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Review Article

Carriers of Healing Agents in Biological Self-Healing Concrete

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Concrete is the most widely used material in civil engineering, but due to its inherent brittleness, the generation of cracks easily occurs. Crack healing is an effective method for restoring the mechanical properties of concrete and improving its durability. Of all the current concrete crack healing methods, microbial-induced calcium carbonate precipitation technology is an incredibly promising crack self-healing strategy that has received widespread attention in the field of concrete crack repair. As the biological self-healing agent has difficulty resisting the high alkali and high calcium environment in concrete, protection is required when it is used in concrete cracks.

1. Introduction

Concrete is now the most widely used building material globally due to its high compressive strength, good durability, and low price [1, 2]. However, it is inevitable that cracks will occur in concrete during use as a result of plastic shrinkage, thermal stress, settlement, drying shrinkage, weathering, reinforcement corrosion, or applied loads [1, 3, 4]. Cracks can increase the permeability of concrete while also accelerating the diffusion of corrosive media, including chloride ions, sulphate ions, and carbon dioxide in concrete. This seriously threatens the integrity, durability, and safety of concrete structures [5–8]. In order to avoid the potential threat posed by cracks, concrete crack repair is required for restoring structural integrity and reducing permeability. However, some cracks can occur internally or be difficult to find, which makes manual repair incredibly difficult [9, 10].

Inspired by the healing of human wounds, self-healing concrete has attracted significant interest from researchers [5]. Concrete self-healing methods include autogenous healing and autonomous healing [9, 11]. Autologous healing involves the carbonation of $Ca(OH)_2$ in concrete that is not involved in hydration after cracking, which seals the cracks. However, there is a limited degree of concrete crack healing when this approach is adopted and it can only heal microcracks with a width of less than 60 μm [5]. Self-healing is the process of a healing agent being added to concrete, which then fills cracks when they are created. Current commonly used healing methods include the epoxy resin method, microcapsule method, mineral admixture method, and microbial method [12]. In comparison to other crack repair methods, the microbial method has the advantages of green environmental protection and convenient construction. In addition, the cost of microbial remediation is low and it can be applied to many specific practical projects.

Ramachandran et al. [13] first applied microbial mineralisation for repairing cracks in concrete surfaces in 1998. As research in this area has increased, the most current self-healing concrete is made from urease-producing bacterial spores (such as *Bacillus pasteuri* [14], *Bacillus sphaericus* [15], *Bacillus megaterium* [16], and *Bacillus cereus* [17, 18]), which are added to concrete. When cracks appear in the concrete, bacteria decompose urea and form carbonate precipitation through metabolic activities [19], thereby sealing the cracks [20]. However, Jonkers et al. [21] discovered that if the bacterial spores are directly added to the concrete, their survival time is significantly reduced. In order to increase the survival time and self-healing efficiency of microorganisms, researchers placed microorganisms in a protective carrier before placing them in concrete for self-healing, achieving ideal results [18, 22–24]. To obtain the best protective carrier, researchers experimented with a variety of materials, such as expanded clay aggregate, diatomaceous earth, silica gel and polyurethane (PU) in glass tubes, melamine-based microcapsules, and alginate hydrogel capsules [25, 26]. In recent years, researchers have studied and tried many carrier materials in order to obtain biological self-healing concrete with superior performance, and even some repeated attempts have wasted a lot of time and energy of researchers, which is obviously not conducive to the development of biological self-healing concrete. In this study, the carrier of biological self-healing agent currently used and the repair effect achieved are reviewed, with a view to developing a better biological self-healing concrete, which will lay a foundation for its entry into the market and engineering application.

2. Protective Carriers for Biological Self-Healing Agents

The protective carriers of biological self-healing agents currently include organic polymer, porous lightweight aggregate, microcapsule, inorganic material, microbial self-protection, and nanomaterial.

2.1. Organic Polymer Carrier. The organic polymer carrier is lightweight and has a high specific surface area. Day et al. [27] attempted to immobilise microbial cells in porous polyurethane (PU) foam, finding that it can effectively protect the survival of bacteria in the high alkali environment in concrete. Bang et al. [28] found calcite deposition in the entire PU-microbial foam, thereby indicating that PU foam can serve as a nucleation site for calcite deposition while also encapsulating bacillus as a means of protecting it from high damage from the alkaline environment of concrete. Figure 1 shows that bacteria are distributed in the pores of the PU foam and calcium carbonate deposits appear inside the pores. This is because the porous structure of PU foam minimises the transfer of substances into the interior. The author also found that the elastic modulus and tensile strength of the polyurethane were increased by 26% and 42%, respectively, due to calcite in the polyurethane [28]. However, PU foam is a polymer material and it has negative environmental effects. Therefore, there is a likelihood that these defects will be obstacles to the use of PU foams as microbial remediation materials.

The research group of Prof. De Belie from Ghent University in Belgium has made many attempts with the bacterial protection carrier. Wang et al. [29] investigated the possibility of the use of silica gel or polyurethane as a carrier for protecting bacteria (Figure 2). The results showed silica gel to be more active than polyurethane for the immobilisation of bacteria, the former producing 14% higher calcium carbonate than the latter when immobilising bacteria. However, when both carriers were used for the repairing of concrete cracks, the strength recovery rate (60%) of polyurethane-immobilised bacteria samples was found to be higher and the water permeability coefficient (10^{-10}–10^{-11} m/s) was found to be lower [29]. This proves that polyurethane has greater potential than silica gel as a bacterial carrier for concrete crack repair.

Wang et al. [30] encapsulated Bacillus spores in a modified alginate-based hydrogel (AM-H), which demonstrated good compatibility with bacteria and cement-based materials. The experimental results found the encapsulated bacterial spores to have certain viability (the oxygen consumption is 4–8 μM), and the encapsulated bacterial spores are able to precipitate a large quantity of $CaCO_3$ in the hydrogel matrix (approximately 70% by weight) [30]. The modified alginate-based hydrogel-encapsulated*Bacillus coccidioides* spores were added to the mortar samples, and the in situ activity of the bacteria was confirmed through a simulation of the oxygen consumption on the surface of the crack (Figure 3).

Wang et al. [31, 32] used hydrogel and modified hydrogel AM-H as protective carriers, using five groups of urea decomposition experiments for studying microorganism activity: ① UV irradiation, ② UV irradiation + freeze crushing, ③ UV light irradiation + freeze crushing + freeze drying, ④ in cement mortar, and ⑤ removal after soaking in cement mortar. The repairing agent that was encapsulated by the hydrogel was found not to affect urea hydrolysis activity in environments ①, ②, and ③, but urea hydrolysis activity was inhibited in environments ④ and ⑤. In addition, the study found microbial spores have difficulty germinating in a high pH environment and microbial spores will not be inactivated when protected by the hydrogel. As a protective carrier, hydrogel is able to provide sufficient moisture for microorganisms, and the results showed that the maximum healed crack width was about 0.5 mm, and the water permeability was decreased by 68% in average [31, 32]. Figure 4 shows a high-definition X-CT three-dimensional image that contains gel healing agent and it can be observed that the distribution of healing products is mainly in the surface layer, while the subsurface layer and the inner depth of the sample decrease sharply [32].

Wang et al. [33] also developed a chitosan-based hydrogel that possessed pH-responsive properties. Their study found swelling ability to be good at pH 7–11. After the samples that contained the hydrogel-immobilised bacterial spores healed, water permeability was reduced by 81–90% and 32% of the cracks were completely healed. However, the addition of the hydrogel resulted in a decrease of approximately 5% in the compressive strength of the samples.

Shahid et al. [34] encapsulated various bacterial spores in sodium alginate microbeads before adding them to concrete. When the concrete was cracked and had been cured for 30 days, obvious healing was observed on the cracked surface. Xu et al. [23] used rubber particles of different sizes to immobilise bacteria and discussed their potential application in concrete self-healing. The study found that rubber particles with a size of 1–3 mm could completely heal cracks with a width of 0.86 mm after being cured for 28 days.

