



Understanding the Impacts of Healing Agents on the Properties of Fresh and Hardened Self-Healing Concrete: A Review

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Abstract: Self-healing concrete has emerged as one of the prospective materials to be used in future constructions, substituting conventional concrete with the view of extending the service life of the structures. As a proof of concept, over the last several years, many studies have been executed on the effectiveness of the addition of self-healing agents on crack sealing and healing in mortar, while studies on the concrete level are still rather limited. In most cases, mix designs were not optimized regarding the properties of the fresh concrete mixture, properties of the hardened concrete and self-healing efficiency, meaning that the healing agent was just added on top of the normal mix (no adaptations of the concrete mix design for the introduction of healing agents). A comprehensive review has been conducted on the concrete mix design and the impact of healing agents (e.g., crystalline admixtures, bacteria, polymers and minerals, of which some are encapsulated in microcapsules or macrocapsules) on the properties of fresh and hardened concrete. Eventually, the remaining research gaps in knowledge are identified.

Keywords: self-healing concrete; crystalline admixture; bacteria; microcapsules; macrocapsules; fresh properties; hardened properties

1. Introduction

Concrete is one of the most consumed materials all over the world and it is regarded as an essential construction material in the global construction and infrastructure sector. The ability of concrete to withstand high compressive stresses contributes to its high loadbearing capacity. In contrast, concrete is relatively weak in tension and needs reinforcement to withstand tensile forces and to make it more ductile. Even with embedded reinforcement inside the concrete, the cracks may inevitably occur due to numerous factors such as extreme exposure, high tensile stresses, etc. Cracks continuously grow from the micro size to the macro size and they can emerge in different locations. The formation of these cracks is one of the major causes of concrete degradation. The ingress of water, harmful liquids, acidic gaseous pollutants and other substances into the crack will jeopardize the internal structure of concrete elements by corroding the steel reinforcement and deteriorating the microstructure of concrete. Efforts have been spent to patch existing cracks using different techniques; however, they are costly, cause indirect costs (e.g., economic losses from traffic jams which occur due to the repair works in the field), and in a lot of cases the repair is temporary. Therefore, there is a need to find a sustainable way of healing cracks. To mitigate this issue, over the last decade, self-healing technologies have received great attention from researchers due to their effectiveness in closing cracks. These aforementioned technologies enable the cementitious composite to repair cracks independently, without human intervention, by stimulating autogenous healing and autonomous healing mechanisms.



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Crystalline admixture (CA), bacteria and encapsulated agents are some types of acknowledged healing agents that have been introduced lately. CA is defined as a type of permeability-reducing admixture (PRA), as reported by the ACI Committee 212 [1], with a hydrophilic nature, reacting easily with water. The self-healing phenomenon of mortar containing CA was studied earlier by Sisomphon et al. [2] and they found that cracks with a width up to 250 µm were completely sealed. Calcium carbonate (CaCO₃) was found to be the major healing product. The healing capacity of CA for micro cracks is relatively effective, but macro cracks are hard to be sealed [3]. García-Vera et al. [4] reported an improvement in the durability behaviour of mortar containing CA (a greater compressive strength, a lower mass loss and a lower reduction of Young's modulus than the control mortar after 90 days of sulphuric acid attack). Ferrara et al. [5] upscaled the utilization of CA to produce high-performance, fibrereinforced cementitious composites and revealed that the mechanical performances (the load capacity, stiffness, ductility and toughness) of cracked specimens were significantly recovered after a short healing period of about one month.

On the other hand, the implementation of bacteria as a self-healing agent in the concrete matrix emerges as one of the most promising approaches in sealing cracks. Jonkers et al. [6] started to investigate the viability of bacteria spores (Bacillus pseudofirmus and *Bacillus cohnii*) in cement paste with the addition of calcium precursor compounds as nutrient for bacteria growth. This showed that the number of viable bacterial cells significantly decreased with increasing specimen age, indicating the low viability under a highly alkaline environment. To address the issue of bacteria vulnerability, several encapsulation techniques were proposed to protect the bacteria using hydrogels [7-9], nanoparticles [10], aggregates [11] or capsules [12]. Furthermore, Mondal et al. [13] suggested the optimal bacterial (*Bacillus subtilis*) concentration of 10^5 cells/mL for strength enhancement and 10^7 cells/mL for durability purposes (reduction in water absorption and water penetration depth). Pei et al. [14] supported the fact that the incorporation of *Baciluss subtilis* into the mortar mixtures improved the compressive strength and decreased the porosity at a specific dosage. The properties of the fresh cement paste/mortar mixture containing bacteria are still unclear. Previous work of Schreiberová et al. [15] showed, for instance, that the addition of nutritional admixtures, that bacteria need for their growth, resulted in an increased fluidity of the fresh cement paste.

The concept of encapsulation technology was first introduced by White et al. [16] in polymer systems. Encapsulation can be defined as an advanced technique to entrap the healing agent inside a capsule-like material. The encapsulated agents are present in the composite and when a crack penetrates into it, the inert shell of the encapsulated material is ruptured, releasing the healing agent from the core to start the healing action. Based on their size, macrocapsules and microcapsules can be distinguished. Giannaros et al. [17] developed microcapsules with mean sizes of 130 and 500 µm for autonomic self-healing of hardened cement paste. The microcapsules were successfully added into the fresh cement paste and an increased viscosity was noticed in the paste containing microcapsules. As a proof of concept, Kanellopoulos et al. [18] performed a three-point bending test on hardened cement paste prisms with the addition of microcapsules. After loading, the specimens were fractured and, from the split sections of cracked specimens, it was observed that there were an unquantified number of 'wet' spots, indicating the ruptured microcapsules. A substantial reduction in compressive strength and Young's modulus of mortar containing organic microcapsules (with urea formaldehyde and epoxy as shell and core materials, respectively) as compared with the control mortar was reported by Wang et al. [19]. However, after being subjected to a healing scenario, the porosity and total pore volume of mortar were reduced remarkably.

For the application of macrocapsules, the 'good' capsules are specially designed to be able to break when the specimen is subjected to cracking while the capsules should not be destroyed during the mixing. Hilloulin et al. [20] suggested that the brittleness of (polymeric) capsules should be designed as high as possible but also allowing to be mixed in. Van Tittelboom et al. [21] used different types of glass and ceramic capsules in mortar specimens. After the capsules were ruptured and specimens were subjected to healing, an improved strength regain and a reduction in water permeability were noticed due to the activation of a suitable healing agent (two-compound system of a prepolymer of polyurethane (PU) and accelerator). Cementitious capsules were also successfully experimented in previous works [22–25] and positive results with regard to healing efficiency were shown. The properties of the fresh concrete mixture as well as the mechanical strengths were in most cases not evaluated due to the reason that the utilization of capsules focused solely on the quantification of the self-healing capacity.

Self-healing concrete promotes a longer life-span of concrete structures and reduces maintenance costs. During the past decade, there have been many publications reporting the feasibility of different healing agents in the application of cementitious mortars, while very limited publications have reported on upscaling to the concrete level. In fact, it remains rather unclear on how the results observed in the mortars will be transferrable to the concrete. In most cases, the healing agents are simply added to the normal mix, without making any adaptations to the design of the concrete mix. In other words, the mix design for self-healing concrete still keeps maintaining the same proportion of each component from the reference mix design. Although researchers have demonstrated the crack healing achieved by self-healing concrete, it is very important to examine the workability of self-healing concrete mixtures and assess the long-term performance of the hardened self-healing concrete before healing to guarantee that the healing agents do not negatively affect the concrete properties to some extent. Knowledge on the consequences of incorporating healing agents in concrete will allow to define adequate mitigation strategies. Finally, this paper offers a comprehensive review of the specific alteration of the concrete properties due to the inclusion of promising/novel healing agents (Section 2) to further understand the behaviour of self-healing concrete in fresh and hardened states (Section 3). In addition, the self-healing properties of the concrete will be discussed concisely.

2. Novel Self-Healing Agents

Stimulated autogenous healing as well as autonomous healing of concrete primarily occur due to the incorporation and activation of healing agents. In general, the healing agents can be added directly, via a vascular system or after encapsulation. CA, bacteria and micro- or macro-encapsulated agents, such as polymers, minerals, etc., are some types of acknowledged healing agents that have been introduced lately in the application of cementitious composites. The detailed descriptions of each healing agent are summarized below.

CA mainly consists of active chemicals, reactive silica and some catalysts [2]. According to an XRD pattern as shown in Figure 1, the main constituents of CA are brucite, gypsum, calcite, and quartz, in addition to C_3S , C_2S , C_3A and C_4AF , similar to the clinker minerals in ordinary Portland cement (OPC) [26]. Figure 2 shows a scanning electron microscopy (SEM) image of CA. The morphology of CA is similar to cement grains and their sizes are typically in the range of 1–20 µm with irregular shape [27].



Figure 1. XRD pattern of CA. Reproduced with permission from [26]. Copyright 2018, Elsevier.



Figure 2. SEM observation of CA at 1000x magnification. Reproduced with permission from [27]. Copyright 2020, Elsevier.

Due to the proprietary nature of this admixture, the chemical composition of CA is kept confidential by all producers. CAs are commercially available in the form of dry powder or liquid. The product was originally used as a waterproofing agent for an exposed concrete surface. These admixtures will block water from any direction because the concrete itself becomes the water barrier. In practice, there are three methods to apply the CA as a waterproofing system: (1) coating on the surface of existing concrete, (2) adding the admixture at the time of batching and (3) dry-shaking to the surface of fresh concrete [4]. Adding CA into the mixes leads additionally to the stimulated autogenous healing of cracks. When combined with water during concrete production, these chemicals react with calcium hydroxide and the other products resulting from cement hydration to form millions of needle-shaped crystals within the concrete. The crystalline structures continuously grow and fill pores and capillaries in the concrete in the presence of moisture [4]. The crystalline products increase the density of the calcium silicate hydrate (C-S-H) phase [5]. In this way, they become an integral part of the concrete matrix and the crystals block the passages, thus preventing the ingress of water and other liquids that may deteriorate the concrete. The capability of the CA to stay dormant and then become active again in the presence of water promotes the self-healing ability to the concrete [28]. If a crack forms, any water ingress triggers the formation of crystals to fill and block this crack. The benefits of the concrete treated with CA are (1) improved water tightness, (2) good immunity to damage and (3) high effectiveness against hydrostatic pressure. Additionally, CA offers an installation advantage as no encapsulation is needed, reducing sample preparation time. The functionality of CA can also be combined with other healing agents, for instance, superabsorbent polymer (SAP), to seal macro-cracks more efficiently [3].

Bacteria are microscopic unicellular organisms which live everywhere and exist in many forms. In nature, bacteria are literally isolated from a medium such as soil, and they are extracted through serial cultivation processes. The presence of a nutrient source is a prerequisite to fully stimulate the growth of the bacteria. The selection of the nutrient is mainly based on the mode of metabolic activity of the used bacteria [15]. For instance, ureolytic bacteria are known as one of the exceptional species of microorganisms in producing excessive amount of carbonates, and bacteria such as *Sporoscarcina pasteurii* need urea and calcium sources to precipitate CaCO₃ [29]. On the other hand, *Bacillus* is a genus of bacteria which is frequently used in the research field due to the fact that they can produce the binding filler material and urease enzyme needed to precipitate the calcite crystals [30]. Figure 3 depicts the rod shaped structure of *Bacillus* bacteria in a solution taken by SEM and optical microscopy. According to the available reports, some prospective bacteria that have been used extensively in concrete are *Bacillus sphaericus* [10,31], *Bacillus subtilis* [32–34], *Bacillus aerius* [35], *Bacillus megaterium* [30], *Sporoscarcina pasteurii* [29,36–38], *Shewanella oneidensis* [39] and a mixed ureolytic culture (*MUC*⁺) [40]. Bacteria are often

proposed as a healing agent to promote an autonomous self-healing repair system based on a biotechnology approach. When cracks appear in the concrete and water penetrates through cracks, the metabolic activation of the dormant bacteria induces the precipitation of CaCO₃ into the pores and cracks, leading to a densification of the concrete matrix. The rate of CaCO₃ precipitation is dependent upon the type of bacteria and the concentration of bacteria. A higher concentration of bacteria typically generates higher precipitation of calcite, which is beneficial for the purpose of concrete protection. In general, there are three proposed techniques to incorporate bacteria into the concrete: (1) bacteria are added directly without carriers at the time of batching, (2) bacteria are impregnated into pellets or aggregates and (3) bacteria are encapsulated via capsules or a vascular network. The utilization of carriers is regarded as one of the most promising solutions to enhance the possibility of bacterial survival [33] because the concrete's high pH and the shear stress during the mixing stage may lower the viability of bacteria [10]. Concrete treated with bacteria offers a wide variety of advantages, such as (1) self-repair of cracks without any external aids, (2) good improvement in mechanical properties and (3) more sustainable and durable concrete.



