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A Review of Self-healing Concrete Research Development

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Abstract

Self-healing concretes are being widely recognized as a remedial technique to improve the durability of concrete. Although, few review papers on self-healing concrete were published, a strong review on all aspects of self-healing concrete cannot be found. In this paper, natural, chemical and biological processes of self-healing concrete technologies were completely reviewed. The main focus of the study is for the biological processes. The review presents a new insight into the research for the treatment of unexpected cracking of concrete. The information presented in this paper can be considered significant for biotechnologists and bioprocess engineers to have comprehensive updates on the current status-quo of self-healing concrete.

Keywords: Self-healing concrete, chemical self-healing process, biological self-healing process, biological precipitation

1- Introduction

Self-healing concrete is mostly defined as the ability of concrete to repair its small cracks autonomously [1]. The idea of self-healing concrete was inspired from the natural phenomenon by organisms such as trees or animals. Damaged skin of trees and animals can be repaired autonomously [1, 2]. Remediating cracks in concrete structure is important for its service durability and structural safety [3].

The main keyword of this article is self-healing concrete. However, other similar keywords in this area are self-healing, self-repair, autonomous healing, automatic healing, auto-treatment, self-treatment, bio-concrete, bio-inspired, biological concrete, calcite bio-mineralization, and calcite precipitation. Recently, developing self-healing concrete technology has become an important objective for researchers in biotechnology and civil engineering sciences [4-10]. During the 1980s, only very few articles can be found related to self-healing concrete, more over serious studies in this area were not established until late 1990's. Among the self-healing designing methods, biological methods are the latest ones.

Several processes are proposed for the design of self-healing concrete. This paper reviewed all processes of self-healing concrete technologies containing (1) natural (2) chemical and (3) biological processes. Figure 1 shows the comprehensive taxonomy for self-healing concrete research.

In the aspect of self-healing concrete, several reviews are found. A latest review on self-healing concrete was by Wu et al. (2012) who highlighted on the natural and man-made self-healing. Their review also covered comprehensive explanation on the chemical and biological methods [11]. Siddique and Chahal (2011) detailed the use of ureolytic bacteria for the designing of self-healing concrete [12]. Toohey et al. (2007) reviewed micro-vascular as self-healing material [20]. Jonkers (2007) reviewed on biological methods to design self-healing concrete based on calcium carbonate precipitation [13]. Al-Thawadi (2011) identified the mechanism of strength enhancement of sand using ureolytic bacteria and calcium carbonate formation [14]. Although several review papers have been published on self-healing concrete, a comprehensive reviewed on physical, chemical and biological processes have not yet been reported. For a biologist, the importance of a comprehensive review paper is to establish a quick macro snapshot from the body of knowledge. Thus, this paper aims to present a comprehensive review on self-healing concrete based on three key taxonomy, i.e. natural self-healing, chemical self-healing and biological self-healing. All the corresponding sub-taxonomies for all three key taxonomies are described in the subsequent sections.

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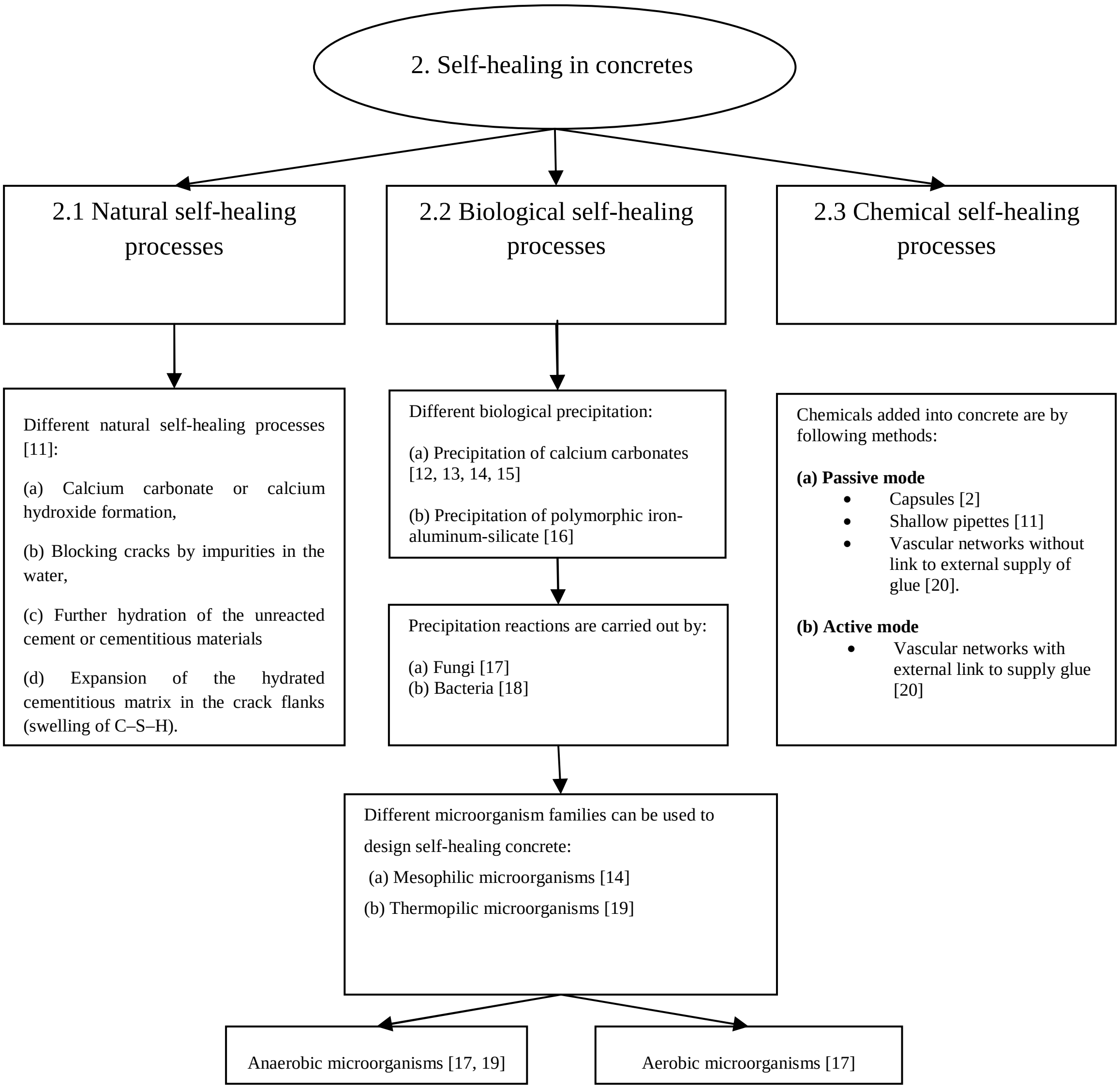