Palin et al. [35] prepared bio-calcium alginate gel particles and preliminarily discussed their feasibility for the repair of concrete cracks in low-temperature marine environments, and the results showed that 0.112 g of beads (or

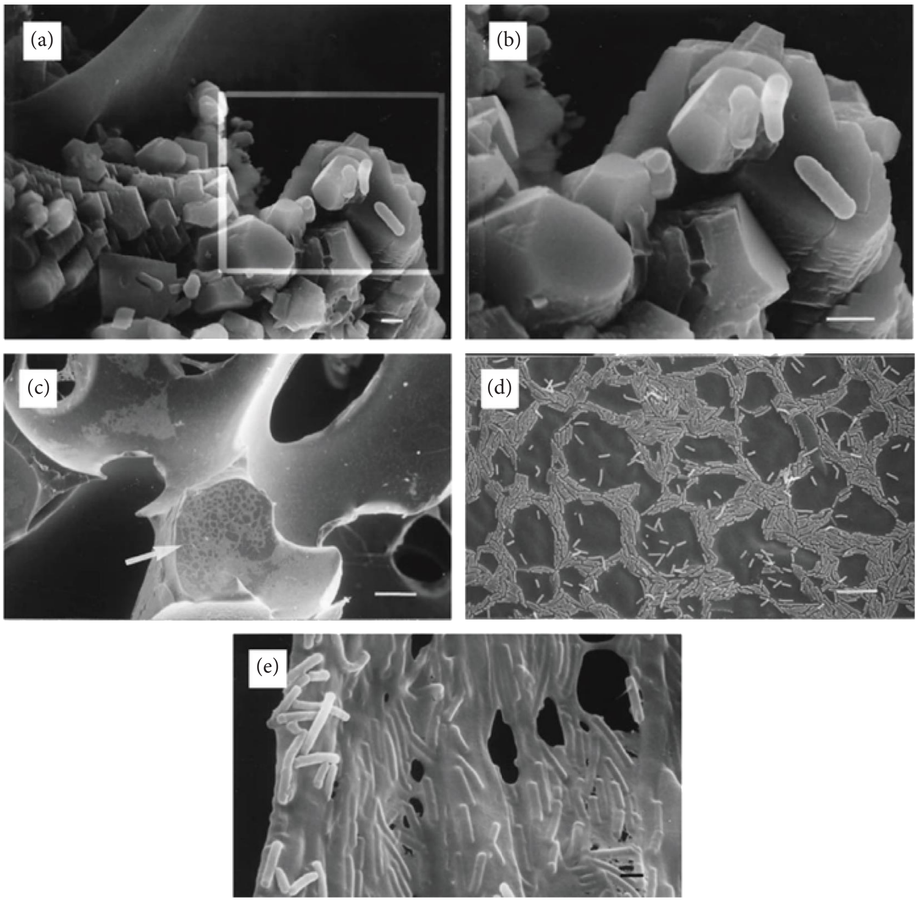


Figure 1: Scanning electron micrographs of calcite. Cells associated with calcite crystals in the PU matrices (a-b). A magnified section boxed in (a) and B. pasteurii immobilised in PU (c). Large area of PU matrices distributed with microorganisms (d-e). Reproduced from Reference [26] with permission of Elsevier Ltd., © 2001.

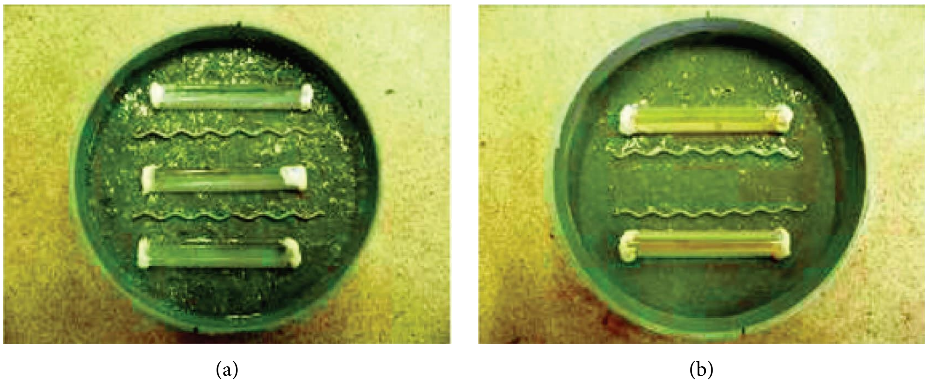

(a) (b)

Figure 2: Cylinders with the glass tubes which were filled with healing agents: (a) silica sol as carrier and (b) PU as carrier. Reproduced from ref. [27] with permission of Elsevier Ltd., © 2012.

~30 beads with a 1 mm diameter) were able to produce ~1 mm^3 of calcite over 14 days [35]. Aimi et al. [34] used calcium alginate gel as a microorganism protective carrier. When the content of biogel particles is 15% of the volume of the specimen, the repair rate of concrete cracks is highest and cracks with a width ranging from 0.13 mm~0.76 mm can be completely repaired. Fahimizadeh et al. [26] wrapped non-urea-decommitting bacteria *B. pseudofirmus* in alginate hydrogel capsules and found that cracks of 0.1–0.3 mm could be completely healed after 28 d of dry-wet cycle curing. This bacterium has more potential than urea-degrading bacteria to improve the depth of crack healing.