Figure 3. (a) *Bacillus* bacteria cell under SEM. Reproduced with permission from [30]. Copyright 2016, Elsevier. (b) Isolation of bacteria colonies under a stereo microscope. Reproduced with permission from [38]. Copyright 2019, Elsevier.

The encapsulation method is constantly developed in the field of concrete technology, ranging from the microscale to the macroscale.

(1)Microcapsules have a nominal size of no more than 1 mm and are produced with a variety of production methods (i.e., interfacial polymerization, in situ polymerization, spray drying, ionic gelatin and complex coacervation–as discussed by Kanellopoulos et al. [18]). Table 1 shows the different types of microcapsules which have been successfully applied in concrete. Morphologically, microcapsules have mostly a spherical shape, as shown in Figure 4. The production of microcapsules has to be carefully performed because many parameters may change the physical properties of the final product. Three important design parameters of interest are capsule size/diameter, shell thickness and surface texture [41]. Other parameters such as type of formation, materials and volume will certainly affect the size distribution. The size of microcapsules significantly affects self-healing efficacy. Comparing the same amount of healing agent in smaller or larger capsules, smaller microcapsules open the possibility to heal more scattered cracks due to their high distribution inside the matrix, while larger microcapsules carry more healing agents that may cover a larger healed area, which are effective to seal wider cracks and can simultaneously heal smaller cracks in a nearby region. Hence, it is still unclear what would be the best size of the microcapsules in order to achieve optimal self-healing performance. In general, thin-walled microcapsules would fail during the production process and concrete mixing, while thick-walled microcapsules are reluctant to break as the propagated crack will hardly penetrate [17]. The morphology, size and shape of prepared microcapsules are dependent on numerous factors including temperature, pH and agitation rate [17,18,42,43]. The microcapsules are typically stored in the preserving solution to prevent shrinkage and the premature hardening of microcapsules as may occur in the dry condition. To incorporate the microcapsules in the concrete, direct addition during the mixing stage is done in numerous studies.

(2) Macrocapsules are literally bigger in size (>1 mm) and can store a larger amount of healing agents than microcapsules. Macrocapsules are commercially available, such as borosilicate glass or ceramic capsules which are cut from a long tube, or the capsules can be manufactured by means of an extruder through an extrusion process [22,23,44]. Table 2 presents the various types of capsules used in the application of self-healing concrete. The physical appearance of some cylindrical capsules is shown in Figure 5. Glass capsules could affect negatively the concrete durability due to the undesired alkali-silica reaction (ASR) [45,46], while polymeric capsules could cause premature curing of an entrapped agent such as PU [44]. To avoid these drawbacks, ceramic capsules [47] and cementitious capsules [22–25] were successfully experimented. To incorporate the capsules into the concrete, other aspects such as capsule dimensions (i.e., diameter, thickness and length) also play an important role in the self-healing scenario because the capsule should be able to break when a crack propagates. Thin-walled capsules are effective for capsule breakage during cracking of the concrete as they are relatively fragile; however, they would fail when the capsules are added during the mixing. Conversely, thick-walled capsules are highly resistant to withstand mixing forces, but they are reluctant to break as the propagated crack will hardly penetrate through the planar surface of the capsules and this might lead to a lower self-healing efficiency. The same problem occurs with the length of capsules. Short capsules may cause a slip when a crack appears, while long capsules will be more difficult to be incorporated into the concrete because of the interaction with aggregates which will disturb the packing system. Thus, the optimal design of macrocapsules remains an interesting topic of research. To authors' knowledge, there are two methodologies to incorporate macrocapsules in concrete mixes, namely manual placement and direct addition. In the first method, the most practical application is manually placing the capsules in the cover zone of mortar/concrete (as shown in Figure 5a,b), while in the second method, a previous work [46] attempted to incorporate the capsules directly into the fresh mixture during the mixing stage. The random distribution of mixed-in capsules was observed in the hardened concrete core, as shown in Figure 5c.



Figure 4. Optical microscopic images of produced microcapsules; with permission from ASCE [48].



Figure 5. (a) Manual placement of two cementitious capsules in a small-scale mortar mould [22]. (b) Manual placement of glass capsules onto a network of wires in a large-scale concrete beam mould. Reproduced with permission from [49]. Copyright 2016, Elsevier. (c) Reconstructed CT scan of a sliced concrete core with a glass capsule crossed by a crack (left) and the 3D distribution of capsules in the concrete cores as a result of direct addition of capsules during concrete mixing (**right**). Reproduced with permission from [46]. Copyright 2018, Elsevier.

Ref.	Production Method	Microcapsule Shell	Cargo	Capsule Diameter (µm)	Shell Thickness (µm)	Remarks
[42]	In situ polymerization	Polyurethane/urea- formaldehyde	Sodium silicate	Not specified	Not specified	Spherical double-walled microcapsules with rough surface
[41]	Interfacial polymerization	Polyurethane	Sodium silicate	Not specified	Not specified	Self-synthesized microcapsules with rough surface
[18,50]	Complex coacervation	Gelatin/gum Arabic shell	Sodium silicate	290	5–20	Microcapsules with the shape of "rugby-ball" which have switchable mechanical properties
[19]	In situ polymerization	Urea-formaldehyde	Epoxy resin	45–185	5.46	Spherical-shaped organic microcapsules that can produce ductility for the cementitious composites
[51]	In situ polymerization	Urea-formaldehyde	Epoxy resin	110–190	Not specified	Round-shaped microcapsules with non-smooth surface which has a good thermal stability
[52]	In situ polymerization	Urea-formaldehyde	Calcium nitrate	22–59	Not specified	Smooth surface and non-porous texture
[48]	In situ polymerization	Urea-formaldehyde	Calcium nitrate	22-109	Not specified	Smooth exterior surface coated with Span60 emulsifier
[43]	In situ polymerization	Urea-formaldehyde	Calcium nitrate	41–107	0.60–1.31	Spherical-shaped microcapsules with smooth exterior surface and rough interior surface
[53]	In situ polymerization	Urea-formaldehyde	Dicyclopentadiene	80–600	0.20-0.25	Rough permeable outer layer and smooth interior shell free of cavities; more uniform

Table 1. Different microcapsule materials with the corresponding parameters and characteristics used in concrete application.

The major purpose of using micro- or macro-capsules containing healing agent is to introduce autonomous self-healing by storing sufficient amount of healing agent internally

inside the concrete to allow in situ repair at any time a damage or crack occurs. For instance, in the case of using polymeric healing agent, after the capsule rupture, the healing agent will react with the catalyst and the polymerization occurs along the crack plane [16], leading to the crack healing phenomenon. Furthermore, the selection of a suitable healing agent is also of great importance. Several healing agents are proposed as a cargo of microcapsules. The utilization of sodium silicate, which was originally implemented in the application of geopolymer composites, has been adopted in self-healing concrete due to the fact that the presence of sodium silicate in the concrete triggers the chemical reaction with portlandite (Ca(OH)₂) resulting in the formation of C-S-H gel [41]. Calcium nitrate is proposed as a healing agent due to its low cost and because it can react with the unhydrated cement grains to form hydroxy nitrate salts that contribute to the accelerated synthesis of C-S-H and the densification of the microstructure [52]. Dicyclopentadiene ($C_{10}H_{12}$) is another healing agent which is normally used as a monomer in the polymerization reaction [53]. Several advantages of using epoxy resin as healing agent inside the microcapsules include high bond strength, good stability, wide adhesion and improved mechanical properties [54]. For the cargo of macrocapsules, PU is mostly used due to the ability of the agent to harden upon contact with humidity inside the concrete matrix [44,49]. Water-repellent agent can also be used which could render the crack faces impermeable [46]. Although the addition of capsules tends to reduce mechanical strength, the encapsulation-based self-healing agents positively offer several advantages such as (1) improved crack-width and crack-depth reduction, (2) permeability reduction and (3) effective strength recovery after healing [50].

Rof	Type of	Specimen	n Macrocapsules				Cargo	Dosage of	Placement	Romarks	
iter.	Composite	Size (mm)	Shell	OD (mm)	ID (mm)	Length (mm)	Coat		Capsules	Method	KUIIIIKS
[49]	SR-SCC	$\begin{array}{c} 150\times250\times\\ 3000 \end{array}$	Glass	3.35	3	50	-	PU	350 cap- sules/beam	Manual	Capsules started to break when the crack width amounted to 50 $\mu\text{m}.$
[46]	SR-SCC	$200\times400\times\\2500$	PMMA	6.5	5.1	50	-	WRA	22 capsules/L of concrete	Direct addition	Survival probability of the PMMA capsules increased as the wall thickness of the capsules increased. Capsules were able to rupture at crack width of 116 µm.
	SR-SCC	$200\times400\times\\2500$	Glass	5	3.4	50	-	WRA	22 capsules/L of concrete	Direct addition	Good survivability with the thicker capsule and more uniform distribution using glass capsules. Capsules were able to rupture at a crack width of 30 µm.
[47]	FRC	$\begin{array}{c} 100\times100\times\\ 650\end{array}$	Glass, ceramic	Not specified	3	60, 400	Mortar layer, cement paste bar	PU	Not specified	Manual, direct addition	Capsules broke during the mixing stage, while they remained intact when the capsules were placed manually using wire.
[44]	TC	$\begin{array}{c} 120 \times 120 \times \\ 500 \end{array}$	Glass	2.3	1.7	25, 50	Ethyl cellu- lose	PU	2% v/v	Direct addition	The dip-coated capsules showed a higher survivability than uncoated capsules. Capsules were able to rupture at a crack width of 400 $\mu m.$
	Mortar	40 imes 40 imes 160	Ethyl cellulose	5	3	50	-	PU	2 cap- sules/prism	Manual	Some capsules were not broken after complete cracking and polymeric capsules showed an incompatibility issue that the stored healing agent is prematurely cured inside the capsule.
[55]	Mortar	$50\times50\times220$	Glass	7.05	6.15	50	Thin PVC film	TEOS, SS, CS, C	2 cap- sules/prism	Manual	Capsules and its corresponding cargo could survive in a high pH solution (pH = 12) similar to cement, except cyanoacrylate which started to harden within 4 days after encapsulation.
[20]	Mortar	40 × 40 × 160	Polymers– PLA, PS, P(MMA/n- BMA	5	3	50, 100	-	Water	2–4 cap- sules/prism	Manual, direct addition	Moderate resistance during mixing stage. P(MMA/n-BMA) capsules showed a high brittleness and they ruptured when subjected to relatively small deformation.
[23]	Mortar	40 imes 40 imes 160	Cementitious	10	7.5	50	Ероху	WRA, PU, bacteria	1–2 cap- sules/prism	Manual	Cementitious capsules were able to sequester and release the healing agents. They showed a good protection between agents and harsh environment of the matrix.

Table 2. Different macrocapsule materials with the corresponding parameters and characteristics used recently in mortar and concrete applications.