Figure 1: A novel taxonomy for research in self-healing concretes

2- Self-healing of concrete

2-1- Natural Self-healing process

As shown in Fig. 2, several natural process can partially repair concrete cracks as shown in Fig. 2(A). In natural processes, four following processes can block crack (1) the formation of calcium carbonate or calcium hydroxide is another process to block crack (2) crack is blocked by impurities in the presence of water as shown in Fig. 2(B). (3) Crack is further blocked by hydration of the unreacted cement or cementitious material (Fig. 2(C)). (4) Crack is blocked by the expansion of hydrated cementitious matrix in the crack flanks (swelling of calcium silicate hydrate gel) as shown in Fig. 2(D) [11]. In many cases, more than one of these process or mechanisms (Fig. 2A to 2D) can happen simultaneously. In fact, most of these mechanisms can only partially fill the entrance of some cracks and cannot completely fill the cracks. This will be useful to prevent the development of cracks or prevention of deep penetration of harmful chemicals such as acids into the crack.

Among the proposed self-healing mechanisms in the natural process, formation of calcium carbonate and calcium hydroxide (Figure 2A) are the most effective methods to heal concrete naturally [21, 22, 18, 23, 24, 25]. This view is supported by the fact that some white residue can be found on the outer surface of the concrete cracks. This white residue is found to be calcium carbonate and has been widely reported including Wu et al. [11]. The fundamental mechanisms for the formation of calcium carbonate and calcium hydroxide [21] are represented in Eqn. (1) to (3). At the first step, carbon dioxide is dissolved in water.

$$H_2O + CO_2 \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-} \qquad \text{Eqn. (1)}$$

Free calcium ions are released as a result of cement hydration and dissipatation through concrete as well as along the cracking surfaces, reacts with CO_3^{2-} and HCO_3^-. As a result, calcium carbonate crystals are formed. Reaction (2) and (3) can only happen at pH above 8 or between 7.5 and 8. The crystals grow both at the surface of the cracks and finally fills the gap.

$$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3 \quad \text{Eqn. (2)}$$

$$Ca^{2} + HCO_3^{-} \leftrightarrow CaCO_3 + H^{+} \quad \text{Eqn. (3)}$$

Neville (2002) claimed that, further hydration of anhydrate cementations components is mainly due to the natural self-healing properties in concrete. However, this process only applies to very young concrete and the formation of calcium carbonate most likely causes self-healing at later ages [26]. Natural self-healing can be useful for cracks with widths up to 0.1–0.2mm [27].

2-2- Chemical self-healing process

Chemical healing process mainly refers to the artificial healing by injecting chemical compounds into the crack for healing. Self-healing concrete is designed by mixing chemical liquid regents (i.e. glue) with fresh concrete in small containers. This paper explains the two common chemical methods that make use of glue addition to the concrete for healing purposes: (1) hollow pipettes and vessel networks containing glue (2) encapsulated glue. The details of each method is shown below.

(A) Formation of calcium carbonate (B) Blocking by impurities (C) Hydration of unreacted cement (D) Expansion of the hydrated cement

Figure 2: Possible mechanisms for natural self-healing in cementations materials

2-2-1- Hollow pipettes and vessel networks containing glue

The chemical self-healing mode for concrete can be divided into two categories: a) active mode b) passive mode. Active mode uses vessel network linked with external supply of glue for the distribution of glue whereas the passive mode uses hollow pipettes, capsules or vessel network to distribute glue that is not linked to an external glue source.

Either the hollow pipettes or the vessel networks can be used to design a self-healing concrete based on the active or passive mode. Hollow pipettes have been applied at different length scales by various researchers to design different self-healing materials such as polymers and polymeric [28–32]. Hollow pipettes contain glue that can be mixed with fresh concrete (Figure 3a) and will be ruptured during crack propagation and the glue is released into the cracks and finally it heals the crack. Self-healing concrete containing hollow pipettes is inspired from blood vessels in creatures. According to Wu et al. (2012), suitability of hollow pipettes to release glue into cracks were proven in many cases (Figure 3b) [11]. Pang and Bond [31, 32] improved the current practice on the self-healing processes using hollow pipettes where the pattern of glue distribution within the cracks was monitored, when a mixture of glue and fluorescent dye was released following the rupture of hollow pipettes.

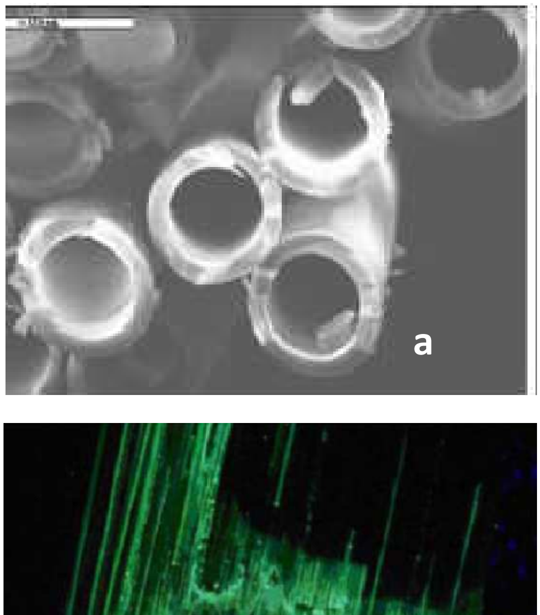


Figure 3: (a) Hollow glass fibers (b) damage visual enhancement in composite laminate by the bleeding action of a fluorescent dye from hollow glass fibers [32].

Some examples of glue that are applicable for filling the hollow pipettes in concrete are methyl methacrylate, ethyl cyanoacrylate, acrylic resin, epoxy resin [25, 33, 34, 35-38].

Besides the hollow pipette filled with glue type of self-healing concrete design, Dry (1994) used a vessel network within a concrete specimen for the distribution of glue (Figure 4). This vessel network was brittle and placed inside a concrete specimen, with one end linked to the supply of glue and the other end sealed. Other researchers such as Mihashi et al. [39] and Joseph et al. [33] also conducted similar studies. Mechanisms of vessel networks are shown in Figure 5.