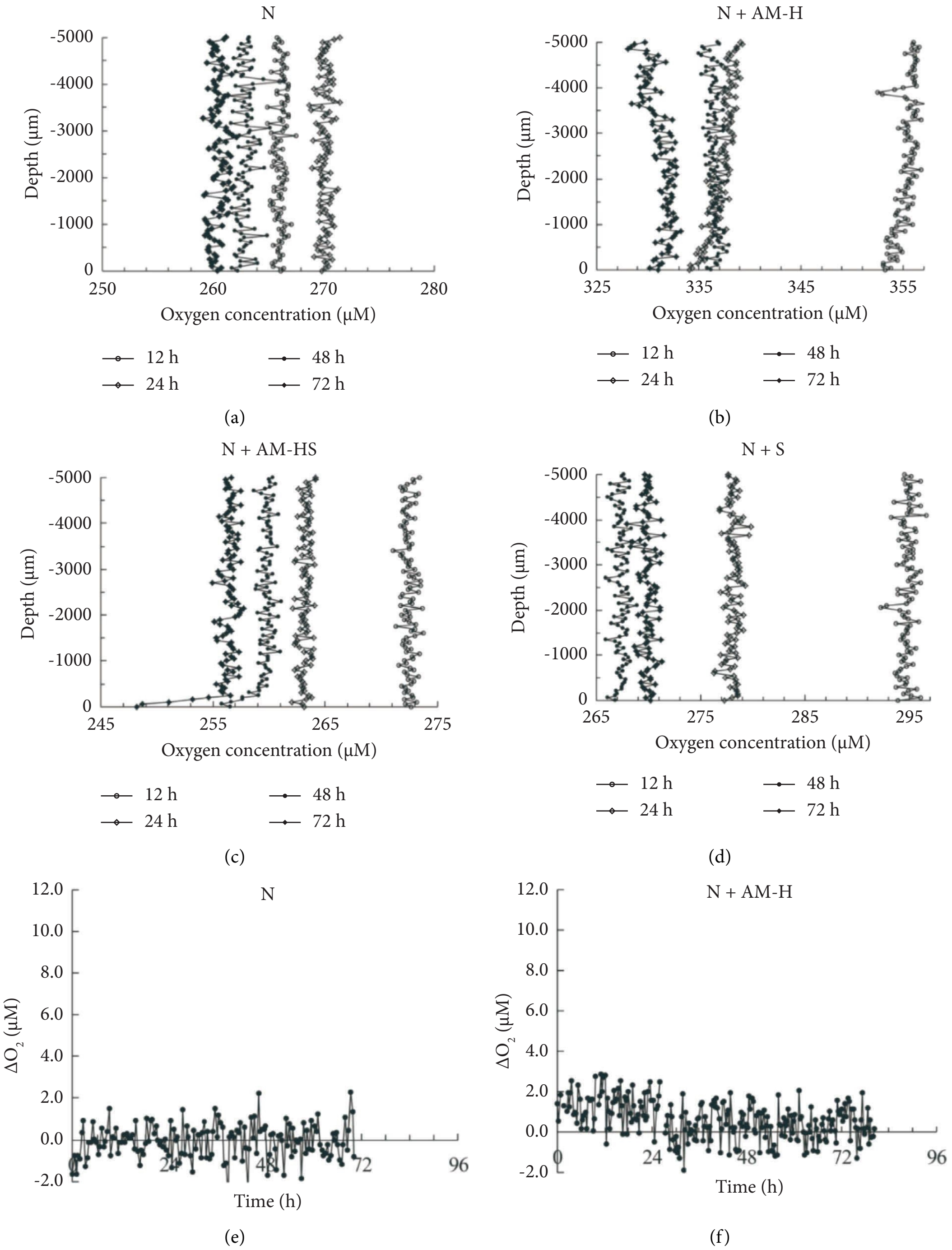
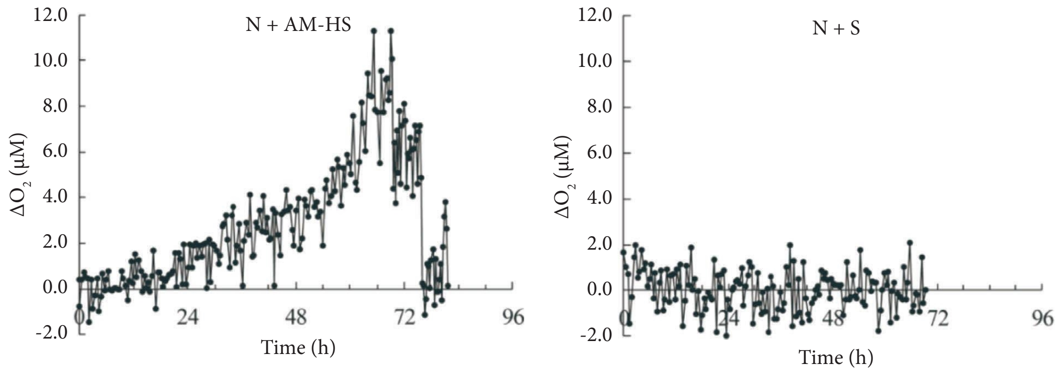


Figure 3: Continued.



(g)

(h)

Figure 3: Oxygen concentration profiles toward the surfaces of different submerged mortar prisms (a-d). Oxygen consumption in the boundary layer of the different prism surfaces (e-h). Reproduced from Reference [28] with permission of Frontiers Ltd., © 2015.

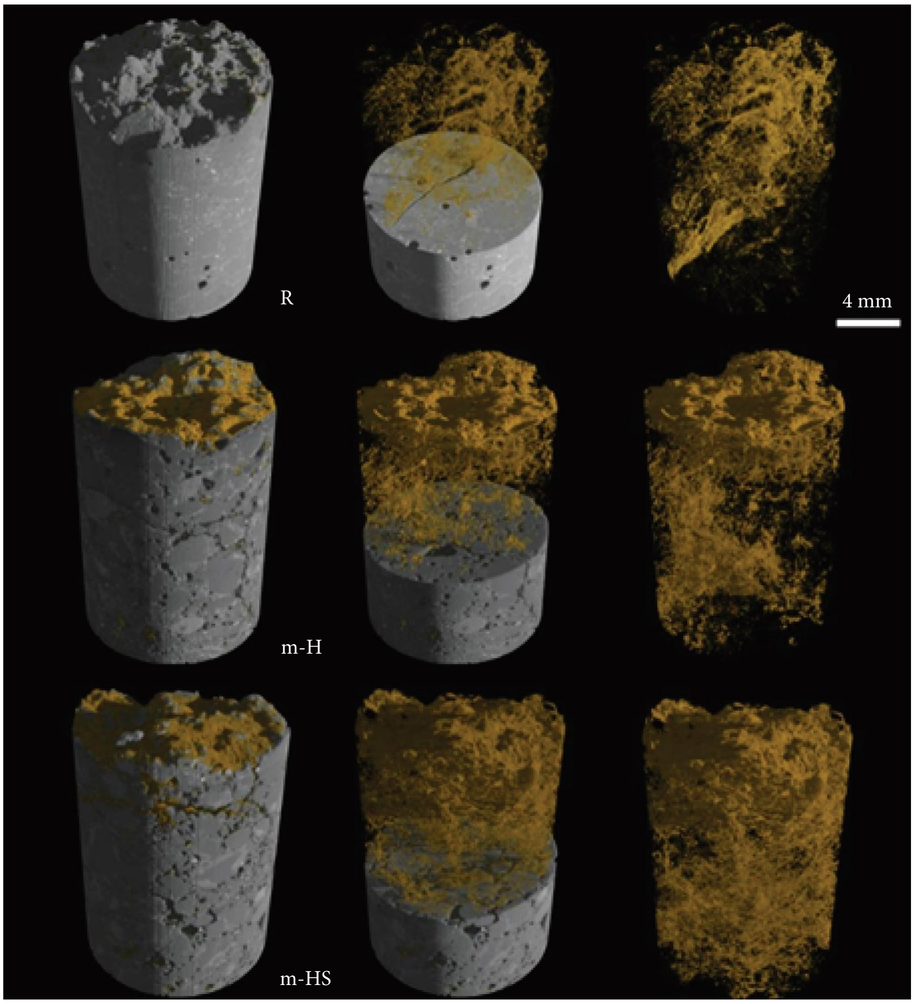


Figure 4: 3D rendered view of the spatial distribution of healing products (in yellow) in the sample R, m-H, and m-HS after treatment (left: outlook of samples plus the precipitation; middle: distribution of precipitates inside; and right: the whole precipitates in the sample). Reproduced from ref. [30] with permission of Elsevier Ltd., © 2014.