Note: OD-outer diameter, ID-internal diameter, SR-SCC-steel reinforced self-compacting concrete, TC-traditional concrete, FRC-fibre reinforced concrete, PMMA-poly(methyl methacrylate), PLA-poly(lactic acid), PS-polystyrene, P(MMA/n-BMA)-poly(methyl methacrylate/n-butyl methacrylate), PU-polyurethane, WRA-water-repellent agent, SS-sodium silicate, TEOS-tetraethyl orthosilicate, CS-Colloidal silica, C-Cyanoacrylate.

3. Comparative Study on the Inclusion of Self-Healing Agents into the Concrete Mix

In general, studies on self-healing cementitious composites (i.e., mostly in mortar) focus mainly on the evaluation of self-healing efficiency. However, to deeply understand the concrete behaviour as a consequence of incorporating healing agents, it is necessary to highlight some key parameters that affect the properties of fresh and hardened self-healing concrete. The main aspects covered in this review are:

- The main strategies of incorporating healing agent with or without capsules into the self-healing concrete mixes, as described in Figure 6;
- Effect of addition of healing agents on the properties of fresh and hardened concrete before healing (especially for micro- and macro-encapsulated agents, these properties will be evaluated based on the physical presence of capsules in the concrete matrix);
- Brief evaluation of self-healing phenomenon in the cracked concrete after healing (Note: the term of healing efficiency/ratio refers to the crack width reduction or crack closure by microscopic investigation, while the sealing efficiency/ratio is determined by permeability test). Testing methods to evaluate self-healing/sealing capacity of the concrete will not be addressed in this review, but can be found in [56].

Healing agent (HA)	Main strategies of incorporating HA into concrete (current practices)	Parameters and materials considered
Crystalline admixture (CA)	 Utilization of CA as: + a direct addition on top of normal concrete mix (without changing the mix design) + a partial replacement of filler (e.g. limestone powder) + a partial replacement of cement + a partial replacement of aggregate 	 Effective dosage of CA (typically 0.8–4.5% by weight of cement)
Bacteria	 Direct addition of bacteria on top of normal concrete mix (without changing the mix design) Encapsulation of bacteria to improve the cell viability (e.g. immobilization, impregnation, etc.) 	 Bacteria genus and species; and the concentration of bacteria (typically 10³-10¹⁰ cfu/ml) Selection of a suitable nutrient/precursor and its dosage Selection of compatible chemical admixtures
Microencapsulated HA ©©©	Direct addition of microcapsules on top of normal concrete mix (without changing the mix design)	 Size and concentration of microcapsules (typically 0.5–10% by weight of cement) Shell material of microcapsules and its cargo
Macroencapsulated HA	 Direct addition of microcapsules on top of normal concrete mix (without changing the mix design) Instalment of the capsules (in relation to the capsule distribution): + manual placement in the mould by the means of wire (capsules are not added during mixing stage) + random distribution and orientation of the capsules (capsules are added during mixing stage) 	 Type of capsule material and the dimension of the capsule (length, diameter and thickness) Survivability of capsules during mixing stage: (1) evolving capsule brittleness by plasticizing agents or by heating and (2) increasing capsule thickness Dosage (or number) of capsules added into the concrete Selection of healing agent stored inside the capsule

Figure 6. Main strategies to introduce healing agents in the recent application of self-healing concrete.

3.1. Effects of CA on Concrete Properties

3.1.1. Properties of the Fresh Concrete Mixture

Based on previous studies [57,58], workability of fresh CA-based concrete, termed as CA concrete, is mostly assessed by its slump value (at least for traditional concrete mixes), determined in accordance with EN 12350-2:2009. It should be mentioned in this regard that for most studies, the CAs were just added to the reference mix, while only a small number of studies have made modifications to the self-healing concrete mix design.

Roig-Flores et al. [58] characterized the workability of fresh fibre-reinforced concretes between two mix batches (control and CA) with 4% addition of CA by weight of cement. According to their mix design, the amount of CA was opted as a replacement of limestone powder (LP), while the total quantity of the powder materials (cement + LP + CA) was kept constant for both mixes. A slight adjustment was made to the nominal amount of aggregates. For instance, in the composition of CA concrete, the amount of gravel 4/12 increased from 950 to 959 kg/m³ as compared with the control concrete, while the amount of natural sand decreased from 899 to 875 kg/m³. Steel fibre was added equally for all mixtures with the purpose of controlling crack width during the self-healing test. The slump values for control concrete and CA concrete were 130 mm and 150 mm, respectively. The difference of slump test results between these two mixes was minor because the slump was deliberately maintained in a similar value (140 \pm 20 mm) by adjusting the dosage of superplasticizer. In another study by the same authors [57], the same concept of adding CA as an LP replacement was applied on precast concrete C45/55 and standard concrete C30/37. The results showed that slump values for all mixes were identical because the amount of superplasticizer was adjusted to reach a similar slump value (~150 mm), and thus the effect of CA was not apparent.

The application of CA on high performance fibre reinforced concrete (HPFRC) was introduced by Escoffres et al. [59]. The amount of CA was fixed at 2% by weight of cement (equivalent to 11 kg/m³), while all concrete components, including steel fibres, were kept constant with respect to the reference mixture except for the aggregates. The amounts of both fine and coarse aggregates were slightly reduced to compensate for the addition of CA. The amount of sand was reduced from 814 to 808 kg/m³, while coarse aggregates from 658 to 653 kg/m³. Chemical admixtures, such as a superplasticizer and viscosity agent, were added in the same amount. The workability of the concrete mixtures was measured by the slump flow test and the results showed that the HPFRC mixtures without and with CA had slump flow values of 530 and 540 mm, respectively. There was no significant effect of CA addition on the flowability of concrete.

Moreover, Azarsa et al. [60] investigated the properties of the fresh normal strength concrete mixtures with two different cement classes named OPC and Portland Limestone Cement (PLC). CA in powder form was added in addition to the normal mix with a dosage of 2% by weight of cement. No superplasticizer was introduced in these mixes. In the case of the OPC mixtures, the inclusion of CA resulted in a reduction of the slump value from 130 to 110 mm and the air content was slightly increased by 0.2%. On the other hand, the slump value decreased significantly on the PLC mixtures from 130 to 85 mm and a 0.3% increase of the air content was observed. One possible reason for the reduced workability can be associated with the nature of the CA as a hydrophilic material. Azarsa et al. [60] claimed that due to its unique characteristics, in the initial stage of mixing the concrete, CA tends to absorb water which results in a lower workability. Although the addition of CA showed a reduction in slump values and a slight increase in the air void content, the plastic densities between CA concretes and reference concretes were found to be similar. It is noteworthy to mention that different studies use different types of CAs, with varying chemical composition and physical properties. However, most CA producers argue that the addition of their commercial CAs shows little or no effect on the workability aspect.

3.1.2. Properties of the Hardened Concrete

While an introduction of CA into the concrete mix is designated to enhance autogenous self-healing [27], the mechanical properties of concrete treated with CA show a significant improvement regardless of the type of concrete. The compressive strength of CA-based concrete is directly associated with the addition of CA and the proportioning of concrete constituents. The 28-day strength improvement of CA concrete is presented in Figure 7 and the results are compared with the corresponding reference concretes. In addition, Table 3 shows the description of each mix code including concrete type, type of cement, water-to-cement ratio (w/c), CA dosage and the role of CA.



Figure 7. Concrete strength increments due to the addition of CA at 28 days; data are taken from available literatures and the details of mix code can be seen in Table 3. The dot and dash-dot lines represent the value of compressive strength enhancement by using Xypex Admix (2–3% CA) and Penetron CA (0.8–1% CA), respectively, according to the technical data sheets [61,62].

Wang et al. [63] studied the strength characteristics of lightweight concrete (mix code M1) produced by incorporating CA up to 4.5% as a cement replacement and found that after 28 days of curing, the mean compressive strength enhanced from 29.04 to 31.50 MPa. Additionally, the flexural strength of this concrete slightly increased from 8.19 to 8.62 MPa. Mix codes of M2, M3.1 and M3.2 were casted by Roig Flores et al. [57,58] to produce fibre-reinforced concretes with the addition of 4% CA by the weight of cement and the addition of CA partially replaced the amount of limestone powder to keep the binder amount constant. The strength improvements of M2 and M3.1 mixtures were recorded at 15.1% and 14.5%, respectively, while the M3.2 mixture had a small increment approximately at 7.9% which may be explained by the influence of higher w/c and lower binder content. Another study [64] also fabricated fibre reinforced concrete (mix code M5) with a lower CA dosage. Here, CA was added as a cement replacement by 1.1% and the strength of the CA-based concrete was 14.6% higher than for the reference concrete.

Moreover, the mix codes of M4.1, M4.2, M6.1 and M6.2 are basically classified as normal strength concretes with a relatively low CA dosage in the range of 0.8–2%. Azarsa et al. [60] investigated the influence of different cement classes as OPC type I (mix code M4.1) and PLC type GUL (mix code M4.2) in combination with CA on the compressive strength of self-healing concrete. CA was directly added to the reference mix and the mix composition was featuring the same cement content, w/c and aggregates proportions. The result showed that the highest strength improvement of approximately 11.6% was achieved by the M4.1 mixture while an improvement of 8.4% was observed on the M4.2 mixture. Sideris et al. [65] incorporated 0.8% CA by the weight of cement in addition to the C20/25 mixtures (mix code M6). As can be seen from Figure 7, the addition of CA at a low percentage of 0.8% slightly increased the compressive strength by 5.5%.

Ref.	Mix Code	Concrete Type	Cement Type	wlc	CA Dosage (% Wt. Cement)	Role of CA	Age of Cracking	Healing Time	Crack Width	Healing Ratio (Scale 0–1)	Exposure
[63]	M1	LWC	Not specified	0.45	4.50%	Cement replacement	7 days	28 days	0.15 mm	-	Water immersion
[58]	M2	FRC	II 42.5R	0.45	4.00%	Limestone powder replacement	2 days	42 days	\leq 0.3 mm	0.90–1.00	Water immersion
[57]	M3.1	Precast FRC	II 42.5R	0.45	4.00%	Limestone powder replacement	2 days	42 days	0.1–0.4 mm	0.80-1.00	Water immersion
	M3.2	FRC	II 42.5R	0.60	4.00%	Limestone powder replacement	2 days	42 days	0.1–0.4 mm	0.80-1.00	Water immersion
[60]	M4.1	NSC	I 42.5R	0.53	2.00%	Direct addition (on top of concrete mix)	28 days	4–5 days	0.1–0.4 mm	0.98–1.00	Water immersion
[60]	M4.2	NSC	GUL	0.53	2.00%	Direct addition (on top of concrete mix)	28 days	4–5 days	0.1–0.4 mm	0.97–0.99	Water immersion
[64]	M5	FRC	OPC 53	0.45	1.10%	Cement replacement	2 days	42 days	\leq 0.4 mm	-	Water immersion
[65]	M6	NSC	II 32.5R	0.64	0.80%	Direct addition (on top of concrete mix)	-	-	-	-	Curing chamber (T = 20 °C,RH > 98%)
[66]	M7	NSC	OPC 43	0.40	2.00%	Direct addition (on top of concrete mix)	3 days	42 days	\leq 0.4 mm	-	Water immersion
[5]	M8	HPFRCC	II 42.5R	0.63	1.00%	Direct addition	42 days	365 days	0.2 mm	0.60	Open air

Table 3	Summary of	of CA concr	ete compositior	and the scenario	o of self-healing	assessment.
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Note: LWC-lightweight aggregate concrete, FRC-fibre-reinforced concrete, NSC-normal strength concrete, HPFRCC-high performance fibre reinforced cementitious composite, GUL cement (General Used Limestone)–Portland Limestone cement which follows Canadian standard for cement.