Other study showed that concrete containing hollow pipettes after flexural test and glue releasing into its cracks can stand up to 20% more load under a subsequent flexural test [25]. Although several researchers have reported hollow pipettes and vessel networks containing glue as methods for designing self-healing concrete, the method needs to be verified for the use in actual projects [28-39].

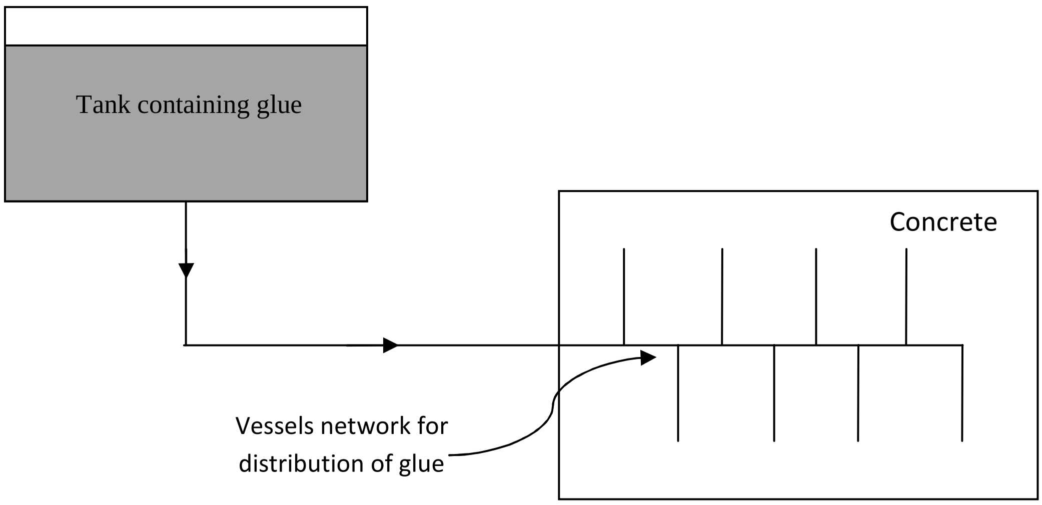
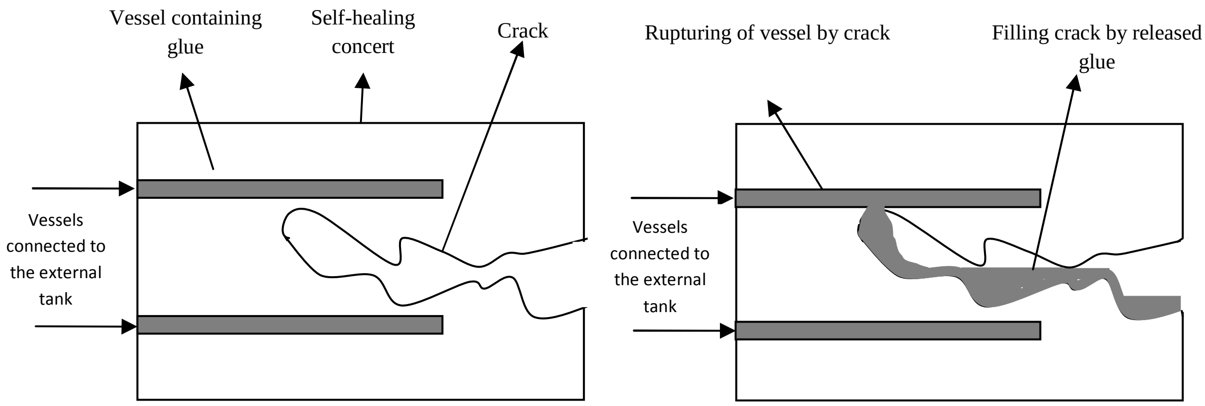


Figure 4: Schematic diagram for vessel networks



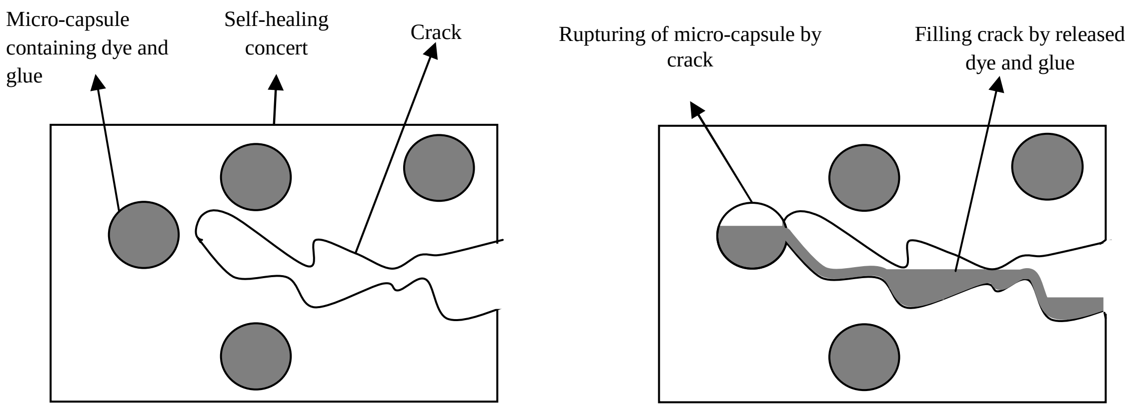
(A) Crack being propagated into concrete

(B) Crack ruptures the vessel and glue released into the crack and is filled

Figure 5: Crack-healing mechanism using vessels containing glue

2-2-2- Encapsulated glue

Encapsulation of glue is evolved from the eggs of bird (in macro-scale) or cells (in micro-scale) [40]. The size for capsules containing glue used for self-healing concrete varies from microcapsules to nanocapsules [35]. Microencapsulation was developed beginning with the preparation of capsule containing dyes. These capsules containing dyes were introduced into paper for copying purposes and were eventually replaced. White et al. [41] introduced the application of microcapsules containing glue for designing self-healing concrete and the concept is shown in Figure 6. Normally cracks would rupture the embedded microcapsules hence the glue is released into the crack faces through capillary action and the crack gets filled.



