S. Ding, X. Yu, B. Han, J. Ou. Multifunctional cementitious composites modified with

nano titanium dioxide: A review. Composites Part A. 2018, 111 115–137.

[158] L. Guadagno, L. Vertuccio, C. Naddeo, E. Calabrese, G. Barra, M. Raimondo, A. Sorrentino, W.H. Binder, P. Michael, S. Rana. Self-healing epoxy nanocomposites via reversible hydrogen bonding. Composites Part B. 2019, 157: 1–13.

[159] C. Lv, J. Wang, Z. Li, K. Zhao, J. Zheng. Degradable , reprocessable , self-healing PDMS / CNTs nanocomposite elastomers with high stretchability and toughness based on novel dual-dynamic covalent sacrificial system. Composites Part B. 2019, 177: 107270.

[160] S.A. Haddadi, A.S.A. Ramazani, M. Mahdavian, P. Taheri, J.M.C. Mol, Y. Gonzalez-garcia. Self-healing epoxy nanocomposite coatings based on dual-encapsulation of nano-carbon hollow spheres with film-forming resin and curing agent. Composites Part B. 2019, 175: 107087.

[161] B. Han, L. Zhang, S. Zeng, S. Dong, X. Yu, R. Yang, J. Ou. Nano-core effect in nano-engineered cementitious composites. Composites Part A. 2017, 95: 100–109.

[162] W. Zhang, B. Han, X. Yu, Y. Ruan, J. Ou. Nano boron nitride modified reactive powder concrete. Construction and Building Materials. 2018, 179: 186–197.

[163] D. Wang, W. Zhang, Y. Ruan, X. Yu, B. Han. Enhancements and mechanisms of nanoparticles on wear resistance and chloride penetration resistance of reactive powder concrete. Construction and Building Materials. 2018, 189: 487–497.

[164] B. Han, Z. Li, L. Zhang, S. Zeng, X. Yu, B. Han, J. Ou. Reactive powder concrete reinforced with nano SiO2-coated TiO2. Construction and Building Materials. 2017, 148: 104–112.

[165] X. Cui, J. Ou, N. Ma, X. Yu, Y. Wang, B. Han, L. Zhang. Study on the reinforcing mechanisms of nano silica to cement-based materials with theoretical calculation and experimental evidence. Journal of Composite Materials. 2016, 50 (29): 4135–4146.

[166] E. Mohseni, B.M. Miyandehi, J. Yang, M.A. Yazdi. Single and combined effects of nano-SiO2, nano-Al2O3 and nano-TiO2 on the mechanical, rheological and durability properties of self-compacting mortar containing fly ash. Construction and Building Materials. 2015, 84 331–340.

[167] W. Li, Z. Huang, F. Cao, Z. Sun, S.P. Shah. Effects of nano-silica and nano-limestone on flowability and mechanical properties of ultra-high-performance concrete matrix. Construction and Building Materials. 2015, 95 366–374.

[168] T. Manzur Yazdani, Nur, Emon, Md Abul Bashar. Potential of carbon nanotube reinforced cement composites as concrete repair material. Journal of Nanomaterials. 2016, 1421959.

[169] H. Du, H.J. Gao, S.D. Pang. Improvement in concrete resistance against water and chloride ingress by adding graphene nanoplatelet. Cement and Concrete Research. 2016, 83: 114–123.

[170] X. Cui, B. Han, Q. Zheng, X. Yu, S. Dong, L. Zhang, J. Ou. Mechanical properties and reinforcing mechanisms of cementitious composites with different types of multiwalled carbon nanotubes. Composites Part A. 2017, 103: 131–147.

[171] R. Palla, S.R. Karade, G. Mishra, U. Sharma, L.P. Singh. High strength sustainable concrete using silica nanoparticles. Construction and Building Materials. 2017, 138: 285–295.

[172] A. Mignon, D. Snoeck, P. Dubruel, S. Van Vlierberghe, N. De Belie. Crack mitigation in concrete: Superabsorbent polymers as key to success? Materials. 2017, 10 (3): 237.

[173] O.M. Jensen, P.F. Hansen. Water-entrained cement-based materials - I. Principles and theoretical background. Cement and Concrete Research. 2001, 31 (4): 647–654.

[174] O.M. Jensen. Internal uring of concrete-state-of-the-art Report of RILEM Technical Committee 196-ICC. RILEM Report. 2007, 41.

[175] E. Boquet, A. Boronat, A. Ramos-Cormenzana. Production of calcite (calcium carbonate) crystals by soil bacteria is a general phenomenon. Nature. 1973, 246 (5434): 527.