(on top of concrete mix)

Generally, it can be observed that the addition of CA in the range of 0.8-4.5% by weight of cement increases the compressive strength up to 15%. However, it is interesting that the gradual CA addition does not linearly increase the strength in the same way. It might be explained by the fact that each study selected different variables, dosages and materials which accordingly makes it difficult to compare the results. On the other hand, commercial CA producers such as, for instance, Xypex and Penetron indicated that the addition of their CA, named Xypex Admix [61] and Penetron Admix [62], resulted in 10% and 13% increase of compressive strength at 28 days, respectively. The recommended dosages suggested by the CA producers are 2–3% by weight of cement for Xypex Admix and 0.8–1.0% by weight of cement for Penetron Admix. For instance, the mix code of M1 used 4.50% Xypex Admix CA and the concrete had a better compressive strength of 8.4% [63]. One interesting result was found by Pazderka et al. [28] discussing the influence of two types of CAs on the C20/25 concrete mixture. They utilized Penetron Admix and Xypex Admix C-1000NF at the constant dosage of 2% of the cement weight. The compressive strengths of concrete without CA, concrete with Penetron Admix and concrete with Xypex Admix were 36.8, 36.2 and 36.3 MPa. The results were almost identical for all specimens and, in fact, it was in contrast with other results presented earlier. Pazderka et al. [28] hypothesized that the addition of CA in an amount of 2% caused a mild deceleration of the hardening of concrete.

The phenomenon of strength enhancement might be explained by three reasons: (1) the filling effect of CA [57,58], (2) the role of CA as cement hydration activator by promoting the further densification of the microstructure [60] and (3) the production of $CaCO_3$ by CA inside the concrete matrix upon presence of moisture [66]. Microstructural analysis based on XRD and SEM revealed the presence of CaCO₃, Ca(OH)₂, C-S-H, crystalline Mg-phase and ettringite in CA concrete specimens [63]. As a matter of fact, there are several factors such as type of CA, w/c and curing time that could result in higher strength. The utilization of CA has a great potential to make concrete more durable and impermeable due to its waterproofing effect to plug the pores by depositing precipitated CaCO₃ crystals. Incorporation of CA also reduces the water penetration depth remarkably. For concrete treated with CA, the penetration depth of water can be reduced by 40–50%, indicating the superior water-tightness effect of this admixture [60]. It was also reported that commercial CAs from Xypex and Penetron reduced the water vapor permeability by 16% and 20%, respectively [28]. In addition, CA helped the concrete structure to withstand the chloride attack and induces lower carbonation depth, thus enhancing the concrete durability and prolonging the service life of the structure [65].

3.1.3. Self-Healing Properties

The healing ability of CA is beneficial for extending the lifetime of concrete. In fact, the evaluation of the self-healing phenomenon is generally dependent on many variables, such as the age of cracking, healing time, crack width and curing condition. Some researchers have performed cracking of specimens at different ages by doing splitting tests or three-point bending tests and the healing period was mostly fixed up to 42 days. It was suggested by Roig-Flores et al. [58] to crack the specimens during early ages (~2 days) to prevent initial cracking due to shrinkage. Conversely, Chandraiah et al. [64] argued that the cracking age does not necessarily affect the process of healing. In general, the initial crack width is typically controlled in the range of 0.10–0.40 mm. The maximum crack width that can be healed with CA varies between 0.15 and 0.30 mm [5,57–60,63,67], and if combined with other techniques, such as CA with expansive agents, the healed crack width can be increased up to 0.40 mm [2]. There are some exposure scenarios that have been applied to CA concrete, such as water immersion, water contact, wet-dry cycles and storage in a humidity chamber and open air; however, the best exposure to effectively stimulate autogenous healing seems to be the water immersion [57,58].

Due to the diversity of testing methodologies and their associated parameters, it is not easy to compare the results presented in different studies. In general, Table 3 summarizes the research programs and parameters used to evaluate the self-healing efficiency. As a note, the healing ratio is assessed by measuring the value of crack width after and before healing by means of microscopic investigation. The crack width reduction vs. the original crack width is considered as the healing ratio. The crack widths reduced significantly in the samples which were fully immersed in water when compared with other exposures. Healing ratios in the range of 0.80–1.00 were obtained [57,58] for concretes treated with CA, while the reference concrete can achieve a healing ratio between 0.50–1.00 [57]. When the cracked concrete specimens were subjected to air exposure as a curing condition, interestingly, CA were still able to promote crack sealing by up to 60% after several months [5]. It is evident that the presence of moisture plays a key role in activating the CA to further encourage the crystallization process. As a visual observation, there were whitish formations near the mouth of the crack and they were confirmed to be calcite crystals with a rhombohedral morphology mainly containing Ca, C and O [63]. The CaCO₃ precipitation, as the self-healing product, in the presence of CA is coherent with the observations of Sisomphon et al. [2], Roig-Flores et al. [57,58], and Escoffres et al. [59]. In addition, the use of CA is also beneficial for the recovery of mechanical properties that could achieve more than 78% strength regain [66]. Consequently, CA acts as a stimulator of the autogenous healing mechanism of concrete [45] and simultaneously may promote a durable concrete. Sideris et al. [65] estimated that the service life of their concrete slabs without CA was about 40 years, while concrete slabs treated with 0.8% CA could reach 48 years and even more than 50 years in case an improved curing was applied, indicating the positive effect of the combination between the utilization of CA and the extension of the curing period.

3.2. Effects of Bacteria on Concrete Properties

3.2.1. Properties of the Fresh Concrete Mixture

The workability of fresh bacterial concrete is an important property that should be investigated thoroughly. The inclusion of bacteria is normally combined with a suitable nutrient to supply the food for their growth inside the concrete matrix. On the one hand, nutrients play an important role for bacteria activation as long as water and moisture are present, while, on the other hand, this additive may also affect the properties of the fresh concrete mixture to a certain extent. According to previous studies, bacteria are often implemented as an additional agent placed into the normal concrete mixes, while the mix composition remains the same as for the reference concrete. From the authors' point of view, this concept might raise a concern as changes in the properties of the fresh concrete might be expected. It is still uncertain whether the water demand and setting time of the concrete mix with a fixed dosage of bacteria will change abruptly or still remain stable. Thus, a comprehensive review, as presented below, is needed to investigate the workability issues due to the addition of bacteria and nutrients.

Vijay et al. [32] studied the combination effect of Bacillus subtilis bacteria spore powder and calcium lactate on the workability of two concrete mixes, i.e., normal concrete and basalt-fibre reinforced concrete. The concentration of bacteria was fixed at 10⁵ cfu/mL (cfu = cell or colony-forming unit) with the purpose of improving the strength of concrete, and calcium lactate was used as nutrient source for bacteria at the dosage of 0.5% by weight of cement. Both bacteria and nutrient were added to the normal mix while maintaining the volume of aggregates and no superplasticizer was used in the mix design. Coarse aggregate with the nominal size of 20 mm and fine aggregate were used. The results showed that the addition of Bacillus subtilis together with calcium lactate increased the slump value of normal concrete. The workability of bacterial concrete improved due to the role of calcium lactate as a retarding agent in the concrete that may increase the setting time and fluidity of the concrete. Furthermore, basalt fibres were introduced in the bacterial concrete mix and the slump value was nearly the same as for the normal concrete without bacteria. Due to the internal friction between fibres and cement, the traditional bacterial concrete is more workable than the fibre-reinforced bacterial concrete. Siddique et al. [35] added isolated ureolytic bacteria Bacillus aerius strain AKKR5 with a concentration of 10⁵ cfu/mL to the normal concrete mix, while the nutrient for bacteria growth was not incorporated in the

mixture. The w/c and aggregate-to-binder (a/b) ratios were kept constant at 0.50 and 4.44, respectively, and superplasticizer was not utilized in this study. Coarse aggregate with a maximum size of 12.5 mm and fineness modulus (FM) of 6.38 and fine aggregate with an FM of 2.58, were used in the mix design. The results indicated that no effect was found on the slump value of bacterial concrete as compared with the reference concrete. A similar result was also found by Mohammed et al. [39]. The inclusion of iron-respiring bacteria, which was cultured in Tryptone Soya Broth (TSB), showed no effect on the fresh density and slump value of CEM I concretes. However, different behaviour was observed on the CEM III concretes as there was a small reduction in the concrete unit weight and a 9% reduction of slump value. Nevertheless, all concrete mixes achieved medium workability, which was classified as S3 according to EN 12350-2:2009.

Ameri et al. [38] performed the evaluation of self-compacting concrete (SCC) mixtures with different Bacillus pasteurii cell concentrations by performing slump flow, T₅₀, V-funnel, U-flow, and L-box tests. Calcium lactate was selected as the nutrient source and added to the mixtures at a dosage of 5% by weight of cementitious materials. Here, the concrete mixes were designed using the optimum rice husk ash (RHA) content (15% by weight of cement) and three bacteria cell concentrations of 10^3 , 10^5 and 10^7 cells/mL. The water content for all mixtures was kept constant with a water-to-binder ratio (w/b) of 0.40. Pumice was used as coarse aggregate with a maximum aggregate size of 19 mm, while natural sand was used as fine aggregate with a particle size between 0 and 4.75 mm. Superplasticizer was incorporated in all mixes with a dosage of 2.5% by weight of cementitious materials. To obtain comparative results, reference concrete was made with the same composition as bacterial concrete with RHA as secondary cementitious material (SCM), only without adding bacteria and nutrients. It is worth noting that for all workability tests, all mixes showed identical results despite different bacteria concentrations. For instance, the slump flows of reference concrete and bacteria concretes with cell concentrations of 10^3 , 10^5 , and 10^7 cells/mL were 680, 684, 689 and 690 mm. This result is in contrast to the results found by Vijay et al. [32] regarding the influence of bacteria and nutrient on workability aspect. While it is difficult to judge which parameter influences workability, interesting research undertaken by Nguyen et al. [34] can be taken into account to understand the impact of nutrients and bacteria with nutrients in concrete applications. In their study, three concrete mix designs were formulated, maintaining the same proportions of cement, water, aggregates and superplasticizer. In other words, two parameters of interest were chosen, i.e., nutrients and bacteria cells. (1) The first mix was the control concrete with a slump target about 180 \pm 20 mm (or consistency class of S4) without nutrients and bacteria. (2) The second mix consisted of control concrete with the addition of two types of nutrients. Peptone and yeast extract were incorporated to the mixing water with a dosage of 1.00% and 0.50%, respectively. Lastly, (3) the third mix was the bacterial concrete which was the combination of the second mix and Bacillus subtilis bacteria with a concentration of 1.82×10^{10} cells/m³. Both nutrients and bacteria with nutrients were just added to the control mix. Based on the slump test results, comparing the second mix and the first mix, the addition of nutrients increased the slump value from 185 to 205 mm, while, comparing the third mix and the first mix, the combination of bacteria and nutrients increased the slump value from 185 to 195 mm. Eventually, it can be concluded that, in this case, the nutrients used as growth media for culturing bacteria were mainly responsible for the changes of workability, while the addition of bacteria in the fresh concrete with nutrients slightly decreased the slump value but still maintained the same consistency class as the control concrete.

3.2.2. Properties of the Hardened Concrete

A general overview of the recent application of bacteria at the concrete level assessed by compressive strength, flexural strength, split tensile strength and water absorption is presented in Table 4. The changes in mechanical and durability properties in relation to the control concrete without bacteria, nutrients and SCMs are expressed in percentage. The performance of concrete embedded with the different genus of bacteria and suitable nutrient(s) normally shows an improvement on the mechanical properties due to the precipitation of calcite. As a matter of fact, it should be stressed that no adaptations in the mix designs were done for the introduction of bacteria-based healing agents.

One of the main issues in introducing bacteria into concrete mixes is the limited cell viability when the bacteria are directly incorporated to the fresh concrete due to the concrete's high pH and the shear forces occurring during the mixing stage. To address this issue, Seifan et al. [10] designed immobilized bacteria cells with magnetic iron oxide nanoparticles (IONs). *Bacillus sphaericus* was selected as the microorganism which was cultured in the calcium chloride, urea and yeast extract. The designed healing agent was added to their normal concrete mix and superplasticizer was not used. As compared with the reference concrete, the compressive strength of bacterial concrete was enhanced by 43% and 15% at 7 and 28 days, respectively. The optimum improvement of mechanical properties of bacterial concrete based on *Bacillus sphaericus* was found by Reddy et al. [31] for a cell concentration of 10⁵ cells/mL. However, the inclusion of a bacterial agent led to a higher free shrinkage due to the chemical reaction of nutrients during cement hydration [10].