(A) Crack is being propagated into concrete

(B) The crack ruptures the microcapsule and glue released into the crack and is filled

Figure 6: Crack-healing mechanisms using encapsulated glue

Micro-capsules containing epoxy resin (as glue) and acrylic resin (as a hardener) were used by Nishiwaki (1997) to research on the improved materials for self-healing concrete [34]. Both splitting and compression tests were carried out. The results elaborated that: (a) two healing agents are difficult; (b) very small amount of healing agent could be filled in one microcapsule; (c) the bonding strength between the microcapsules and the cementitious matrix had to be stronger than the strength of the microcapsules. In order to solve these problems: (1) one of the healing agents might be used as core material; (2) diameter of the microcapsule should be big enough; (3) bonding strength between the encapsulated shell material and the cementitious matrix should be improved. Finally, it was concluded that there were a lot of technical problems.

According to Homma [25], a self-healing concrete specimen containing microcapsules was loaded to the point of almost breaking. The results elaborated that; self-healing concrete specimen could recover 26% of its original strength as compared to the control specimen that recovered 10%. Based on this study, increasing the quantity of glue can raise the strength recovery ratio of self-healing concrete.

2-3- Biological self-healing process

The use of microorganisms to design self-healing concrete has been categorized as biological strategy by several researchers [11, 12, 13]. Microorganisms can grow allmost everywhere such as soil, water and oil reservoir, acidic hot springs and industrial wastewater. The use of microorganisms to design self-healing concrete has been suggested by several researchers [42, 43]. Gollapudi et al. introduced biological self-healing concrete as environment friendly process [16]. Microorganisms are mostly divided into three important categories: bacteria, fungi, and viruses. Among these microorganisms, special strains of bacteria capable of precipitating certain chemicals are used to design the biological self-healing concrete. Precipitation of polymorphic iron-aluminum-silicate ($(Fe_5AI_3)(SiAl)O_{10}(OH)_5$) and calcium carbonate ($CaCO_3$) are the most important processes use for designing the biological self-healing concretes.

Microorganisms can be added to the biological self-healing concrete through different approaches. These includes the addition of microbial broth directly into the fresh concrete; additions in the form of spores, immobilized form onto silica gel or activated carbon, encapsulated form, or using the vascular networks as described under the chemical method to distribute the microorganisms [11, 20, 44].

The pH, temperature and moisture content of the concrete are typically not suitable for the growth of bacteria. Hence, in certain cases, resistant form of bacteria (spore) is used instead of using fresh microbial broth. Alternatively, encapsulated microorganisms can also be used to withstand the harsh condition of concrete. Encapsulation of microorganisms are however an expensive and complex method. The use of vascular networks to distribute the microbial broth throughout the cemetitious matrix is another way of protecting the microorganisms from inappropriate conditions. However, these methods are complicated and subjected to lack of constructability using current technology.

The use of immobilized microorganisms onto silica gel or activated carbon is a suitable way in terms of financial aspect. However, the effect of using these materials on strengthening of concrete is still not completely clear. Jonkers et al., (2010) showed that applying $6\times10^8/cm^3$ bacterial spores to design self-healing concrete resulted in a decrease in strength of less than 10% for 3, 7 and 28 days cured specimens [76]. This study showed that the effects of bacteria on concrete straightness are not considerable. However, it can be very effective to repair cracks and extension of concrete durability.

2-3-1- Biological precipitation of calcium carbonate

The pH of fresh concrete is usually between 10 to 13. The temperature of fresh concrete can go up to 70°C. After the drying of concrete, there is not enough water. Therefore, the selected bacteria needs to exhibit high resistance against high pH, temperature, and serious limitation of water. Usually mesophilic microorganisms cannot grow normally in these conditions. To solve this problem Ghosh and Mandal (2006) successfully used thermophilic bacteria to design self-healing concrete [19].

Microbial calcium carbonate can be precipitated as a by-product during urea hydrolysis, photosynthesis, and sulfate reduction [45]. As a microbial sealant, calcium carbonate showed its positive potential in selectively consolidating simulated fractures and surface fissures in granites and in the consolidation of sand. Calcium carbonate can be found in three-precipitated form of mineral crystals. They have similar chemical formula but different structures, namely calcite, aragonite and vaterite. The most stable form of calcium carbonate is calcite. Aragonite is meta-stable and can be converted into calcite over time. Vaterite is rarely found in nature [46]. Only calcite is of greater interest for developing self-healing concrete.

Several factors affecting the precipitation rate of biological calcite are (1) concentration of the dissolved inorganic carbon content, (2) pH, (3) concentration of calcium ions (Ca^{2+}) concentration, (4) presence of nucleation sites. Microbial metabolisms can provide first three of these factors and the cell wall of the bacteria acts as nucleation site [27].

Bacterial calcium carbonate precipitation on concrete surface can reduce permeability towards gas and capillary water uptake. Carbonate precipitation is found throughout the world, especially in the oceans [48, 49]. This type of bacterial culture and medium composition has a profound impact on the morphology of calcium carbonate crystal. For example, precipitation of calcite can be raised by magnesium [50]. Several microbial metabolic pathways can contribute to the precipitation of biological mineral. For instance, the famous pathways to precipitate calcium carbonate are anaerobic sulphide oxidation, ammonification, denitrification, sulfate reduction and photosynthesis [51, 52].

The primary role of bacteria to precipitate calcium carbonate is attributed to their ability to increase the pH of the environment through different bacterial metabolisms [53]. Apparently, biological calcium carbonate precipitation using ureolytic bacteria is one of the most popular way to design self-healing concrete. These bacteria are able to produce extracellular urease enzyme. The hydrolysis of urea to carbon dioxide and ammonia can be catalyzed by urease enzyme. The hydrolyzed ammonia and carbon dioxide increases the pH and carbonate concentration in the bacterial environment, respectively. A series of biochemical reaction takes place to form calcium carbonate as shown in Eqn. (4) to (10) [11].