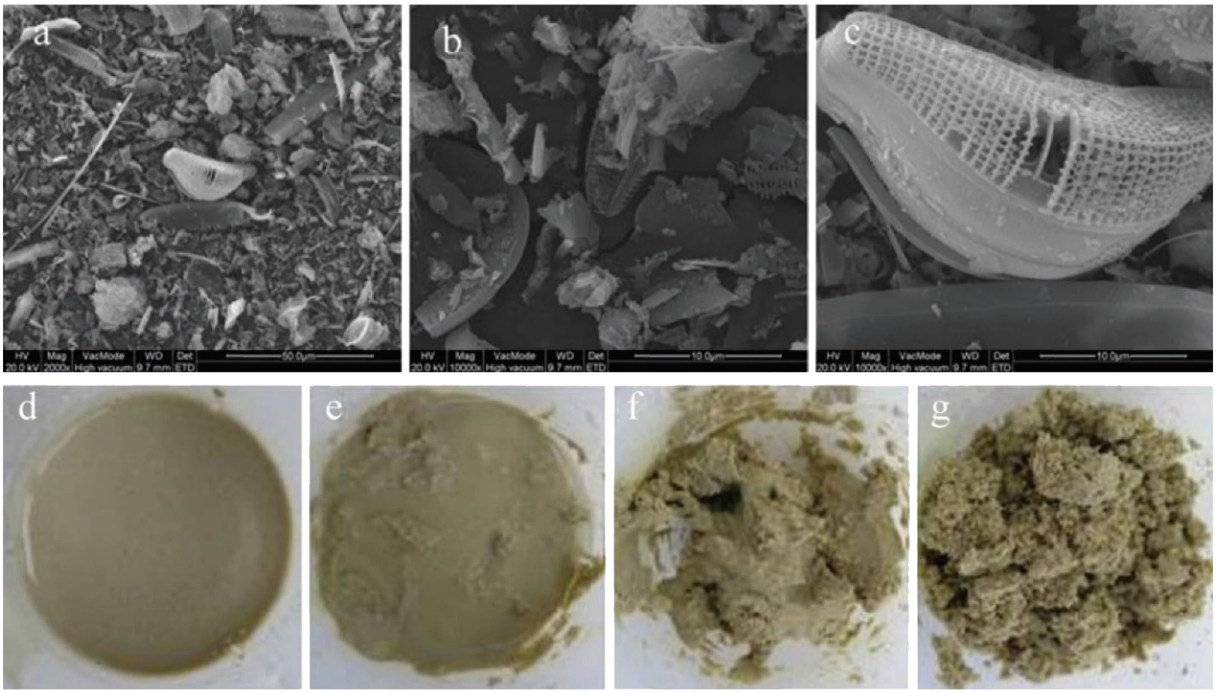


Figure 5: Morphology of the DE powders (a–c); digital photos of the mixture of DE and BS at different concentrations of DE (DE concentration in (d), (e), (f), and (g) were 40, 50, 60, and 70%, respectively). Reproduced from ref. [37] with permission of Oxford Academic Ltd., © 2012.

From the aforementioned research, it can be seen that organic high-grade materials ensure bacteria survival and play a positive role in concrete crack repair. However, the preparation of some organic polymer protective is complicated and their strength decreases following their addition to concrete.

2.2. Porous Lightweight Aggregate Protective Carrier. Porous lightweight aggregate is a natural inorganic porous material that has a good compatibility with the concrete matrix and is favoured by many scholars. Wiktor and Jonkers [36] used expanded clay particles as a protective carrier, encapsulating the repair agent in lightweight aggregate using the vacuum impregnation method and testing the performance of microbial self-healing concrete. In this test, microorganism activity in concrete was evaluated through the measurement of oxygen consumption, and the microorganisms protected by the expanded clay particles were found to still be active several months after the specimens were placed.

Khaliq et al. [37] explored the possibility of the use of lightweight aggregates (LWAs) and graphite nanoplatelets (GNPs) for the immobilisation of *Bacillus subtilis* to heal cracks in cement-based materials. The results showed that samples with graphite nanoplatelets as the carrier had uniform bacteria distribution in the precracked samples for three and 7 days, had a protective effect on bacteria, and demonstrated the highest crack healing efficiency; that is, the maximum healing width of LWA and GNP was 0.61 mm and 0.81 mm, respectively [37]. However, when precracked at a later stage, the crack healing of these specimens was found to be significantly reduced; although the samples added light aggregates as bacterial carriers, the early precracked sample efficiency was not as good as that of graphite nanoplatelets; however, the crack healing efficiency of both samples was the same in the later samples. In addition, the compressive strength of cement-based materials added with immobilised bacteria in lightweight aggregate increased by 12% [37]. Wang et al. [38] used diatomaceous earth (DE) as a means of protecting the bacteria in the high pH environment of cement-based materials (Figure 5). The test results found DE to have a good protective effect on bacteria. The urease activity of immobilised bacteria was found to be significantly higher than that of unimmobilised bacteria. It was found that the optimal DE concentration for immobilisation was 60%. Under an optical microscope, the immobilised bacteria were observed to have the ability to heal cracks with a width of 0.15~0.17 mm. The mineralisation near the cracks was characterised by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). For calcium carbonate, the results of the capillary water absorption test showed the sample with immobilised bacteria to have the lowest water absorption rate, which indicates that the mineralised products in the cracks increased the water permeability resistance of the cracked samples. Hydrogel [31] was also used as a bacterial coating material for crack healing in cement-based materials, and the study found the hydrogel-coated bacterial spore mortar specimen to have obvious self-healing advantages. In addition, the maximum healed crack width was approximately 0.5 mm and average water permeability decreased by 68%.

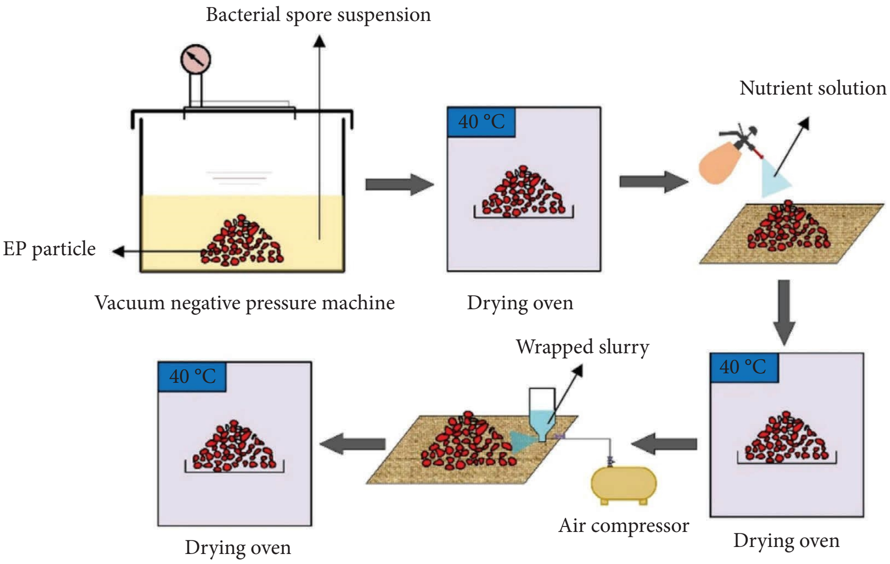


FIGURE 6: Process routing of self-healing agent. Reproduced from ref. [22] with permission of Elsevier Ltd., © 2020.

Huynh et al. [39] used diatomite as a microorganism, immobilising microorganisms, and nutrients in diatomite simultaneously. When the dosage was 1.26% of the cement mass, the compressive strength of the mortar was found to increase by 7% and flexural strength increased by 22%. The maximum repaired crack width reached 1.8 mm.

The research group of Professor Li Zhu at Taiyuan University of Technology has conducted a great deal of research on the self-healing of concrete cracks using bacteria immobilised on expanded perlite. Zhang et al. and Jiang et al. [22, 40] demonstrated the use of expanded perlite (EP) as a bacterial carrier, and the preparation process for the biological self-healing agent can be seen in Figure 6, which shows that the feasibility of crack healing in cement-based materials is quantified by the immobilisation of *Bacillus cocynii*. They investigated the effect the direct introduction of bacteria has and expanded clay-immobilised bacteria into cement-based material specimens for crack healing. The experimental results revealed that the incorporation of EP immobilised bacteria had the best healing effect on the sample. After 28 days, the fully healed crack width reached 0.79 mm, and SEM and XRD analysis found that the minerals on the crack surface were precipitated as calcite crystals. The researchers also found the healing efficiency of concrete cracks to be greatest without the coating material, followed by the cement-coated bio-healing agent, while the metakaolin polymer-coated self-healing agent was the worst. In order to self-heal concrete cracks, they added *Bacillus corii*, facultative anaerobic bacteria, and mixed anaerobic bacteria to expand perlite. Once the concrete had been artificially cracked and cured for 28 days, the crack healing rates of the samples that were immobilised with various bacteria were found to be 73.3%, 83.3%, 63.3%, and 41.5%. The morphologies of the mineralised products that were filled with different mineralising bacteria in the cracks were different in each case. Using expanded perlite containing 0–90%, silica fume and polyethylene fibres were mixed with concrete to increase its split tensile strength by 25% and 34.1%, respectively. In addition, they used the biological self-healing agent for studying the water permeability of repaired concrete, and the results showed the water permeability coefficient of the repaired sample to be 72.28% lower than without the biological self-healing agent.