The introduction of Bacillus subtilis with calcium lactate as the nutrient source in concrete applications was experimented upon by Vijay et al. [32] and Khaliq et al. [33]. As observed at 28 days, the compressive strength of concrete with Bacillus subtilis at a cell concentration of 10^5 cells/mL is at least 20% higher than that of concrete without bacteria [32]. From the microstructure findings, it was revealed that the strength enhancement occurred due to the formation of calcite which filled in the voids. Khaliq et al. [33] designed bacterial concretes with three different approaches. (1) In the first mix, bacteria were added directly into the fresh concrete without any protective carriers. (2) In the second mix, lightweight aggregates (LWA) were used as a protective carrier of bacteria, replacing the natural coarse aggregates. LWA were soaked in the bacterial solution for 24 h prior to mixing. (3) In the same way as the second mix, the third mix used graphite nanoplatelets (GNP), instead of LWA, as a bacteria carrier compound. The reference mix without bacteria was designed for a compressive strength of 4000 psi (28 MPa). The concrete mix designs for bacterial concretes were not adapted and still maintained the same proportion as the reference mix. Retarding admixture and superplasticizer were added into the mixes at 1% by weight of cement to produce free-flowing concrete for the application in hot climates. The results showed that the compressive strengths of all mixes were increased for all bacterial incorporation techniques. The highest strength improvement of 12% was achieved by the bacterial concrete specimens containing LWA as compared to the control concrete. One possible reason for this improvement is attributed to the smaller size of LWA in comparison to regular sized coarse aggregates which may have resulted in better packing and compaction of the concrete matrix. The use of GNP induced a positive effect as the compressive strength increased by about 9.8%. It was claimed that the small size of GNP decreased the formation of a weak interfacial transition zone (ITZ) in the concrete by filling the porous and crystalline microstructure within the ITZ. A decrease in ITZ makes the mortar matrix denser and more compact, resulting in a higher compressive strength [33]. This may be explained by the fact that the ITZ has a significantly higher porosity and shows multiple microcracks, leading to the common view of the ITZ as the weak link in concrete [68]. Nevertheless, the direct inclusion of Bacillus subtilis bacteria without carrier also showed an approximately 5% enhancement of compressive strength. The presence of bacteria and its organic precursor densify the internal structure of the concrete due to the bacterial activity producing CaCO₃.

Andalib et al. [30] formulated concrete mix designs with a target compressive strength of 30 MPa by using several dosages of *Bacillus megaterium* with the purpose of obtaining the optimum concentration for strengthening structural concrete. One single parameter was initially chosen namely cell concentration in the range of 10³–10⁷ cells/mL. The mix design for bacterial concrete was not adapted, thus maintaining the same proportions as the control one. To effectively germinate the bacteria, 5% of mixing water as bacterial

broth medium culture was added during the mixing stage. The results showed that the compressive strength of bacterial concrete increased optimally (7.8% improvement) at a cell concentration of 10^5 cells/mL, whereas a higher concentration showed a negative effect resulting in a lower strength. This result was supported by SEM images showing that the bacterial concentration of 10^7 cells/mL yielded a higher porosity of the concrete microstructure. Furthermore, a more detailed investigated in the narrower range between 10×10^5 and 50×10^5 cells/mL was executed to find the optimal concentration in relation to the strength improvement. While the strength differences are insignificant within this range, the highest strength was achieved with the bacterial concentration of 30×10^5 cells/mL for the application of structural concrete.

Table 4. Comparison of various bacteria applications in normal strength concrete and their effects on the mechanical and	nd
durability properties.	

Rof	Bacteria	Bacteria	Nutrient	SCM	Cł	anges at 28 Da	iys	Water Absorption		
Kei.	Dacteria	Concentration	Munch	bein	Compressive Strength	Flexural Strength	Split Tensile Strength	Control Concrete	Bacterial Concrete	
[10]	Bacillus sphaericus	250 µg/mL	YE, UR, CaCl	-	$\uparrow 15\%$	-	-	-	-	
[31]	Bacillus sphaericus	10 ³ cells/mL 10 ⁵ cells/mL 10 ⁷ cells/mL	YE, UR YE, UR YE, UR	- - -	↑ 10% ↑ 20% ↑ 17%	↑ 2% ↑ 35% ↑ 22%	↑ 16% ↑ 25% ↑ 19%	- - -	- - -	
[32]	Bacillus subtilis	10 ⁵ cells/mL	LAC	-	$\uparrow 21\%$	↑ 17%	-	-	-	
[33]	Bacillus subtilis	$\begin{array}{c} 3\times 10^8 \\ cells/mL \end{array}$	LAC	-	↑ 12%	-	-	-	-	
[34]	Bacillus subtilis	10^8 cells/mL	YE, Peptone	-	-	-	-	6.3%	5.3%	
[35]	Bacillus aerius	10 ⁵ cells/mL	Not specified	-	$\uparrow 11\%$	-	-	2.3%	1.2%	
[00]	Ductitus ucrtus	10^5 cells/mL	Not specified	10% SF	† 31%	-	-		0.8%	
[30]	Bacillus megaterium	10 ³ cells/mL 10 ⁵ cells/mL 10 ⁷ cells/mL	LAC, UR LAC, UR LAC, UR	- - -	↑ 3% ↑ 5% ↓ 5%	- - -	- - -	- - -	- - -	
[29]	29] Sporoscarcina pasteurii	10 ⁷ cells/mL	Not specified	-	↑ 5%	-	$\uparrow 11\%$	-	-	
[29]		10^7 cells/mL	Not specified	10% NZ	$\uparrow 20\%$	-	$\uparrow 20\%$	-	-	
[36]	Sporoscarcina pasteurii	10 ³ cells/mL 10 ⁵ cells/mL 10 ⁷ cells/mL	Not specified Not specified Not specified	- - -	$egin{array}{c} \uparrow 4\% \ \uparrow 17\% \ \uparrow 8\% \end{array}$	- - -	- - -	17.7%	14.0% 13.0% 13.7%	
		10 ³ cells/mL	Not specified	10% FA	No changes	-	-	17.7%	4.0%	
		10^5 cells/mL	Not specified	10% FA	↑ 15%	-	-		3.3%	
		10^7 cells/mL	Not specified	10% FA	$\uparrow 4\%$	-	-		3.7%	
[27]	Sporoccarcina nastaurii	10 ³ cells/mL	Not specified	10% SF	↑ 52%	-	-	17.5%	0.1%	
[57]	Sporoscuretnu pusteurn	10^5 cells/mL	Not specified	10% SF	↑ 66%	-	-		0.1%	
		10 ⁷ cells/mL	Not specified	10% SF	$\uparrow 45\%$	-	-		0.8%	
[00]	Commentation and the state	10 ³ cells/mL	LAC	15% RHA	↑ 13%	↑ 2 3%	↑ 2 1%	4.8%	3.2%	
[38]	Sporoscurcina pasteurii	10^5 cells/mL	LAC	15% RHA	↑ 20%	↑ 2 9%	† 29%		1.4%	
		10 ⁷ cells/mL	LAC	15% RHA	$\uparrow 17\%$	↑ 26%	↑ 25%		1.1%	
[39]	Shewanella oneidensis	$2.3 imes 10^8$ cells/mL	TSB	-	↑3%	-	-	-	-	
	Bacillus sphaericus	2.3×10^8 cells/mL	TSB	60% GGBS	$\downarrow 10\%$	-	-	-	-	

Note: LAC-calcium lactate, YE-yeast extract, UR-urea, TSB-tryptone soya broth, FA-fly ash, SF-silica fume, NZ-natural zeolite, RHA-rice husk ash, GGBS-ground granulated blast-furnace slag.

Many studies frequently utilized *Sporoscarcina pasteurii*, which is also known as *Bacillus pasteurii* from older taxonomies, for the application of self-healing concrete due to the fact that this bacteria has the ability to solidify organic nitrogen source through the process of

biological cementation [36]. Due to its high urease activity, urease catalyzes the hydrolysis of urea to form ammonia and carbonic acid, in which ammonia later forms ammonium and hydroxide ions in water, while carbonic acid also forms bicarbonate and hydrogen ions in water. This leads to the formation of carbonate ions. In the presence of calcium ions in the cement system, CaCO₃ crystals can be precipitated [69]. The role of Sporoscarcina bacteria as a bio-based healing agent has been known to exhibit significant improvement from the perspective of mechanical properties [29,36–38] at the concrete level by utilizing the most frequently proposed cell concentrations of 10^3 , 10^5 and 10^7 cells/mL. For instance, Chahal et al. [36] designed concrete mixtures to have a compressive strength of 28 MPa at 28 days. Cement was partially replaced with 0, 10%, 20%, and 30% fly ash by weight of cement and Sporoscarcina pasteurii bacteria was cultured to obtain different concentrations of cells. Nutrient broth was also prepared in advance prior to the mixing stage, but the ingredients of this nutrient were not specified. Similarly to other studies, the mix designs were not adapted for the introduction of bacteria. For bacterial concrete specimens without cement substitution, the compressive strength improvement was 4%, 17% and 8% for a cell concentration of 10^3 , 10^5 and 10^7 cells/mL, respectively. Moreover, from a durability point of view, the utilization of fly ash in combination with bacteria greatly improved the water tightness of the concrete as in fact, the water absorption was found to be reduced nearly four times [36]. Based on another report by the same authors [37], 10% cement substitution by silica fume greatly boosted the compressive strength of bacterial concrete up to 52%, 66% and 45% with the corresponding cell concentrations of 10^3 , 10^5 and 10^7 cells/mL, respectively, compared to control concrete without the bacteria and silica fume. A similar pattern was also found when substituting the cement with rice husk ash [38] or natural zeolite [29]. Microstructure analysis by means of SEM confirmed the presence of CaCO₃ in the bacterial concrete.

Mohammed et al. [39] attempted to produce bacterial concrete with *Shewanella oneidensis* and high cement replacement by blast furnace slag of up to 60%; however, a substantial drop of the concrete's strength was observed. In Siddique's experiment [35], self-healing concrete mixes were designed using *Bacillus aerius* bacteria in combination with silica fume as a partial replacement of cement. The advantage of the *Bacillus* species is high pH tolerance, thus increasing the viability under alkaline environments. The *w/b* was fixed at 0.47 and the aggregate proportions were maintained the same for all mixes. With no cement substitution and the inclusion of 10^5 cells/mL *Bacillus aerius* bacteria, an 11% enhancement in compressive strength in comparison to the normal strength concrete was observed. By using the same bacteria cell concentration and 10% cement replacement by silica fume, there was a steep increase of the strength up to 31%, which was mainly due to microbial calcite precipitation and a denser microstructure.

The results based on the flexural strength and the split tensile strength basically follow the same trend as the compressive strength [29,31,32,38]. Moreover, as shown in Table 4, the concretes containing bacteria are more durable than the normal concrete as a reduction in water absorption was clearly observed. The reduction was more pronounced when the SCMs (e.g., fly ash, silica fume, natural zeolite and rice husk ash) were utilized in the bacterial concrete mixes as cement replacement. The highest reduction of water absorption was observed in the bacterial concrete containing *Sporoscarcina pasteurii* bacteria and 10% silica fume. The deposition of CaCO₃ in the concrete capillary pores caused the reduction in water absorption and porosity which in turn increases the durability of the concrete [35–38]. It is noteworthy to highlight that the optimum bacteria cell concentration for strengthening the concrete was achieved at 10^5 cells/mL. A higher bacterial cell concentration would be more efficient where protection of concrete is more important than strength [13].