Urea is hydrolyzed to carbamate and ammonia in the presence of urease as shown in Eqn. (4).

$$CO(NH_2)_2 + H_2O \xrightarrow{Urease\ enzyme} NH_2COOH + NH_3 \quad \text{Eqn. (4)}$$

Carbamate is spontaneously hydrolyzed to form ammonia and carbonic acid as in Eqn. (5).

$$NH_2COOH + H_2O \rightarrow NH_3 + H_2CO_3 \quad \text{Eqn. (5)}$$

Carbonic acid is hydrolyzed to form carbonate ion and hydrogen ion as shown in Eqn. 6.

$$H_2CO_3 \leftrightarrow HCO_3^- + H^+ \quad \text{Eqn. (6)}$$

Ammonia spontaneously hydrolyses to form ammonium and hydroxide ion as shown in Eqn. 7.

$$2NH_3 + 2H_2O \leftrightarrow 2NH_4^+ + 2OH^- \quad \text{Eqn. (7)}$$

The reaction in Eqn. (7) continuously produces hydroxide ion, this gives rise to a pH increase, which shifts the overall equilibrium of bicarbonate ion (HCO_3^-) towards the formation of carbonate ions as shown in Eqn. (8).

$$HCO_3^- + H^+ + 2NH_4^+ + 2OH^- \leftrightarrow CO_3^{2-} + 2NH_4^+ + 2H_2O \quad \text{Eqn. (8)}$$

Bacterial cell wall has negative charge and for this reason, cell wall is able to draw positively charged calcium ions (Ca^{2+}) to deposit on their cell wall surface (Eqn. 9). The Ca^{2+} ions then react with the CO_3^{2-} ions leading to the precipitation of calcium carbonate ($CaCO_3$) at the cell surface as shown in Eqn. (10). This precipitation serves as the nucleation site.

$$Ca^{2+} + Cell \rightarrow Cell - Ca^{2+} \quad \text{Eqn. (9)}$$

$$Cell - Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 - Cell \downarrow \quad \text{Eqn. (10)}$$

A schematic diagram of the microbiological precipitation of calcium carbonate into concrete cracks based on above reactions is seen in Fig. 7.

Based on the microbial pathway for the precipitation of calcium carbonate, urea has to be present in the self-healing concrete to initiate the necessary biochemical reactions. Biological precipitation of calcite can be detected using x-ray diffraction (XRD). Calcite crystals can also be observed by scanning electron microscopy (SEM) [49]. Talaiekhozani et al. (2013) have prepared some pictures of biological calcium carbonate precipitation on the surface of concrete. This study is carried out through the isolation of microorganisms from soil. The isolated microorganisms could help in concrete healing process after one-month observation. Healed concrete cracks are show in figure 8 (from (a) to (c)) [74]. Also, similar type of microscopic picture has been prepared by Zwaag and Routes (2010) that can be observed in figure 8(d). In this picture, bacteria and their calcium carbonate precipitation are clearly observed [75].

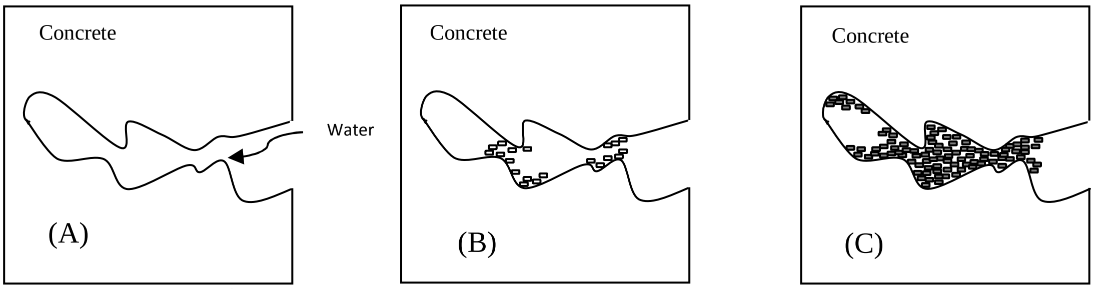
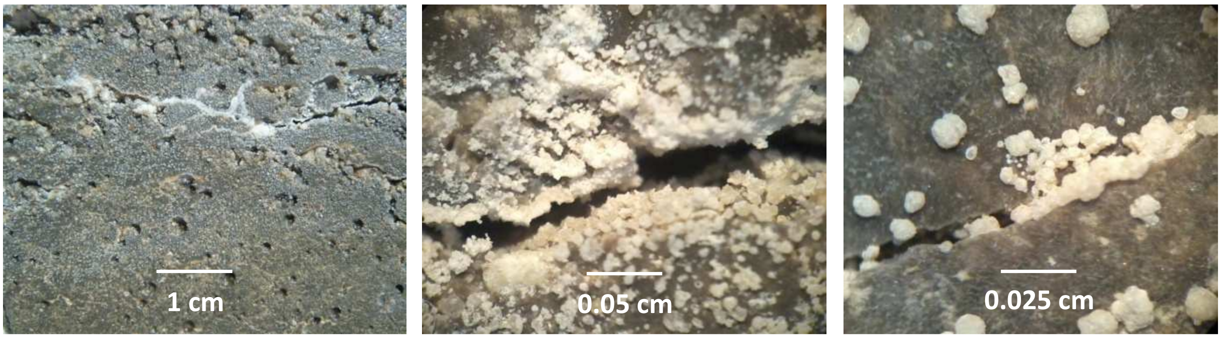
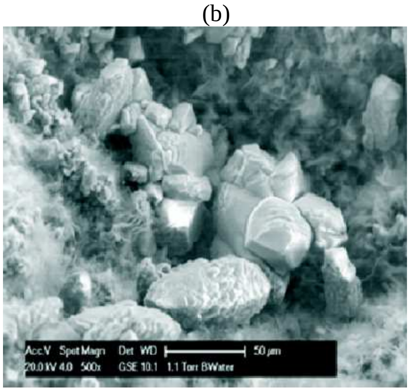


Figure 7: Schematic scenario of crack healing by microorganisms (A) crack is propagating into concrete; (B) microorganisms can be activated into crack; (C) microorganisms grow and precipitate calcium carbonate around their wall cells and can fill the crack



(a) (b) (c)



(d)

Figure 8: Four different pictures of microbiological precipitated calcium carbonate on the concrete cracks, figure (a) is without magnification, figure (b) with 20x magnification, (c) with 40x magnificationand (d) [74] ESEM picture of bacterial activates and precipitation of calcium carbonate with 20000x magnification [75]

A large domain of bacteria [56, 57, 58, 59, 60] have been reported to produce self-healing concrete. Unfortunately, the pH of the fresh concrete is between 10 and 13, which is rather harsh for the survival of majority of bacteria. In addition, the temperature of the fresh concrete (~70˚C) is also too high for cell growth. Upon drying of the concrete, there is not enough water for cell growth to occur. Therefore, the suitable bacteria have to exhibit high resistance against high pH, temperature, and serious limitation of water. Typically, mesophilic microorganisms cannot grow under these conditions. Unlike the live bacteria, bacterial spore is very resistant against the harsh conditions as mentioned and some bacterial spores can live for more than 60 years. In many studies, instead of the direct use of bacteria in the fresh concrete, bacteria spores were used [15].