Alazhari et al. [41] also immobilised microbial spores and nutrients in perlite by observing the surface cracks and the measurement of surface water absorption in the cracked area of the specimen, it was proven that the immobilised system has the ability to repair cracks. The research results found that when the two-component self-healing agent replaces 20% of the mass of sand with the appropriate ratio of microbial spores and calcium acetate (8×10^9 spores per gram of calcium acetate), it exhibits an excellent crack repair effect. The effects different medium environments have on microbial spore production, microbial growth, and induced calcium carbonate deposition were also studied.

Bhaskar et al. [42] studied the effect zeolite-immobilised bacteria and mineral matrix has on the self-healing behaviour of common mortar and fibre-reinforced (FR) mortar specimens. The study found the compressive strength of the ordinary mortar and fibre-reinforced mortar to increased as bacterial addition increased, and the presence of bacteria reduced the water absorption of mortar samples by 5.77–14.13% [42]. Ordinary porous mortar and fibre-reinforced mortar that contain bacteria and nutrients exhibit good resistance to chloride ion penetration. XRD analysis found the main crystal form of bacteria-treated mortar to be calcite.

Ersan et al. [43] chose to use expanded clay particles and activated carbon particles as protective carriers for nitrate-reducing bacteria. The maximum crack width healed by the bacteria was $370 \pm 20\,\mu$m at 28 days and $480 \pm 16\,\mu$m at 56 days. When the crack width was $465 \pm 21\,\mu$m, the water permeability coefficient recovered as high as 85% after being cured for 56 days (as can be seen in Figure 7). They also

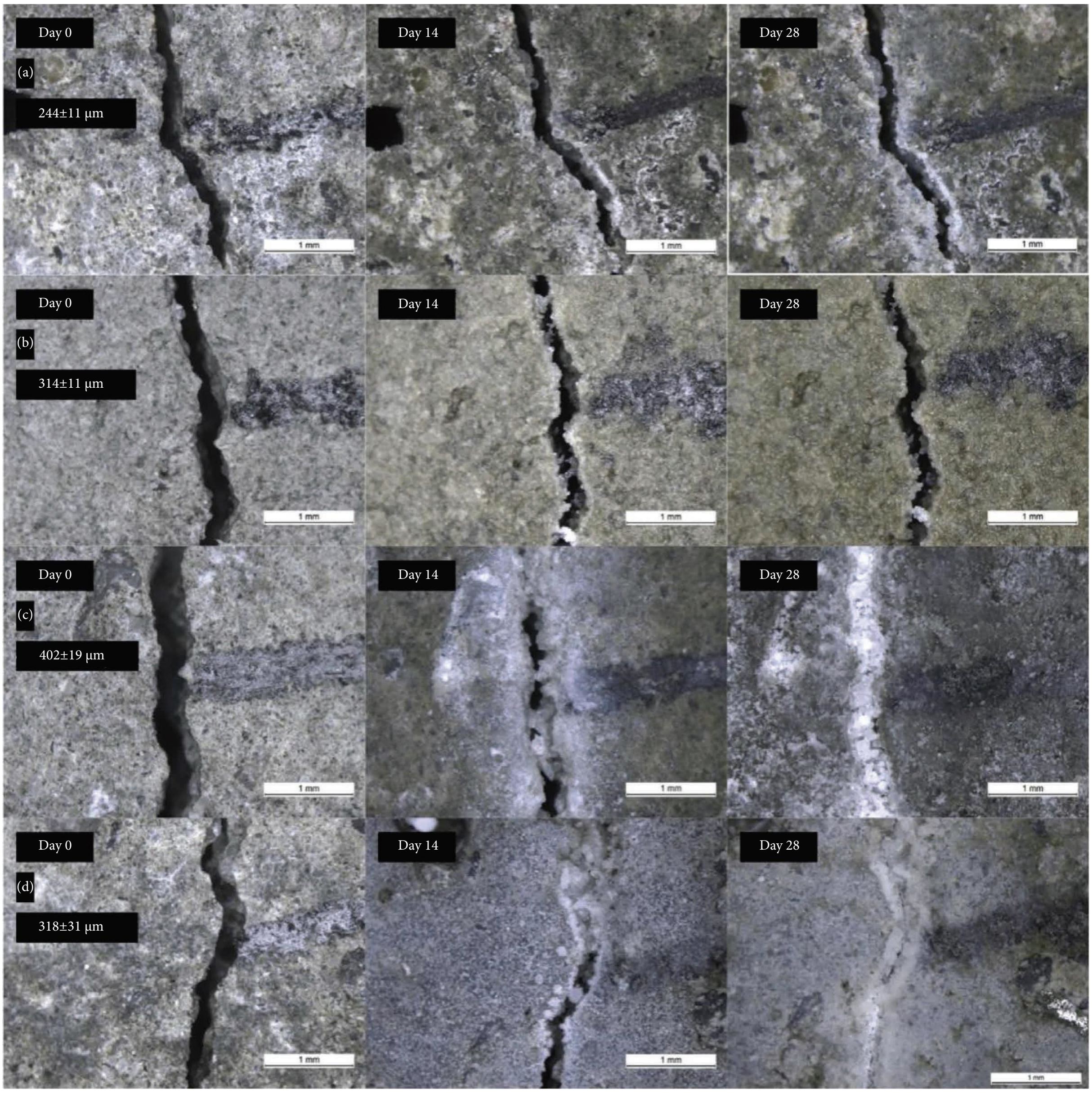


Figure 7: Photomicrographs showing biweekly evolution of cracks during 28 days of water immersion: (a) reference mortar, (b) abiotic control, (c) mortar containing diaphorobacter nitroreducens loaded expanded clay particles, and (d) mortar containing Pseudomonas aeruginosa loaded expanded clay particles (given values represent the average width of the shown crack ± standard deviation). Reproduced from ref. [42] with permission of Elsevier Ltd., © 2016.

studied the immobilisation of denitrification-reducing bacteria, calcium formate, and calcium nitrate in expanded clay, adding them to the mortar. The samples that contained bacteria were found to completely heal cracks 350 μm in width after being soaked in water for four weeks [44].

Chen et al. [45] studied the effect bacteria and nutrients has on the self-healing effect of cement mortar cracks. The test results found carbonic anhydrase bacteria and yeast paste to be immobilised with half of the ceramsite carrier. The other half only immobilised glucose in the specimen group exhibited the best crack repair effect. Following 28 days of crack repair and maintenance, the crack depth repair rate achieved 87.5%. The restoration rate of the specimens that were only mixed with immobilised bacteria and yeast paste ceramsite was 27.1%, while the restoration rate of the specimens that were mixed with empty ceramsite was 8.7%.

Bang et al. [46] used porous glass beads as a protective carrier for studying the effect pH has on the repair agent by calcium ion kinetics. They found the remediation agent that was treated with the protective carrier was able to produce precipitation at a higher pH value (pH = 8.1), thereby proving that the protective carrier improves the adaptability of the microbial remediation agent to the alkaline environment.

Although the aforementioned inorganic porous materials and microcapsules can provide effective microbial growth and metabolism protection, these materials generally have low cylinder compressive strength and the incorporation of carriers significantly reduces the mechanical properties of concrete. Therefore, the main issue that needs to be solved urgently for studying the self-healing effect of concrete cracks when using inorganic porous materials as microbial carriers is how to reconcile the contradiction between self-healing and mechanical properties.