Additionally, the nutritional admixtures for the growth of bacteria may also affect the strength of concrete considerably. However, due to the fact that a limited number of studies in this domain on concrete is available, a review of impact of different nutrients was done at the mortar level. Schreiberová et al. [15] fabricated mortar specimens which were combined with the most frequently proposed nutrients including calcium lactate, calcium nitrate, calcium formate, yeast extract and urea; bacteria were not incorporated in the mortar mixtures. As shown in Table 5, it was observed that the pre-selected calcium sources did not endanger the strength values at any ages except calcium nitrate at 28 days. Moreover, the inclusion of calcium lactate and calcium formate increased the compressive strength. It is evident that based on the available results presented in Table 5, the addition of calcium lactate [30,32,33,38] with the relevant bacteria has a similar tendency to enhance the strength of the concrete. One possible reason of strength enhancement by calcium lactate may be explained in the following reactions [6]:

$$\begin{aligned} \text{CaC}_6\text{H}_{10}\text{O}_6 + 6\text{O}_2 \rightarrow \text{CaCO}_3 + 5\text{CO}_2 + 5\text{H}_2\text{O} \\ \\ 5\text{CO}_2 + \text{Ca}(\text{OH})_2 \rightarrow 5\text{CaCO}_3 + 5\text{H}_2\text{O} \end{aligned}$$

As a result of metabolic conversion of calcium lactate, the minerals are formed and are likely $CaCO_3$ -based. Further, the produced CO_2 molecules react with $Ca(OH)_2$ which results in more production of $CaCO_3$ -based minerals.

Furthermore, the addition of urea exhibited a positive result during the early ages while at the later age of 28 days the mortar strength was similar to the control. On the contrary, a drastic drop of the mortar compressive strength was observed when the yeast extract was added into the mix, which is in agreement with the result reported by Jonkers et al. [6]. Chen et al. [70] proved that the addition of yeast extract (0.06% by weight of cement) into the mortar mixes lowered the compressive strength, approximately from 38 to 32 MPa. This may be explained due to the fact that the air content of mortar containing yeast extract was almost doubled in relation to the reference mortar without nutrients; increasing from 2.1 to 3.8%. The result suggests that the addition of nutritional admixtures will have a considerable effect on the performance of concrete and the appropriate dosage should be optimized in order to not negatively affect the mechanical properties while still maintaining the ability to supply the "food" for the bacteria's consumption.

		viean values of Compressive Strength								
Nutrient	Dosage (% Weight of Cement)	3 Days		7 Days		28 Days				
		(MPa)	(%)	(MPa)	(%)	(MPa)	(%)			
Control	-	22.88	100	28.93	100	45.31	100			
Calcium lactate	3.00	27.70	121	36.02	125	58.76	130			
Calcium nitrate	3.00	26.44	116	33.47	116	41.13	91			
Calcium formate	3.00	37.96	166	44.23	153	57.63	127			
Yeast extract	0.85	10.65	47	19.61	68	35.12	77			
Urea	2.50	30.80	135	34.77	120	44.39	98			

Table 5. Effect of nutritional admixtures on the compressive strength of the mortar (without bacteria) [15].

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3.2.3. Self-Healing Properties

The incorporation of bacteria into the concrete mixture with a suitable nutrient source essentially promotes an autonomous healing mechanism. The precipitation of calcite crystals in the cracks takes place upon the presence of water, hence, blocking the passage of water and other liquids that may jeopardize the structure of the concrete. In order to simulate the self-healing capability, in laboratory conditions, concrete specimens treated with bacteria were typically cracked at the age of 28 days and the healing time varied between 28–44 days; for instance, with the use of *Bacillus subtilis* [32–34]. After a healing period under water immersion, it can be observed visually that the crack mouth was filled with white sedimentation, identified as CaCO₃ crystals. The morphology of calcite was observed

in tetrahedron and pyramid shapes by [32]. Concrete containing *Sporoscarcina pasteurii* bacteria, cracked to a width of 0.28 mm, was nearly fully healed after 30 days of curing in aqueous molar solution of urea and calcium chloride, as shown in Figure 8 [29]. The sealing efficiency of the bacterial concrete was recorded at 90% when the cracked specimen immersed in water for 27 weeks [40]. The incorporation of *Bacillus subtilis* bacteria by the use of LWA and GNP, which act as protective carriers to ensure the viability of bacteria, were effective to stimulate crack closing up to 0.52 mm and 0.38 mm, respectively [33]. As a matter of fact, the need for liquid water is vital to activate the dormant bacteria in producing CaCO₃. The best performance of bacteria concrete in terms of self-healing capacity was achieved by using the bacteria cell concentration of 10⁷ cells/mL, where it possessed maximum reduction in water absorption and maximum surface crack and pore healing [13].



Figure 8. Development of crack closing in the bacterial concrete after 30 days based on microscopic image. Reproduced with permission from [29]. Copyright 2020, Elsevier.

3.3. Effects of Micro-Encapsulated Agent on Concrete Properties

3.3.1. Properties of the Fresh Concrete Mixture

Microcapsules are regarded as 'vessels' for healing agents which are fabricated through serial synthesis by, for instance, emulsification and polymerization to entrap the core in a shell structure. The final product of the microencapsulated healing agent normally exists in the liquid or slurry form containing an unquantified amount of microcapsules. These microcapsules are added during the mixing process into the concrete in a small dosage for self-healing purposes. However, the presence of microcapsules may affect the properties of the fresh concrete mixture.

Only a few studies investigated the effects of microcapsules on the properties of the fresh concrete mixture. Sidiq et al. [41] designed the concrete mixes with a w/c and sand-to-cement ratio (s/c) of 0.54 and 1.83, respectively. The coarse aggregates were chosen with two nominal sizes of 7 mm and 10 mm. The microcapsules were prepared with two different dosages of 2.5% and 5% by weight of cement and in fact, the mix designs were not adapted for the introduction of microcapsules. The microcapsules were mainly composed of sodium silicate solution as core material and PU as shell material. To prevent high damage on microcapsules, the healing agent solution was added into the concrete mixer after three minutes of mixing, followed by one more minute after the addition. It was reported that the fresh concrete mixture experienced a loss of plasticity as a result of incorporating the microcapsules at the time of batching. This phenomenon may be explained by two reasons: (1) the microcapsules were regarded as powder-like material in the solution thus the incorporation of microcapsules increased the ratio of powder material to the water content of the mix and (2) a partial reduction of water content due to the

hydrophilic character of the PU as shell material. Despite this unsatisfactory effect, both mixes still remained workable.

Milla et al. [52] incorporated the microcapsules carrying calcium nitrate with ureaformaldehyde as shell material in the production of steel fibre reinforced concrete. Calcium nitrate was claimed to enhance the autogenous healing capacity in concrete. The microcapsules were technically produced with and without Span 60 emulsifier and the characteristics were assessed by means of slump and air content tests. The dosages of all microcapsules were fixed at 0.50% and 0.75% by weight of cement. The proportions of the concrete mixes were kept constant for all mixes with w/c of 0.41. Limestone was used as coarse aggregate with the maximum aggregate size of 19 mm, while sand was used as fine aggregate with the maximum particle size of 4.76 mm. Superplasticizer was used to ensure workability and a defoaming agent was also used to counter the increase of air content when combining microcapsules with superplasticizer. The results showed that the air content values were low for all concretes and no significant difference could be found in the air content between the reference concrete and the microcapsule-based concrete. Based on the slump test, by using one type of microcapsules with emulsifier, the workability showed a declined trend owing to the agglomerations and difficulties in dispersing the microcapsules throughout the concrete matrix, resulting in stiff mixtures. In contrast, another type of microcapsules without emulsifier showed a higher slump value than the reference concrete indicating a better workability. However, the difference in workability in the presence of microcapsules (with and without emulsifier) is not yet fully understood.

It should be emphasized that a handful of reports did not explicitly address the influence of microcapsules on the properties of the fresh concrete mixture, despite its superior ability to heal the cracks. Logically, it is plausible that the microcapsules will not entirely survive during the mixing process and there is a certain amount of microcapsules that rupture due to the collision with the aggregates [41,71]. Subsequently the broken microcapsules would release the healing agent, reacting immediately with the cement blend and influencing the hydration process. To date, the compatibility between the microencapsulated healing agents and the cementitious matrix is not yet completely understood. Hence, evaluating the influence of microcapsules on the properties of the fresh concrete mixture is of great importance to realize its application in the fieldwork in the future.

3.3.2. Properties of the Hardened Concrete

One of the main issues by adding the microcapsules into the mixture is the unfavourable tendency on the mechanical properties of the concrete. In view of the previously reported findings [41,48,50,51,72], the compressive strength of the concrete was reduced significantly at any dosage. Two major parameters discussed in this state-of-art review are the concentration and the size of the microcapsules, while the cargo material as healing agent will not be considered in detail owing to the fact that the properties of the hardened concrete in this part are assessed before being subjected to a cracking and healing scenario.

Al-Tabbaa et al. [50] demonstrated the first field application of microencapsulation technology in the UK by fabricating concrete wall panels using gelatin Arabic shell microcapsules containing sodium silicate in the slurry form. The mean diameter of these microcapsules was approximately 290 μ m. The design of ready mixed concrete was formulated to achieve the strength class of C40/50 with an effective w/c of 0.45. Cement type I, limestone aggregates with a nominal size of 10 mm, limestone fines and marine sand were included in the design. A plasticizer and retarder were also used as concrete admixtures. The addition of microcapsules was limited to 2.67% by weight of cement or approximately 0.47% of the total volume of concrete. Before being added into the concrete mixer, the microcapsules were initially washed with water and then filtered from the preserving solution. With regard to the compressive strength before healing, it was confirmed that at 28 days, the strengths of concrete samples without and with microcapsules were 59 MPa and 42 MPa, respectively. This result was in contrast with their previous research in the laboratory field. It was hypothesized that the poor workability and honeycombing during

casting resulted in a significant drop in strength. Similarly, an 8% decrease in the concrete stiffness value was attributed to the presence of the microcapsules. On the other hand, Sidiq et al. [41] proposed their concrete mix design based on microcapsules, which has been introduced previously in the Section 3.3.1. As a result of doubling the microcapsules dosage from 2.5% to 5.0% by the weight of cement, the reduction of compressive strength was recorded at 26.51%. Such reduction may be caused by a higher porosity content and less adhesion/interlocking between cementitious particles due to the presence of microcapsules. In fact, even at a low dosage (0.75% by weight of cement), both compressive strength and flexural strength were reduced by 11% and 14%, respectively, as demonstrated in the work of Al-Ansari et al. [72].

A research conducted by Wang et al. [51] attempted to use a higher concentration of the microcapsules (10% by weight of cement) for application in a tunnel construction project in Shenzhen, China. The microcapsules were prepared in the laboratory and consisted of epoxy resin as cargo material and urea-formaldehyde resin as shell material with mean diameter of 152.4 µm. All concrete specimens with and without microcapsules were designed with the same w/b of 0.32 and the cement content was partially replaced by slag and fly ash. Other agents such as expansive agent and superplasticizer were employed during proportioning. Especially for concrete with microcapsules, a curing agent was added at 5% by weight of the total binders to effectively activate the healing mechanism when the broken microcapsules release the healing agent. Compressive strength tests on specimens at 60 days showed that the strength of the microcapsule-based concrete was approximately 70% of the control concrete. This negative effect was attributed to the presence of the microcapsules which modified the microstructure of the self-healing concrete. At the microscopic level, as shown in Figure 9 from the SEM image, it was clear that the broken microcapsules still remained in the matrix and they took up some large pore spaces that ultimately decreased the density and homogeneity of the concrete matrix. This finding was supported by the fact that the addition of microcapsules led to a greater porosity value of the concrete [41]. In terms of compressive strength, the presence of the microcapsules can be regarded as harmful pores which are not able to withstand the compression load during mechanical tests [51].