The range of bacteria strains useful to design biological self-healing concrete are presented in Table 1. *Bacillus pasteurii* and *Bacillus sphaericus* family are the most common microorganisms used in designing self-healing concrete. *Bacillus pasteurii* is easily found in soil. Five different strains of the *Bacillus sphaericus* family and one strain of *Bacillus lentus* were evaluated for the precipitation of calcium carbonate on the degraded limestone [61]. The results showed that, all *Bacillus sphaericus* family could precipitate calcium carbonate, but in different amounts. Bacillus strains were found to produce the intracellular urease [61, 62]. Ureolytic activity can be used to measure the precipitation of calcium carbonate [63, 15, 57]. The amount of urease available is close to 1% of the cell dry weight [64].

2-3-2- Biological precipitation of polymorphic iron-aluminum-silicate

The silica accumulating bacteria have been reported in several studies [54]. A complex iron-aluminum-silicate was found on the surface of isolated bacteria cells from a lake contaminated with metal sediment [55]. The experiments showed that the chemical formation of polymorphic iron-aluminum-silicate is $(Fe_5AI_3)(SiAl)O_{l0}(OH)_5$. The bacteria *Leuconostoc mesenteroides* plays an important role in precipitating the silica at acidic pH. This bacterium utilizes carbohydrate to produce lactic acid hence creating an acidic environment, the reduced solubility of the colloidal silica results in precipitation. This method is not popular as acidic condition and is not good for the durability of concrete.

Table 1: List of microorganisms applicable for developing self-healing concrete based on respective self-healing mechanisms

Self-healing mechanism	Name of microorganism	References
	Sporosarcina Pasteurii (or Bacillus Pasteurii)	13, 65, 66, 14
	Bacillus megaterium	
	Halomonas euryhaline	12, 67, 68, 77
	Myxococcusxanthus	
	Deleya halophila	42
	Bacillus sphaericus	43
	Bacillus lentus	17
Ureolytic process	*Acinobacter species*	46
	Escherichia coli	19, 69, 70
	Pseudomonas aeruginosa	19
	Shewanella species	72
	Bacillus Cohnii	55
	Bacillus pseudofirmus	55
	Bacillus amyloliquefaciens	71
	Bacillus alkalinitrilicus	73
Silica process	*Leuconostoc mesenteroides*	16

3- Future challenges

Although, self-healing processes containing natural and chemical are well known to design self-healing concrete, biological process is a young promising technology, which has not been fully understood yet.

Till now, many bacteria can be isolated from nature that are useful for designing self-healing concrete (Table 1). Using bacteria have many advantages such as (1) Bacteria are easy to culture. (2) Isolation of bacteria is not very complex and (3) many methods have been describe for adding bacteria to concrete. On the other hand, bacteria are not enough resistance against harsh condition of concrete such as high pH, low level of water, high temperature and etc. Therefore, the study about other type of microorganisms especially fungi is very important. Although, few article on using fungi for self-healing concrete design can be found, the mechanism of fungi for filling cracks or optimum growing condition of fungi have not been completely understood and they can be a good area for future research.

4- Conclusion

This paper reviews a wide range of methods for designing self-healing concrete. A taxonomy was proposed to cover possible methods for the design, namely natural, chemical and biological methods. Chemical methods were the conventional methods that have been used as a sole method to design self-healing concrete. This paper reviews intensively about the great potential of biological method, using the bacteria capable of precipitating calcite, as providing the way forward for developing biological self-healing concrete. The precipitation of calcite will form calcium carbonate that would help in healing concrete cracks. The taxonomy proposed in this paper contributes significantly for researchers in the field of biological to embark on the research work of self-healing concrete.

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Reference

1- S. K. Ghosh (Ed.), (2009) Self-Healing Materials: Fundamentals, Design Strategies, and Applications, Wiley WCH, GmbH.
2- K. van Breugel (2007) Is There a market for self-healing cement-based materials. In: Proceedings of the first international conference on self-healing materials, Noordwijkaan zee, the Netherlands.
3- W. Zhong, W. Yao, (2008) Influence of damage degree on Self-healing of Concrete. Construction and Building Materials, 22: 1137-1142.
4- A. C. Balazs, (2007) Modeling self-healing materials, Mater. Today 10: 18–23.
5- S. Van der Zwaag (Ed.), (2007) Self Healing Materials–an Alternative Approach to 20 Centuries of Materials Science, Springer, Dordrecht, The Netherlands.
6- R. P. Wool, (2008) Self-healing, Materials: a review, Soft Matter, 4: 400–418.
7- M. Nosonovsky, B. Bhushan, (2008) Multiscale Dissipative Mechanisms and Hierarchical Surfaces: Friction, Super hydrophobicity, and Biomimetics, Springer-Verlag, Heidelberg, Germany.
8- M. Nosonovsky, B. Bhushan, (2009) Thermodynamics of surface degradation, self-organization, and self-healing for biomimetic surfaces, Phil. Trans. R. Soc. A. 367: 1607–1627.
9- K. Koch, B. Bhushan, H. J. Ensikat, W. Barthlott, (2009) Self-healing of voids in the wax coating on plant surfaces, Phil. Trans. R. Soc. A 367.