[176] D.P. Bentz, K.A. Snyder. Protected paste volume in concrete: Extension to internal curing using saturated lightweight fine aggregate. Cement and Concrete Composites. 1999, 29: 1863–1867.

[177] K.V. Reddy, M. Tech, V. College. A comparative study of mechanical properties of M25 grade self-curing concrete with conventional concrete. International Journal of Applied Research. 2015, 1 (10): 655–659.

[178] M.R. Geiker, D.P. Bentz, O.M. Jensen. Mitigating autogenous shrinkage by internal curing. ACI Special Publication. 2004, 218: 143–154.

[179] M.T. Hasholt, O.M. Jensen, K. Kovler, S. Zhutovsky. Can superabsorent polymers mitigate autogenous shrinkage of internally cured concrete without compromising the strength? Construction and Building Materials. 2012, 31: 226–230.

[180] M.V.J. Kumar, M. Srikanth, K.J. Rao. Strength characteristics of self-curing concrete. International Journal of Research in Engineering and Technology. 2012, 1 (1): 51–57.

[181] D. Snoeck, J. Dewanckele, V. Cnudde, N. De Belie. X-ray computed microtomography to study autogenous healing of cementitious materials promoted by superabsorbent polymers. Cement and Concrete Composites. 2016, 65 83–93.

[182] Y. Kuang, J. Ou. Self-repairing performance of concrete beams strengthened using superelastic SMA wires in combination with adhesives released from hollow fibers. Smart Materials and Structures. 2008, 17 (2): 025020.

[183] S.B. Li, Q.G. Liang, J.P. Li. Finite element analysis for the crack self-repairing behavior of the concrete beam embedded shape memory alloy. Applied Mechanics and Materials. 2014, 507 (2014): 455–459.

[184] S.R. White, N.R. Sottos, P.H. Geubelle, J.S. Moore, M.R. Kessler, S.R. Sriram, E.N. Brown, S. Viswanathan. Autonomic healing of polymer composites. Nature. 2001, 409 (6822): 794.

[185] Z. Lv, H. Chen. Analytical models for determining the dosage of capsules embedded in self-healing materials. Computational Materials Science. 2013, 68: 81–89.

[186] Z. Lv, H. Chen. A probabilistic method for determining the volume fraction of pre-embedded capsules in self-healing materials. Smart Materials and Structures. 2014, 23 (11): 115009.

[187] G. Perez, E. Erkizia, J.J. Gaitero, I. Kaltzakorta, I. Jiménez, A. Guerrero. Synthesis and characterization of epoxy encapsulating silica microcapsules and amine functionalized silica nanoparticles for development of an innovative self-healing concrete. Materials Chemistry and Physics. 2015, 165: 39–48.

[188] M. Kosarli, D.G. Bekas, K. Tsirka, D. Baltzis, D.T. Vaimakis-tsogkas, S. Orfanidis, G. Papavassiliou, A.S. Paipetis. Microcapsule-based self-healing materials : Healing efficiency and toughness reduction vs . capsule size. Composites Part B. 2019, 171: 78–86.

[189] D. Gardner, A. Jefferson, A. Hoffman, R. Lark. Simulation of the capillary flow of an autonomic healing agent in discrete cracks in cementitious materials. Cement and Concrete Research. 2014, 58 35–44.

[190] S. Castanier, G. Le Me´tayer-Levrel, J.P. Perthuisot. Ca-carbonates precipitation and limestone genesis — the microbiogeologist point of view. Sedimentary Geology. 1999, 126 (1–4): 9–23.

[191] W. De Muynck, N. De Belie, W. Verstraete. Microbial carbonate precipitation in construction materials : A review. Ecological Engineering. 2010, 36: 118–136.

[192] H.M. Jonkers. Self healing concrete: a biological approach, in: Self Heal. Mater., 2007: pp. 195–304.

[193] M. Luo, C. Qian. Influences of bacteria-based self-healing agents on cementitious materials hydration kinetics and compressive strength. Construction and Building Materials. 2016, 121:

659–663.

[194] E. Tziviloglou, V. Wiktor, H.M. Jonkers, E. Schlangen. Selection of nutrient used in biogenic healing agent for cementitious materials. Frontiers in Materials. 2017, 4: 15.

[195] W. Khaliq, M.B. Ehsan. Crack healing in concrete using various bio influenced self-healing techniques. Construction and Building Materials. 2016, 102: 349–357.