Figure 9. The presence of large pores due to broken microcapsules in the cementitious matrix. Reproduced with permission from [51]. Copyright 2019, Elsevier.

In general, the geometry of microcapsules will indirectly affect the performance of the concrete. This fact was addressed in the research of Milla et al. [48], discussing another parameter aside from microcapsules concentration, specifically the average size of microcapsules. During the production process, the size of the microcapsule was controlled by the agitation rate during synthesizing. Higher agitation rates led to smaller microcapsules

and vice versa. Three batches of microcapsules were prepared with varying agitation rates of 450, 800 and 1500 rpm, and the mean particle size for each batch was found to be 109, 50 and 22 μ m, respectively. The concentrations of microcapsules were tested at 0.25, 0.50 and 1.00% by weight of cement. After the preparation of the microcapsules, the optimal mix designs of concrete were composed in accordance to their previous studies to achieve workable mixtures with low w/c. Hence, superplasticizer was used and the w/cwas fixed at 0.41. Due to the fact that the combination of microcapsules and superplasticizer generated a higher air content, a defoamer was utilized. Limestone and sand were employed as coarse and fine aggregates, respectively, with the maximum particle size of 19 mm and 4.76 mm. The microcapsules were added to the normal mix, thus no adaptations on concrete compositions. Figure 10 shows the compressive strength result of the self-healing concrete with two design parameters namely average microcapsule size (22, 50 and 109 μ m) and microcapsule concentration (0.25, 0.50 and 1.00%). The result confirmed that the highest strength was achieved for the control concrete without microcapsules, while mix 50-0.25% attained the highest compressive strength among microcapsules-based specimens. In contrast, specimens made with 22 μ m microcapsules at the dosage of 1% showed the lowest strength. It may be explained by the fact that microcapsules prepared with a higher agitation rate (smaller capsules in size) tended to agglomerate more than the other microcapsules with lower rates [44]. However, the strength differences of the microcapsule-based concretes were relatively low, ranging up to 5.1 MPa. Furthermore, the lowest strength was observed on the concretes with the highest microcapsule concentration of 1% for all microcapsules sizes. The aforementioned results suggested that the embedded microcapsules yielded a substantial reduction of mechanical strength due to the porous microstructure of the concrete and an appropriate concentration should be optimized in order to not affect negatively on concrete properties.



Figure 10. Compressive strength results of microcapsules-based concrete at various microcapsule concentrations (0.25, 0.50 and 1.00%) and mean sizes (22, 50 and 109 μ m). Data from [48].

3.3.3. Self-Healing Properties

The introduction of microcapsules significantly enhances the autonomous crack healing/sealing ability of self-healing concrete as compared with the normal concrete. In order to effectively activate the healing mechanism, capsules should be broken so the healing agent can be released. Therefore, in laboratory studies, cracks are created by means of three-point bending tests [17,18,52] or by applying 60–70% of maximum compressive strength to the samples [41,51]. Depending on the healing agent, these tests are done at a young or later age; and the curing conditions differ. Sidiq et al. [41], for instance, damaged the concrete specimens at 28 days by 70% of maximum compressive strength, and then the specimens were subjected to a healing scenario in a humidity chamber up to 56 days. It was found that after 56 days of healing, the concrete containing a microcapsule content of 2.5% (sodium silicate as the cargo) was fully recovered, meaning the compressive strength of the damaged specimen after healing equals or exceeds the maximum 28-day compressive strength. For the samples with 5% microcapsules, a full recovery was observed at 14 days and the compressive strength was improved by 38% at the age of 56 days [41]. In other words, the strength recovery was greatly enhanced on the specimens with the higher amount of microcapsules. Similar findings have been found in other studies confirming the positive impacts of the micro-encapsulated healing agents on the mechanical performance after undergoing a healing scheme [43,48,50–52,72]. Sidiq et al. [41] found that crack width up to 122 µm was effectively healed with embedded microcapsules containing sodium silicate and the crack healing ratio achieved up to 60%. It can be concluded that the inclusion of microcapsules generated dual effects on the mechanical properties of self-healing concrete [51]. Firstly, before the healing period, the addition of microcapsules undeniably induced an adverse effect on the mechanical performance due to the large pores in the cementitious matrix. Secondly, after being subjected to the healing scenario, the healing efficiency of the concrete was significantly increased in terms of mechanical strengths. Moreover, Wang et al. [51] and Al-Ansari et al. [72] reported on the durability performance of the self-healing concrete which improved remarkably with increased healing time. Wang et al. [51] performed the rapid chloride migration (RCM) test on concrete disc specimens containing 10% microcapsules (urea-formaldehyde as the shell and epoxy resin as the core) by weight of binders. Initially, the 60 days old concrete specimens were subjected to a compressive load with 30% of maximum compressive strength to induce microcracks. Then, cracked specimens were stored and healed in a curing room (60 °C, 95% RH) for 3, 5, 7, 14 and 28 days. After healing at a specific age, the specimens were split in half and a silver nitrate solution was sprayed on the freshly split specimens to measure the average chloride penetration depth. During the first week of healing, the chloride migration coefficient decreased rapidly from 5.4 to 4.6 ($\times 10^{-12}$ m²/s) and then the reduction rate slowed reaching a value of 4.2 ($\times 10^{-12}$ m²/s) after 28 days. Another study by Al-Ansari et al. [72] found a significant reduction of air permeability of the concrete samples containing 0.75% microcapsules (urea-formaldehyde as the shell and calcium nitrate as the core) by weight of cement. At first, the hardened concretes were loaded up to 60% of their ultimate load at 28 days, and the air permeability test was executed. After that, the specimens were healed under water curing and the air permeability was re-measured after 3 and 7 days of healing. The results showed that the air permeability coefficient of self-healing concrete were 0.98×10^{-16} m² after loading, 0.62×10^{-16} m² after 3 days of healing and 0.03×10^{-16} m² after 7 days of healing. In addition, the air permeability coefficient of control concrete without microcapsules decreased slightly from 0.57×10^{-16} m² (after loading) to 0.43×10^{-16} m² (after 7 days of healing). Despite the negative effects of the microcapsules in the view of mechanical strengths before the healing period, the concrete with micro-encapsulated healing agent showed a better improvement after the specimens were healed. It is feasible to explain that the healing agent released from the broken microcapsules filled the defects and sealed the microcracks, which decreased the concrete's permeability and promoted a more durable concrete.

3.4. Effects of Macro-Encapsulated Agent on Concrete Properties

3.4.1. Properties of the Fresh Concrete Mixture

To date, macrocapsules are mostly included by pre-instalment of the capsules [47,49,73] in the mould and a fresh mix is later poured after a sufficient time of mixing. Only in a limited number of studies, the macrocapsules have been added during the mixing process. In these cases, the mix design is generally not adapted. Here, a review is made to

observe the characteristics of fresh concrete mixes containing capsules and the evaluation of survivability of capsules after undergoing the mixing scenario.

Hilloulin et al. [20] started to investigate the resistance of several types of polymeric capsules including PLA, P(MMA/n-BMA) and PS capsules (the abbreviations are described in Table 2) towards concrete mixing. All capsules were prepared with a length of 50 mm and filled with water. The outer diameters of PLA, P(MMA/n-BMA) and PS capsules were 3.5, 6.6 and 7.2 mm, respectively. In order to test the survival rate of capsules during concrete mixing, small concrete batches containing 10 capsules per batch were prepared. The mixing techniques were divided into two parts: hot mixing and cold mixing. As the capsules were made from polymers with a low glass transition temperature, the change in temperature of the constituents was sought to modify the mechanical properties of the capsules and subsequently adjust the brittleness of the capsules with temperature, aiming to improve the survivability of the capsules during mixing. As a matter of fact, the physical properties of polymers change considerably around their glass transition temperature (i.e., 50 °C, 60 °C and 100 °C for P(MMA/n-BMA), PLA, and PS, respectively). Specially for the concrete hot mixing test, cement was not added, while only using pre-heated aggregates (85–105 $^{\circ}$ C) and boiling water (100 $^{\circ}$ C) during mixing. The amount of boiling water was kept the same as the water needed in the cold mixing. Additionally, capsules were preheated in an oven (85–120 °C) during 20–40 min prior to addition into hot mixes. The cold mixing scheme followed the traditional concrete mixing procedure. The results showed that the survivability ratio of all capsules used in the hot mixing was higher than in the cold mixing. More than 8 capsules out of 10 capsules could survive during the hot mixing. This might be explained due to the fact that the capsules showed more flexible behaviour after pre-heating. In the cold mixing, PS capsules showed the highest resistance (2–3 broken capsules), followed by P(MMA/n-BMA) capsules (7 broken capsules) and PLA capsules (10 broken capsules). It is logical that the PS capsules were able to survive in the cold mixing rather well due to the bigger diameter and wall thickness. However, the treatment for pre-heated capsules seems complicated from an industrial point of view.

Gruyaert et al. [44] investigated the idea to use polymeric capsules with evolving brittleness (flexible at first and brittle enough in contact with hardened concrete environment) in the concrete application. During the capsule production, capsules were made with two different dosages of plasticizing agent, at 10% and 25%, through a serial extrusion process. Plasticizing agents were added to obtain the characteristic of capsules with evolving brittleness. To measure the resistance of capsules during concrete mixing, 10 capsules (5 mm outer diameter, 1 mm thickness and 50 mm in length) were prepared and tested with a small batch of concrete. The concrete mix design was formulated with a w/c of 0.47 and employing sand 0/4 and crushed limestone with two fractions of 2/6 and 6/20. Capsules were added during the last 2 min of mixing. The results showed that the capsules with 25% plasticizing agent performed better (9 out of the 10 capsules remained intact) in comparison to capsules with 10% plasticizing agent. However, these polymeric capsules tend to react chemically with the healing agent (e.g., PU), resulting in a premature hardening of the precursor inside the capsules before healing takes place. On top of that, the capsules did not break upon crack appearance, indicating less suitability for self-healing concrete application.

Araujo et al. [46] studied the survivability of other types of capsules in two different concrete mixes, prior to the final production of large concrete beams with mixed-in capsules. Initially, two types of capsules were utilized including glass capsules with a wall thickness of 0.8 mm and poly(methyl methacrylate) (PMMA) capsules with different wall thicknesses of 0.2, 0.4 and 0.7 mm. The length of all capsules was fixed at 50 mm, while the external diameters slightly varied in the range of 5.0–6.5 mm. In general, two concrete mix designs were formulated to observe the behaviour of mixed-in capsules in relation to the survivability of capsules towards mixing forces. (1) The first mixture was designed for traditional concrete containing crushed stones as coarse aggregates with two size fractions of 2/6 and 6/20. The w/c was fixed at 0.47 and no admixtures were added. (2) The second mixture was designed for SCC containing gravel with the fractions of 2/8 and 8/16. The w/c was higher than the first mixture (0.55) and superplasticizer was added. The mixing procedure was kept constant for all mixtures where the capsules were added directly into the fresh mixture in the last two minutes of the mixing time. By using their developed techniques, the survival ratios of capsules were evaluated. It was reported that the concrete composition had an exceptional influence on the resistance of capsules. The stresses induced on the capsules were lower in an SCC mix than a traditional mix. This was clearly reflected in the survival percentages of thin-walled PMMA capsules which was higher in the SCC mix. For instance, the survival ratios of PMMA capsules with the thickness of 0.4 mm were 20% and 83% in the traditional and SCC mixtures, respectively. Additionally, the survival ratio of thick-walled glass capsules increased from 70% in the traditional mix to 100% in the SCC mix. The aforementioned results may also indicate that the capsules could have a better survivability and less damage when they are incorporated into the concrete mixes with the use of gravel as coarse aggregates. Since crushed limestones are angular in shape and characterized by their sharp and pointy edges, they will critically damage the capsules during mixing and possess a higher impact than gravel [44]; while gravels are naturally rounded aggregates. Based on these findings, three large concrete beams were fabricated using an SCC mixture: (1) reference concrete, (2) self-healing concrete with PMMA capsules (wall thickness = 0.7 mm, outer diameter = 6.5 mm, length = 50 mm) and (3) self-healing concrete with glass capsules (wall thickness = 0.8 mm, outer diameter = 5.0 mm, length = 50 mm). Both types of capsules were added with a dosage of 22 capsules per liter of concrete (equivalent to 3250 capsules in 150 L of concrete). However, due to the tendency of PMMA capsules to float, the casting of concrete beam was divided into two steps: (1) a SCC mix containing capsules was casted and poured into the mould forming a cover layer of 120 mm, and (2) another SCC mix without capsules was prepared and placed on top of the previous layer. The properties of these fresh concrete mixes were not evaluated.