10- M. Nosonovsky, R. Amano, J. M. Lucci, P. K. Rohatgi, (2009) Physical chemistry of selforganization and self-healing in metals, Phys. Chem. Chem. Phys, 11 :9530–9536.
11- M. Wu, B. Johannesson, M. Geiker, (2012) A review: Self-healing in cementitious materials and engineered cementitious composite as a self-healing material, Construction and Building Materials 28: 571–583.
12- R. Siddique, N. K. Chahal, (2011) Effect of ureolytic bacteria on concrete properties, Construction and Building Materials, 25: 3791–3801.
13- H. M. Jonkers, (2007) Self Healing Concrete: A Biological Approach, Self Healing Materials. An Alternative Approach to 20 Centuries of Materials Science, 195–204.
14- S. M. Al-Thawadi, (2011) Ureolytic Bacteria and Calcium Carbonate Formation as a Mechanism of Strength Enhancement of Sand, Journal of Advanced Science and Engineering Research, 1: 98-114.
15- D. W. Muynck, K. Cox, N. Belie, W. Verstraete, (2008) Bacterial carbonate precipitation as an alternative surface treatment for concrete, Construction and Building Materials,22: 875-885.
16- U. K. Gollapudi, C. L. Knutson, S. S. Bang, M. R. Islam, (1995) A new method for controlling leaching through permeable channels, Chemosphere, 30: 695–705.
17- N. Chahal1, A. Rajor, R. Siddique, (2011) Calcium carbonate precipitation by different bacterial strains, African Journal of Biotechnology, 10: 8359-8372.
18- S. Van der Zwaag, editor. (2007) Self-healing materials: an alternative approach to 20 Centuries of Material Science.
19- P. Ghosh, S. Mandal, (2006) Development of bioconcrete material using an enrichment culture of novel thermophilic anaerobic bacteria, Indian Journal of Experimental Biology, 44:336-339.
20- K. S. Toohey, N. R. Sottos, A. L. Lewis, J. S. Moore, S. R. White, (2007) Self-healing materials with micro vascular networks, Published online, doi:10.1038/nmat1934.
21- C. Edvardsen, (1999) Water permeability and autogenous healing of cracks in concrete. ACI Mater J, 96:448–54.
22- E. Schlangen, (2010) Fracture mechanics. CT5146 Lecture Notes. In: Hua X. Selfhealing of Engineered Cementitious Composites (ECC) in concrete repair system. Master thesis, Delft University of Technology,
23- Y. Z. Yang, M. D. Lepech, E. H. Yang, V. C. Li, (2007) Autogenous healing of engineered cementitious composites under wet–dry cycles. Cem Concr Res, 39:382–90.
24- S. Qian, J. Zhou, M. R. de Rooij, et al. (2009) Self-healing behavior of strain hardening cementitious composites incorporating local waste materials. Cem Concr Compos, 31:613–21.
25- D. Homma, H. Mihashi, T. Nishiwaki, (2009) Self-healing capability of fibre reinforced cementitious composites. J Adv Concr Technol, 7:217–28.
26- A. Neville, (2002). Autogenous Healing 輸 Concrete Miracle. Concrete International, 24(11), 76-82.
27- V. C. Li, & E. Yang, Self healing in concrete materials. In S. van der Zwaag (ed.) (2007) Self healing materials – An alternative approach to 20 centuries of materials science. Springer, The Netherlands, 161–194.
28- C. Dry, (1996) Procedure developed for self-repair of polymer matrix composite materials. Compos Struct, 35:263–9.
29- M. Motuku, U. K. Vaidya, G. M. Janowski, (1999) Parametric studies on self-repairing approaches for resin infused composites subjected to low velocity impact. Smart Mater Struct, 8:623–38.
30- S. M. Bleay, C. B. Loader, V. J. Hawyes, et al. (2001) A smart repair system for polymer matrix composites. Composites A, 32:1767–76.
31- J. W. C. Pang, I. P. Bond, (2005) 'Bleeding composites' – damage detection and self-repair using a biomimetic approach. Composites Part A, 36:183–8.
32- J. W. C. Pang, I. P. Bond, (2005) A hollow fibre reinforced polymer composite encompassing self-healing and enhanced damage visibility. Compos Sci Technol, 65:1791–9.
33- C. Joseph, A. D. Jefferson, M. B. Cantoni, (2007) Issues relating to the autonomic healing of cementitious materials. In: Proceedings of first international conference on self-healing materials, Noordwijkaan Zee, Netherlands.Paper 61.Springer CDROM.
34- C. Nishiwaki, (1997) Fundamental study on development of intelligent concrete with self-healing capability. Master's thesis, Department of Architecture and Building Science, Graduate School of Engineering, Tohoku University.
35- C. Dry, (1990) Alteration of matrix permeability, pore and crack structure by the time release of internal chemicals. In: Proceedings of advance in cementitious materials. American Ceramic Society: Gaithersbury, Maryland, pp. 729– 68.
36- C. Dry, (1994) Matrix cracking repair and filling using active and passive modes for smart timed release of chemicals from fibers into cement matrices. Smart Mater Struct, 3: 118–23.
37- C. Dry, McMillan W, (1996) Three-part methylmethacrylate adhesive system as an internal delivery system for smart responsive concrete. Smart Mater Struct, 5: 297–300.
38- C. Dry, (2000) Three design for the internal release of sealants, adhesives and waterproofing chemical into concrete to release. Cem Concr Res, 30: 1969–77.
39- H. Mihashi, Y. Kaneko, T. Nishiwaki, K. Otsuka, (2000) Fundamental study on development of intelligent concrete characterized by self-healing capability for strength. Trans Jpn Concr Inst, 22: 441–50.
40- A. R. Hemsley, P. C. Griffiths, (2000) Architecture in the microcosm: biocolloids, self assembly and pattern formation. Philos Trans Roy Soc London, 358: 547–64.
41- S. R. White, N. R. Sottos, P. H. Geubelle, J. S. Moore, M. R. Kessler, S. R. Sriram, et al. (2001) Autonomic healing of polymer composites. Nature, 409(6822):794.