2.3. Microcapsule-Type Protective Carrier. The microcapsule or core-shell structure carrier encapsulates the bio-healing agent and achieves all-around protection. The protective layers of microcapsules or core-shell structures can be classified into two categories: organic materials and inorganic materials. Regarding the use of organic materials as the protective layer, Liu et al. [47] prepared a microcapsule with ethyl cellulose as the raw material before studying the activity and crack healing effect of microcapsule-coated bacterial spores. The results found the microcapsules to have a better protection effect on bacteria, and the bacteria that were protected by microcapsules had a better effect on concrete crack healing. However, the crack repair effect was not quantified in this study. Zamani et al. [48] used in situ polymerisation for encapsulating Pseudomonas spores and nutrients in polyurea microcapsules. Figure 8 shows a microcapsule and its preparation process. The results found that bacterial spores and nutrients had no effect on microcapsule chemical structure, and calcium carbonate precipitation was observed when the microcapsules had been solidified for three days. The microcapsules were found to have a better repairing-effect on concrete cracks.

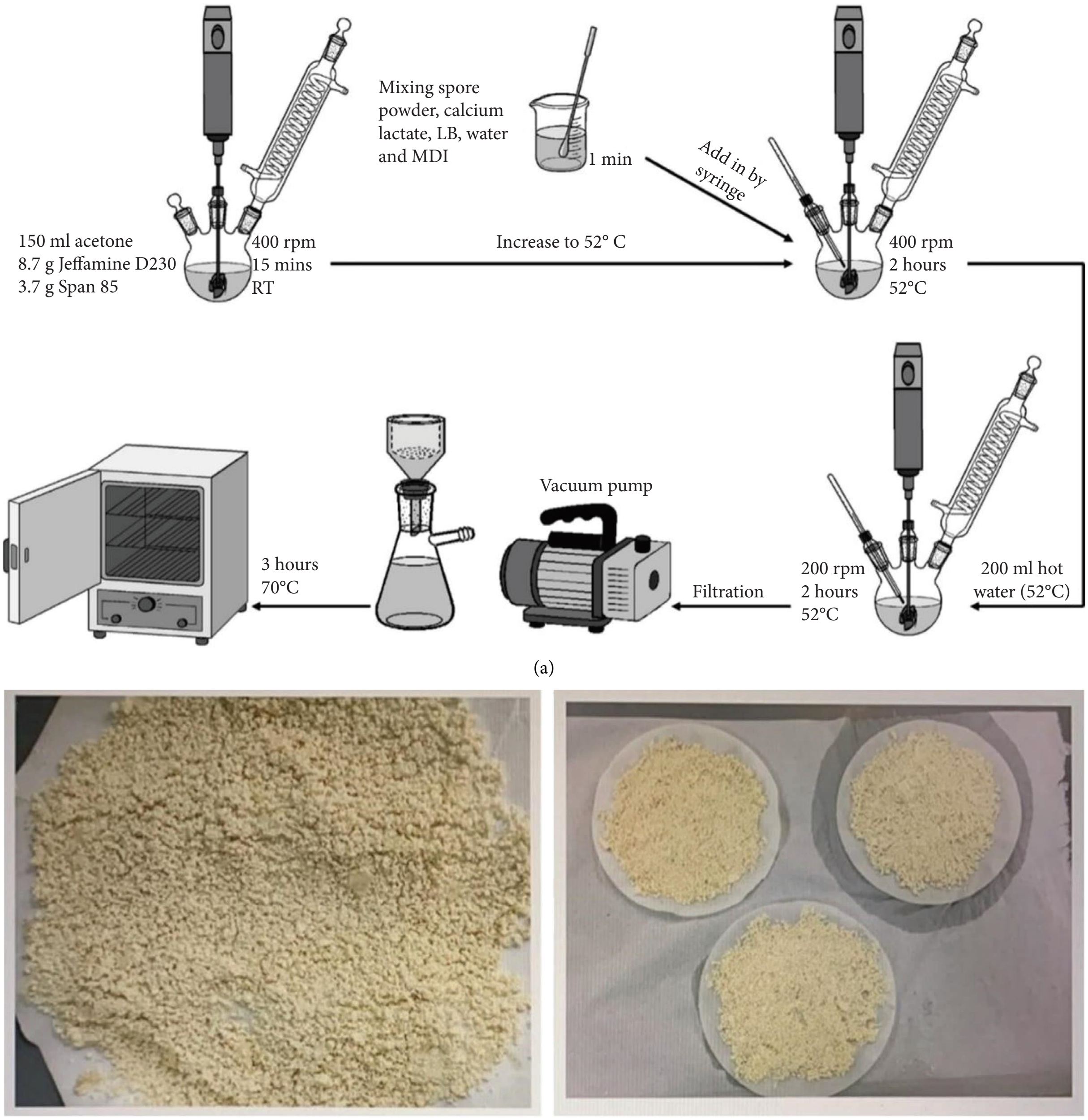
Wang et al. [15] prepared a microcapsule using melamine as the raw material, and the feasibility of this protective carrier for encapsulating microbial spores was evaluated based on the amount of urea decomposition and by microscopic observation. The influence the presence or absence of microbial repair agents has on the self-healing effect of concrete was compared by MICP, microscopic observation, and water permeability test. The results found the fracture healing rate of samples with microcapsules containing bacterial spores to be 48–80%, while for samples that contained microcapsules without bacterial spores, it was between 18 and 50%. Using bacterial spores in microcapsules, the maximum healable crack could be 970 mm, the water permeability of the sample decreased by approximately 10 times, and the liquid water was essential for crack healing. The study also noted that the addition of microcapsules had no significant effect on the bulk density of the sample. However, the addition of microcapsules also reduced the compressive strength of the samples, and when the number of microcapsules was 1–5%, the compressive strength of the samples decreased by 15–34%.

Regarding the use of inorganic materials as the protective layer, Zhang et al. [49] prepared a novel core-shell structure capsule to coat bacterial spores, which has the ability to provide bacterial spores with protection for a minimum of 203 days. Following the addition of the capsules to immobilise bacterial spores, the relative permeability coefficient of the sample after the crack repair was found to be reduced by 80%. In order to improve the healing effect of microorganisms on concrete cracks, Wu et al. [17, 18] screened a strain with the ability to produce urease in high alkali and high calcium environment. A biocapsule was then prepared using the bacterial native environment as a carrier (Figure 9). The study found that after being repaired with the biocapsule, cracks of 550 μm in width could be completely healed. The water permeability coefficient of the healed samples was two orders of magnitude lower than for samples without biocapsules.

Yuan et al. [50] adsorbed bacteria and their nutrients into zeolite and protected the outer surface of zeolite with sulphoaluminate cement. Their study found that as the addition amount of this core-shell structure increased, water absorption, water permeability, and air permeability of the samples were all significantly reduced. Zheng et al. [51] used low-alkaline sulphoaluminate cement as a bacterial carrier for studying the effect the self-healing agent has on concrete cracks. The results demonstrated that the self-healing agent has little effect on the early strength of cement-based materials but shows a certain improvement with the later mechanical properties. Following a certain period of maintenance, cracks with a width of 0.25–0.35 mm could be repaired completely and the average healing depth of the cracks was 2.895 mm. The water permeability of the healed specimens recovered by 97% and chloride ion permeability recovered by 63.2%.

The microencapsulated spores are isolated from the external environment, which protects the spores and is conducive to their dormancy and latency. When cracks appear in the concrete, the microcapsules then burst, resulting in the release of spores. In suitable external environmental conditions, the spores germinate, transforming from a dormant state to vegetative cells, and bioremediation begins.

The self-healing mechanism for bio-self-healing concrete based on capsules is as follows: microorganisms obtain the required nutrients for metabolism, growth, and reproduction from the medium that is provided by microcapsules before absorbing Ca^{2+} from the peripheral environment. This is then combined with CO_3^{2-} which is produced by microbial metabolism, and $CaCO_3$ mineral precipitation is formed. As shown in Figure 10, there are two ways in which microorganisms can metabolise the biological mineral calcium carbonate: microorganisms generate CO_2 during metabolism and CO_2 combines with $Ca(OH)_2$ in the matrix to form $CaCO_3$ deposition or microorganisms directly metabolise calcium-containing substances to form $CaCO_3$ mineral deposits [52, 53]. The resulting $CaCO_3$ is deposited continuously and cracks in the concrete are repaired. The microorganisms are in a state of lack of oxygen and water once more and they enter a dormant period, continuing to lurk in the concrete. When a crack reappears, the spores are awakened and the next round of repair can begin [20, 54].