3.4.2. Properties of the Hardened Concrete

As mentioned previously, the mix designs of the self-healing concretes are identical to the mix designs of their reference concretes; the capsules are either placed manually in the moulds or are added to the concrete mix during mixing. Simultaneously, the evaluation of the properties of the hardened capsule-based concrete is rarely done and the main focus of applying the capsules lies on the assessment of self-healing capabilities. In this paper, a small number of studies reporting on the alteration of the properties of the hardened capsule-based concrete before being subjected to a healing scenario is reviewed.

Formia et al. [25] performed a preliminary test on the use of cementitious capsules to evaluate the changes on compressive strength of SCC due to the presence of capsules inside the concrete matrix. The cementitious capsules having a volume of 4000 mm³ (10 mm in diameter, 50 mm in length) were not filled with healing agent to avoid any possible contributions to the compressive strength and also to simulate the condition of empty capsules. The capsules were added with the dosage of 1.6% by volume of concrete (or in a proportion of four capsules per liter of concrete). In general, these capsules were embedded in the concrete cubes $(100 \times 100 \times 100 \text{ mm})$ with three different orientations: (1) horizontal orientation, (2) vertical orientation and (3) random orientation. For horizontal and vertical orientations, the first layer of SCC was poured in the mould, then one tube was put on the fresh concrete surface. Hence, a second layer of SCC was poured and a second tube was placed; and so on until filling completely the mould with concrete including four capsules. Especially for random orientation, the capsules were installed in each concrete layer with a random position and inclination. In this case, during casting, the capsules were placed by pressing them into the fresh concrete mix in order to guarantee a random orientation in space. SCC was designed using CEM I 52.5R, calcareous aggregates with five different fractions (with the maximum diameter of 10 mm), limestone powder, and plasticizer. The effective w/c was fixed at 0.46. The compressive strengths of concrete specimens with

different capsule orientation were investigated after curing for 28 days at 90% relative humidity. The SCC without capsules had a mean compressive strength of 36.55 MPa; while the mean compressive strengths of SCC with horizontally oriented capsules, SCC with vertically oriented capsules, and SCC with randomly distributed capsules were 36.45, 35.95 and 33.45 MPa, respectively. The results showed that the incorporation of capsule with the dosage of 1.6 vol% did not significantly influence the compressive strength. Concrete with randomly distributed capsules experienced a 8.5% strength reduction due to the poor manual placement of the capsules which led to worse interfacial properties between the concrete matrix and the capsules. However, it was observed that these cementitious capsules had a good bonding system with the concrete matrix because neither slipping nor de-bonding of the capsules was found at the end of the compression test, indicating a promising usage of cementitious capsules for a future research.

In the research of Van Tittelboom et al. [49], two SCC beams were fabricated with the same dimension of 150 \times 250 \times 3000 mm. The mix design consisted of cement CEM I 52.5 N, sand 0/5, gravel with two size fractions (2/8 and 8/16), limestone filler and superplasticizer. Both mix designs of reference concrete and capsule-based concrete were kept the same. The major difference lies on the self-healing concrete beam where about 350 glass capsules (3.35 mm outer diameter and 50 mm in length) were placed inside the mould using a network of plastic wires at a cover depth of 10 mm. The density of the hardened concrete was approximately 2320 kg/m³, and the mean compressive strength at 28 days was recorded at 59.2 MPa. Both reference and capsule-based concrete beams were loaded in four-point bending to reach an average crack width of 250 µm, controlled by means of linear variable differential transformers (LVDTs). During testing, the vertical displacements in the middle of the beam were found to be 20.76 and 22.91 mm for the reference concrete and capsule-based concrete, respectively. At the end of crack formation, the total load was registered around 36 kN for both concretes. There was no significant difference between reference and capsule-based concretes in this test, and it may be due to the fact that the capsules were concentrated in one layer, thus during the cracking process, the influence of capsules in the load-displacement behaviour of concrete beam was not apparent.

There have been many publications [20,21,44,46,47,73] reporting the positive results of introducing the macrocapsules in the application of concrete. However, the results are only limited to the healing efficiency and thus the properties of the hardened capsulebased concrete are often neglected. Similar to the case of microcapsules, the addition of macrocapsules in the concrete matrix may induce a considerable effect in respect to the mechanical properties. The consequence of adding capsules in the concrete may also 'downgrade' other concrete properties before the healing ability is triggered upon cracking and rupture of the embedded capsules. One may argue that the properties of the hardened concrete such as the compressive strength of capsule-based concrete may experience a loss of strength as compared with the control concrete without capsules. It is logical that the notion is presumed by two possible reasons: (1) the presence of macrocapsules, which even have a much larger volume than microcapsules, takes a partial volume of concrete and (2) the presence of macrocapsules disturbs the packing of aggregates which increases the volume of voids; both reasons lead to a reduction of concrete strength. Therefore, the real application of macrocapsules in the concrete is still a bottleneck and more advancements in research are needed to mitigate potential problems induced by the presence of capsules in the concrete matrix. Hence, the application of the macrocapsules should be carefully considered and optimized to not affect negatively the properties of the hardened concrete.

3.4.3. Self-Healing Properties

The major notion of the encapsulated self-healing mechanism is based on the ability of the capsules to rupture when a crack generates and simultaneously release the healing agent into the crack, promoting in situ repair. The selection of the healing agent is also of great importance as the cargo should not be hardened during the entrapment inside the capsule. Thus, the suitability between the capsule material and healing agent are essential to be understood. The self-healing approach using an encapsulation technology steadily rises in the research field; however, most applications stay in the mortar level. Some studies upscale the utilization of capsules in the concrete level as discussed in this section.

The self-healing performance of concrete containing glass capsules was studied by Hu et al. [74]. The capsules with an internal diameter of 8 mm and length of 40 mm were filled with PU and were embedded manually in the concrete. The concrete specimens were cracked under a controlled three-point bending test until a crack width of approximately $300 \ \mu m$ was reached. Cracked specimens were cured in the curing chamber ($20 \ ^{\circ}C, 90\%$ RH) until the testing day. After 2 days of healing, the strength recovery rate and the healing efficiency were recorded at 75% and 67%, respectively. Based on SEM images at the interface between concrete and PU, large amounts of the PU curing products were identified and found to be cemented together with fine sand as well as with the C₃S and C_2S on the concrete surface [74]. In another large-scale test [49], Van Tittelboom et al. incorporated 350 glass capsules (3.35 mm outer diameter and 50 mm in length) with a cargo of PU in a concrete beam using a network of plastic wires at a depth of 10 mm. The agent was chosen due to the fact that it can harden in contact with humidity inside the concrete matrix. After the beam was initially cracked to achieve an average crack width of 250 μm, the beam was stored in standard laboratory climate and was sprayed with water during 6 weeks as a curing condition in order to allow a fair comparison with the other beams tested in that research. As a result of the 6 weeks of showering, a combined effect of autonomous healing (immediately) and autogenous healing (in time) was detected. At the end of healing period, the crack closing ratio was obtained in the range of 10–40%. The wider the crack width, the lower the crack closing ratio. The highest portion of crack sealing occurred at the moment of crack formation and capsule rupture. It should be noted that not all cracks were filled with PU.

Similar work was conducted by Araujo et al. [46] comparing the self-healing efficiency of two concrete beams ($200 \times 400 \times 2500$ mm) with the direct addition of glass capsules (5.0 mm outer diameter and 50 mm in length) and PMMA capsules (6.5 mm outer diameter and 50 mm in length). A water-repellent agent was injected into the capsule by means of a syringe and the both ends were sealed with hot glue or epoxy resin. All beams were stored in a standard laboratory environment until the time of testing. At the age of 14 days, a three-point bending test was performed in each beam by creating six localized cracks. The cracks were created consecutively (one crack per day) by moving the test set-up over the length of the beam. The crack widths were measured at six positions using an optical microscope and found in the range of 0.36–0.67 mm. During the loading of the beams, leaking of agents was noticed, indicating that the crack crossed and broke some capsules inside the beam. In order to evaluate the self-healing efficiency of the concrete beams with the addition of macrocapsules, chloride ingress tests were conducted. To do this test, the beams were positioned slightly tilted in order to allow a 3% NaCl solution to flow over the beams during 24 h per week. The cracked surface was positioned upwards, and thus exposed to the 3% NaCl solution. After the first day of testing, the beams were left in the dry cycle for 6 days and the chloride test was repeated during 6 weeks. At the end of testing, to determine the chloride ingress, two concrete cores with a diameter of 150 mm (with a crack inside) were obtained from each beam. Then, each core was split along the crack surface and by following the testing procedures, concrete powders were collected by grinding in 2 mm layers perpendicular to the crack face at various depths. The total chloride concentration was measured by titration against silver nitrate. The result showed that the chloride concentrations of healed samples were approximately constant at every depth. When compared with the reference concrete (without capsules), the chloride content of healed concrete was considerably reduced due to the release of the healing agent from the capsules.

4. Conclusions

The importance of this study is to understand the effect of the addition of healing agents on the behaviour of concrete in the fresh and hardened state as well as in relation to its self-healing capacity. This paper explores three prospective self-healing materials including CA, bacteria and encapsulated healing agents that can be used for repairing the cracks and improving the self-healing efficiency of concrete. Based on the literature studies, the following conclusions can be drawn as follows:

- (1) There is still no clear explanation regarding the workability of concrete due to the addition of healing agents. Some studies claimed that the addition of CA, bacteria or capsules did not show negative effects on the workability, while other studies argued that they contributed to a longer setting time, loss of plasticity, higher air content and a decrease in slump value. Consequently, there is a need to further investigate the consistency and workability of self-healing concrete and understand the underlying mechanisms leading to the changes and formulate mitigation plans.
- (2) The addition of CA and bacteria with suitable nutrients generally enhances the compressive strength of concrete composites. This may be attributed to: (1) the filling and water-barrier effects of CA as well as the role of CA as hydration activator to promote the further densification of the concrete microstructure and (2) pores clogging phenomenon by microbial calcite precipitation leading to a denser microstructure and the notable effect of suitable nutritional admixtures to react and help producing more CaCO₃-based materials.
- (3) The incorporation of microcapsules caused a steep decrease of the strength value due to the high pore volume as a result of capsules presence inside the concrete matrix. The properties of the hardened concrete with macrocapsules are still not well understood, while, in fact, the presence of macrocapsules may disturb the packing of aggregates.
- (4) The inclusion of healing agents demonstrates adequate healing capabilities to a great extent and the durability performance of self-healing concrete is remarkably improved upon healing activation.

This state-of-art review has shown that self-healing technologies offer a new advancement of using smart materials to preserve the longevity of the concrete structures. However, to date, findings show that the inclusion of healing agents at the concrete level is very limited, suggesting that many improvements are needed in this research. One of the major drawbacks in the current practice is that no adaptations are made in original mix designs for self-healing concrete. Consequently, mix design optimization is highly required and more interdisciplinary works should aim at developing the self-healing concrete composition, selecting the optimum dosage of healing agents, and determining some key parameters that affect the engineering properties of self-healing concrete. Finally, it may be hoped that in the near future there would be technical standards and specifications to optimally compose the mix designs for self-healing concrete in a similar way as designing the conventional concrete in accordance with international standards.

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