42- H. M. Jonkers, A. Thijssen, G. Muyzer, O. Copuroglu, E. Schlangen, (2008) Application of Bacteria As Self-Healing Agent for the Development of Sustainable Concrete. In: Proceedings of the 1st international conference on biogeocivil engineering, Delft, The Netherlands; June 23–25.
43- K. V. Tittelboom, N. D. Belie, W. D. Muynck, W. Verstraete, (2010) Use of bacteria to repair cracks in concrete. Cem Concr Res, 40: 157–66.
44- J. Wang, K. V. Tittelboom, N. D. Belie, W. Verstraete, (2012) Use of silica gel or polyurethane immobilized bacteria for self-healing concrete, Construction and Building Materials, 26: 532–540.
45- H. Knorre, W. Krumbein, (2000) Bacterial calcification. In: Riding RE, Awramik SM (Eds.), microbial Sediments. Springer-Verlag, Berlin, Germany, 25-31.
46- S. Sanchez-Moral, J. C. Canaveras, L. Laiz, C. Saiz-Jimenez, J. Bedoya, L. Luque, (2003) Biomediated precipitation of calcium carbonate metastable phases in hypogean environments: A short review, Geomicrobiology Journal, 20: 491-500.
47- D. Kralj, L. Brečević, A. E. Nielsen, (1990) Vaterite growth and dissolution in aqueous solution I. Kinetics of crystal growth. Journal of Crystal Growth, 104: 793.
48- M. R. Leeder, (1982) Sedimentology, George Allen and Unwin (Publishers) Ltd., London, 344 pp.
49- S. K. Ramachandran, V. Ramakrishnan, S. S. Bang, (2001) Remediation of Concrete Using Micro-organisms. ACI. Materials, 98: 3-9.
50- R. A. Berner, (1975) The role of magnesium in the crystal growth of calcite and aragonite from sea water, Geochim. Cosmochim. Acta., 39: 489-504.
51- S. Castainer, M. G. Le, J. P. Perthuisot, (2000) Bacterial roles in the precipitation of carbonate minerals. In microbial sediments (Ed Riding RE, Awramik SM) Heidelberg, Springer-Verlag, pp. 32-39.
52- R. Riding, (2000) Microbial Carbonates: The geological record of calcified bacterial mats and biofilms. Sedimentology, 47: 179-214.
53- S. Douglas, T. J. Beveridge, (1998) Mineral formation by bacteria in natural Communities. FEMS. Microb. Ecol., 26: 79-88.
54- F. G. Ferris, W. S. Fyfe, T. J. Beveridge, (1987) Metallic ion binding by *Bacillus subtil is*; implications for the fossilization of microorganisms, Geology, 16: 149-152.
55- M. J. Henk, T. Arjan, M. Gerard, C. Oguzhan, S. Erik, (2008) Application of bacteria as self-healing agent for the development of sustainable concrete, Ecological Engineering, 36: 230–235,
56- A. Moldovan, S. Patachia, C. Vasile, R. Darie, E. Manaila, and M. Tierean, Natural Fibres/Polyolefins Composites (I) UV and Electron Beam Irradiation J. Biobased Mater. Bioenergy 7, 58-79.
57- K. V. Tittelboom, N. D. Belie, W. D. Muynck, W. Verstraete, (2010) Use of bacteria to repair cracks in concrete. Cem Concr Res, 40:157–66.
58- P.Y. Chen, J. McKittrick, M. A. Meyers, (2012) Biological materials: Functional adaptations and bio inspired designs, Prog Mater Sci, 57(8): 1492–1704.
59- K. Liu, Y. Tian, L. Jiang, (2013), Bio-inspired superoleophobic and smart materials: Design, fabrication, and application, Prog Mater Sci, 58: 503-564.
60- S. Bauer, P. Schmuki, K. von der Mark, J. Park, Engineering biocompatible implant surfaces: Part I: Materials and surfaces, Prog Mater Sci, 58:261-326.
61- J. G. Holt, N. R. Kried, P. H. A. Senath, J. T. Staley, S. T. Williams (Eds.), (1993) Bergey's Manual of Determinative Bacteriology (pp. 787). Philadelphia. PA: Lippincott, Williams and Wikins.
62- M. T. González-Muñoz, K. Ben-Chekroun, A. Ben-Aboud, J. M. Arias, M. Rodriguez-Gallego, (2000) Bacterially induced Mg-Calcite formation: Role of Mg^{2+} in development of crystal morphology. Journal of Sedimentary Research, 70: 559-564.
63- K. L. Bachmeier, A. E. Williams, J. R. Warmington, S. S. Bang, (2002) Urease activity in microbiologically-induced calcite precipitation. Journal of Biotechnology, 93: 171-181.
64- O. Braissant, E. P. Verrecchia, M. Aragna, (2002) Is the contribution of bacteria to terrestrial carbon budget greatly underestimated? Naturwissenschaften, 89: 366-370.
65- S. S. Bang, J. K. Galinat, V. Ramakrishnan, (2001) Calcite precipitation induced by polyurethane-immobilized Bacillus pasteurii, Enzyme and Microbial Technology 28: 404–409.
66- V. Ramikrishnan, R. K. Panchalan, S. S. Bang, (2005) Improvement of concrete durability by bacterial mineral precipitation, in Proc. ICF 11, Torino, Italy.
67- J. Dick, W. D. E. Windt, B. D. Graef, H. Saveyn, P. V. Meeran, N. Belie, W. Verstraete, (2006) Biodeposition of a calcium carbonate layer on degraded limestone by Bacillus species. Biodegradation, 17: 357-67.
68- M. A. Rivadeneyra, A. Ramos-Cormenzana, G. Delgado, R. Delgado, (1996) Process of carbonate precipitation by *Deleyahalophila*. Current Microbiology, 32: 308-313.
69- K. L. Bachmeier, A. E. Williams, J. R. Warmington, S. S. Bang, (2002) Urease activity in microbiologically-induced calcite precipitation, Journal of Biotechnology, 93: 171–181.
70- P. Ghosha, S. Mandala, B. D. Chattopadhyayb, S. Pal, (2005) Use of microorganism to improve the strength of cement mortar, Cement and Concrete Research, 35: 1980 – 1983.
71- N. Y. Lee, (2003) Calcite Production by Bacillus amyloliquefaciens CMB01, J. Microbiol., 41: 345-348.
72- R. Narayanasamy, N. Villegas-Flores, F. Betancourt-Silva, J. Betancourt-Hernandez, & N. Balagurusamy, (2010, July). Application of Bacteria in Repairing the Concrete Cracks-A Review. In Sixth International Conference on Concrete under Severe Conditions: Environment and Loading.
73- V. Wiktor, H. M. Jonkers, (2011) Quantification of crack-healing in novel bacteria-based self-healing concrete, Cement & Concrete Composites 33: 763–770.

74- A. Talaiekhozan, A. Keyvanfar, S. Samadi, R. Andalib, A. Shafaghat, H. Kamyab, M.Z. Abd Majid, M. Z. Rosli, M. A. Fulazzaky, C.T. Lee, M. W. Hussin, Application of *Proteus mirabilis* and *Proteus vulgaris* mixture to design self-healing concrete, Impress in desalination and water treatment, 2013.
75- S. van der Zwaag, (2010) Routes and mechanisms towards self-healing behavior in engineering materials. Bull Polish Acad Sci, 58:227–36.
76- H. M. Jonkers, A. Thijssen, G. Muyzer, O. Copuroglu, E. Schlangen (2010) Application of bacteria as self-healing agent for the development of sustainable concrete, Ecological Engineering, 36: 230–235.
77- Talaiekhozan, A., Fulazzaky, M. A., Keyvanfar, A., Andalib, R., Majid, M. Z. A., Ponraj, M., ... & Ir, M. W. H. (2013). Identification of Gaps to Conduct a Study on Biological Self-healing Concrete. Journal of Environmental Treatment Techniques, 1(2), 62-68.