(a)

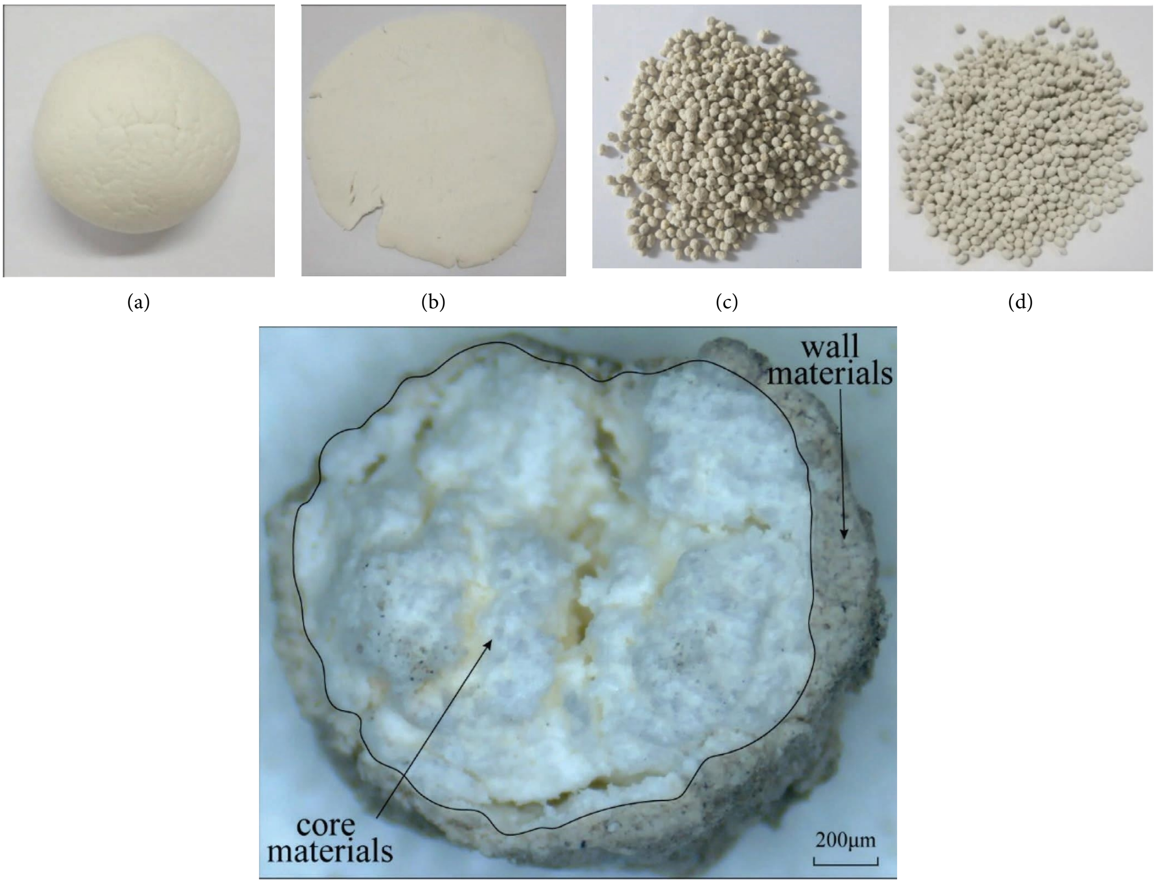
(b)

Figure 8: Schematic illustration of synthesising and encapsulation of bacteria in polyurea capsule (a) and optical images of prepared microcapsules (b) Reproduced from ref. [47] with permission of Elsevier Ltd., © 2020.

2.4. Inorganic Material Carrier. Xu et al. [55] developed a low-alkali, fast-hardening cementitious material with calcium sulphoaluminate cement as a carrier for bacterial spores. As a carrier of bacteria, calcium sulphoaluminate cement has the ability to effectively maintain bacteria activity for a prolonged period of time. The sulphoaluminate cement-coated bacteria were then placed into the cement-based material. The fractures healed to 417 μm within 28 days, and the fracture closure rate was almost 100%. In comparison to ordinary mortar, the recovery rate of compressive strength increased by 130% and watertightness increased by 50%.

The research group of Prof. Kua at the National University of Singapore used biochar to immobilise bacteria [56]. During the three cycles of injury and healing, the healing width of the immobilised bacterial spore specimens in biochar is 500–800 μm, and its healing efficiency has been higher than that of the specimens directly added with bacterial spores and superabsorbent polymers [56].

2.5. Microbial Self-Protective Carrier. Erşan et al. [44] and Silva et al. [57] used the mixed colony as a protective carrier, which is easy to operate and removes the need to introduce



(a) (b) (c) (d)

(e)

Figure 9: Biocapsules preparation process ((a) granulation, (b) pressed cake, (c) core particles, and (d) molding) and image of biocapsule cross section (e) Reproduced from ref. [18] with permission of Elsevier Ltd., © 2020.

additional substances. Erşan evaluated the effect of an activated compact denitrifying core (ACDC) as a protective carrier by performing a comparison of the reducibility of the repair agent at various pH values and the amount of urea decomposition following their incorporation into the mortar. ACDC was found to maintain high activity at every pH value, and it could resist shrinkage stress during the mortar curing process. This proves that ACDC has the ability to maintain high activity in the concrete matrix by using itself as a protective carrier. Silva evaluated the ability of CERUP for maintaining activity through a comparison of the amount of urea decomposition and repair degree of cyclic enriched ureolytic powder (CERUP) and ordinary microorganisms. Compared to the control group, CERUP was found to demonstrate higher urea hydrolysis activity in the first six hours and no significant difference was observed after 24 h. In the CERUP group, the repair rate was approximately 20% higher, demonstrating CERUP's better ability to protect and repair.

3. Precipitation Mechanism of the Microbial Precipitation of Carbonate

The process of microorganism-induced calcium carbonate precipitation (MICP) involves a series of biochemical reactions based on the action of microorganisms [58–61]. The process is observed in many instances in nature, including in hot springs, seawater, freshwater, caves, and soils [62, 63]. In nature, common microbial metabolic processes for inducing calcium carbonate precipitation include denitrification by denitrifying bacteria, antisulphurisation by sulphate-reducing bacteria, oxidation by oxidising bacteria, and urea decomposition by urease-producing bacteria [64–67]. Urease-producing bacteria have great advantages in terms of practical applicability due to their widespread existence in nature, strong adaptability, nonpathogenicity, and the noncorrosiveness of raw materials that are used in the concrete usage process to concrete, which have been studied in depth by scholars, both domestically and abroad [68–70]. The mechanism of calcium carbonate deposition induced by ureolytic microorganisms is currently studied as follows [71–73] (as can be seen in Figure 11).

Firstly, urea is decomposed into ammonia and carbamate by enzymatic hydrolysis, and ammonia and carbamate are hydrolysed to form ammonia and carbonic acid immediately following enzymatic hydrolysis:

$$\begin{aligned} CO(NH_2)_2 + H_2O &\longrightarrow NH_3 + NH_2COOH, \\ NH_2COOH + H_2O &\longrightarrow NH_3 + H_2CO_3. \end{aligned} \tag{1}$$

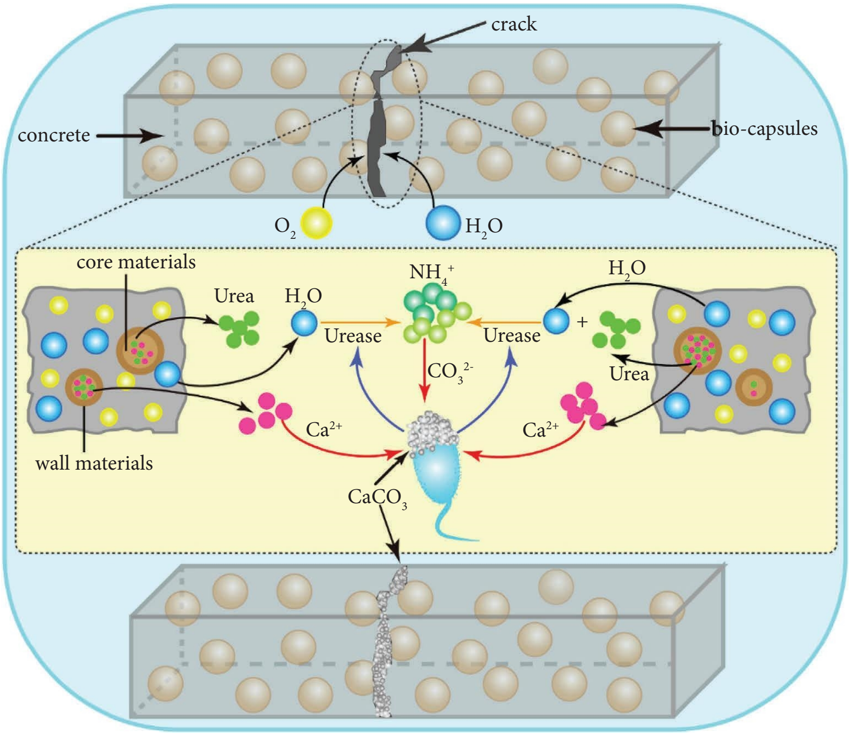


Figure 10: Mechanism of biocapsule self-healing concrete cracks. Reproduced from ref. [18] with permission of Elsevier Ltd., © 2020.

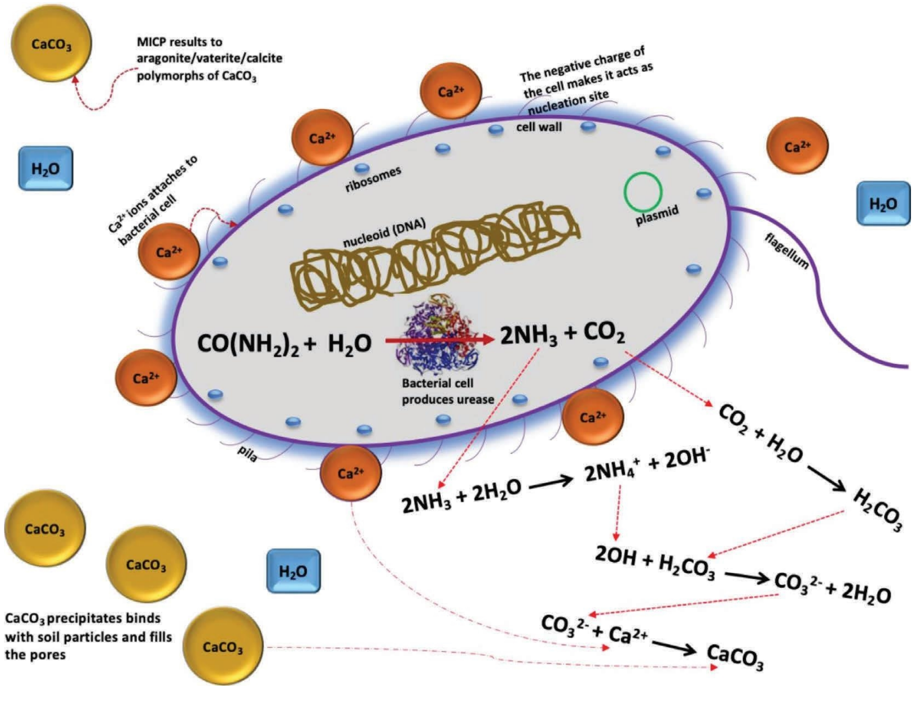


Figure 11: Overview of bio-mediated calcite precipitation using ureolysis. Reproduced from ref. [74] with permission of the Korean Society of Environmental Engineers. © 2021.

Secondly, ammonia forms ammonium and hydroxide ions and carbonic acid forms bicarbonate ions as follows:

$$\begin{gathered}2NH_3 + 2H_2O \longleftrightarrow 2NH_4^+ + 2OH^-,\\ H_2CO_3 \longleftrightarrow HCO_3^- + H^+.\end{gathered} \tag{2}$$

The hydroxide ion increases the pH, which causes a shift in the bicarbonate balance and results in the formation of carbonate ions as follows:

$$HCO_3^- + H^+ + 2NH_4^+ + 2OH^- \leftrightarrow CO_3^{2-} + 2NH_4^+ + 2H_2O. \tag{3}$$

Finally, when calcium ions are present, carbonate ions are precipitated in the form of calcium carbonate crystals as follows:

$$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3. \tag{4}$$

4. Outlook

Concrete self-healing performance is not the only factor to consider when choosing a suitable carrier, as the carrier can affect other concrete properties in addition to self-healing performance. In the event that a property is changed beyond standard or design requirements, the carrier cannot be used in practical engineering applications.

The microbial carrier has two main functions when repairing concrete cracks: protecting the bacteria to buffer the high alkali environment in the concrete and providing space for microorganism growth and metabolism, which is similar to the role of "house." The carrier is used as a space for storing and maintaining bacterial activity and its reasonable selection and application are essential for the successful completion of concrete crack repair. In order for concrete cracks to self-heal, a carrier must possess the following properties: (1) Good biocompatibility: there should be little effect on bacterial activity and it should be nontoxic. (2) High capacity: it should have a good pore structure and strong adsorption capacity as a means of ensuring that it is able to hold a sufficient amount of microorganisms or substrates. (3) Excellent physical and chemical stability: it should be highly resistant to environmental influences, including temperature, pH value, and external enzymes, which is conducive to maintaining bacteria activity. (4) Good biological inertness: it should have resistance to microbial decomposition. (5) Good impact and wear resistance: it should have good mechanical strength and the ability to resist mixing force during the cement slurry concrete mixing process. (6) Good mechanical properties: the particle shape of the carrier should be as close as possible to spherical, meaning that the incorporation of the carrier will not result in too much loss of strength and other properties to the concrete matrix. (7) Good mass transfer performance: the diffusion limit (resistance) of bacteria, substrates, and products is small, which ensures rapid and sufficient reaction between bacteria and substances.

In addition, most of the bacteria used at present are ureahydrolytic bacteria, which will produce NH_3 as a byproduct in the mineralisation process. When selecting the carrier, the carrier that can adsorb NH_3 or convert it into environmentally friendly substances (such as struvite) can be considered. However, the carrier still needs to be found and tried. As Mohammad Fahimizadeh et al. [75] point out, the nonureolytic MICP pathways remove the environmental burden posed by ureolytic MICP by offering environmentally friendly options that can be active under various conditions using various substrates. The biological self-healing concrete using nonureolytic MICP and the carrier meeting the above requirements have a great research potential.

5. Conclusion

This study has reviewed the current carrier materials of bio-self-healing agents in bio-self-healing concrete. Researchers have tested and optimised different bio-self-healing agent carriers for increasing the healing effect of bio-self-healing concrete. Carriers that are currently used include epoxy resin microcapsules, polyurethane, silicone gel, ceramsite, slag, swelling perlite, expanded clay particles, diatomaceous earth, and polyurethane foam and biochar. Although positive results have been achieved through the use of different carriers, bio-self-healing concrete still has a significant room for improvement regarding healing speed and depth of healing and it has high environmental requirements. Therefore, it will be a long time before it is applied in engineering. However, there is cautious optimism regarding the future of bio-self-healing concrete.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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