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Overview of recent work on self-healing in cementitious materials

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ABSTRACT: Cracks, especially microcracks, in concrete are of paramount importance to the durability and the service life of cementitious composite. However, the self-healing technology, including autogenous healing and autonomous healing, is expected to be one of effective tools to overcome this boring problem. In this paper, we focus on the autogenous healing of concrete material and a few of recent works of autonomous healing are also mentioned. The durability and the mechanical properties improved by the self-healing phenomenon are reviewed from experimental investigation and practical experience. Several aspects of researches, such as autogenous healing capability of an innovative concrete incorporated geo-materials, self-healing of engineered cementitious composite and fire-damaged concrete, effect of mineral and admixtures on mechanism and efficiency of self-healing concrete are summarized to evaluate the presented progresses in the past several years and to outline the perspective for the further developments. Moreover, a special emphasis is given on the analytical models and computer simulation method of the researches of self-healing in cementitious materials.

KEYWORDS: Self-healing; Unhydrated cement nuclei; Cracks; Autogenous healing; Autonomous healing

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RESUMEN: *Panorámica de trabajos recientes sobre materiales cementantes autorreparables*. Las fisuras, y sobre todo las microfisuras, tienen una gran repercusión en la durabilidad y en la vida útil de los materiales cementantes. Ante este problema, la tecnología de la autorreparación, tanto autógena como autónoma, se presenta como una solución eficaz. El artículo se centra en la reparación autógena del hormigón, así como en algunos trabajos recientes sobre la reparación autónoma. Se describen las mejoras de las propiedades de durabilidad y de resistencia que proporciona la técnica del hormigón autorreparable, tanto desde el punto de vista de la investigación experimental como del de la experiencia práctica. A fin de evaluar los avances logrados en los últimos años y de trazar las grandes líneas de desarrollo futuro, se resumen varios de los aspectos investigados: capacidad de reparación de un hormigón innovador que incorpora geomateriales; autorreparabilidad tanto de los compuestos cementantes tecnológicos como de los hormigones que han sufrido daños por incendio; influencia de los aditivos minerales en el mecanismo y eficacia del hormigón autorreparable. Además, se destaca el papel de los modelos analíticos y los métodos de simulación informática en la investigación de los materiales cementantes autorreparables.

PALABRAS CLAVE: Materiales autorreparables; Núcleos de cemento sin hidratar; Fisuras; Reparación autógena; Reparación autónoma

1. INTRODUCTION

Cracks, especially microcracks, are very common and could appear during any stage of the service life of concrete structure. Cracks can be caused by different factors including structural/excessive loading, plastic/drying shrinkage, harsh environmental exposure, poor construction procedures and thermal effects. Due to provide an easy path for the transportation of liquids and gasses which potentially contain harmful substances, cracks may lead to deterioration of concrete and corrosion of reinforcement. Hence, mechanical performance and durability of concrete structures are reduced. In addition, cracking is aesthetically poor. Consequently, large costs are involved in inspection, monitoring, maintenance and repair the cracks of concrete structures every year. Therefore the best way to heal cracks is by triggering a healing mechanism without human intervention upon appearance of the crack, inspection and monitoring are consequently needed no longer or at a reduced frequency.

Compared to other engineering materials, concrete is unique because it intrinsically contains micro-reservoirs of unhydrated cement particles which are widely dispersed and available for self-healing. The phenomenon of self-healing in cementitious materials can be traced back to one century ago (1). In old concrete structures, some cracks being lined with white crystalline material were observed. One such example is on an 18th century bridge in Amsterdam, where microcracks were self-healed by the recrystallization of calcite (2). Such phenomenon suggested the ability of concrete to self-seal the cracks with chemical products by itself, perhaps with the aid of rainwater and carbon dioxide in air. In most concrete, particularly those with a low water/cement ratio, the amount of unhydrated cement is expected to reach 25% or higher (3). These unhydrated cement particles are known to present for a long time in matrix. Thus, under favorable conditions, the phenomenon of self-healing in concrete is well established (3, 4).

From experimental investigation and practical experience of self-healing phenomena of cracked concrete, two strategies have proven promising. One is autogenous healing technique, the other is autonomous healing technique. The autogenous healing means that cracks/damages can be naturally sealed by the self of concrete, like a bone to heal (5). Such healing of micro-cracks is attributed to rehydration of unhydrated cement particles in concrete matrix (6–9). For autonomous healing in a composite material self-healing capabilities are achieved by the release of encapsulated repair-agent as a result of cracking from the onset of damage. When cracks happen, the capsules containing self-healing compounds within the concrete material break and the healing agent is released to heal the cracks (10–15). Generally, autogenous healing has more advantages than autonomous healing, like economics which is extremely important for the highly cost-sensitive construction industry (4, 16). In addition, autonomous healing may potentially weaken the strength of materials due to the addition of self-healing capsules.

Due to the attractive potential and practical value, self-healing materials have been intensely investigated over the last 10 years and a significant increase in the number of scientific publications was accompanied (17–19). Evidence of self-healing to material design was apparent at the first international conference on self-healing materials which was held in the Netherlands during April 2007. This conference has also been succeeded by the first two books devoted solely to self-healing materials (20, 21). In 2005 a RILEM technical committee was established charged with investigating self-healing phenomena in cement-based materials, as stated by Joseph (22). The growing development in the arena of self-healing materials was largely exhibited by the second, third and fourth international conference on self-healing materials, held in Chicago in July 2009 and in Bath in June 2011, and in Belgium in June 2013, respectively.

In past several years, the self-healing of cementitious material has been concerned by so many researchers, and a lot of interesting outcomes and test techniques have been presented. Thus, it is necessary to discriminate and classify the recent works of self-healing. In this work, we focus on the autogenous healing of concrete material and while a few of recent works of autonomous healing are also mentioned. The state-of-the-art on the durability and the mechanical properties influenced by the self-healing phenomenon are first reviewed from experimental investigation and practical experience to categorize the approaches described in the literature to-date. Autogenous healing capability of an innovative concrete added geo-materials, self-healing of engineered cementitious composites (ECC) and fire-damaged concrete, effect of mineral and admixtures on self-healing mechanism are summarized to evaluate the present advances and to outline a perspective for future developments. Recent advances of the analytical models and computer simulation technology of self-healing research in cementitious materials is also presented.

2. DURABILITY IMPROVED BY SELF-HEALING ACTION

Autogenous healing of cracks in fractured concrete has been firstly noticed by the French Academy of Science in 1836 in water retaining structures, culverts and pipes (23). According to Hearn (8) the self-healing phenomenon was firstly studied by Hyde (24) at the end of the nineteenth century. Previous researchers have investigated the necessary conditions for autogenous healing in concrete materials. These studies had resulted in identifying three general criteria critical to robust self-healing: the presence of specific chemical species (7, 25, 26), exposure to various environmental conditions (9, 26–28) , and small crack width (9, 25, 29, 30). Meanwhile, it was reported that there were several processes including chemical, physical and mechanical interactions as discussed by Kishi et al. (31) to be responsible for autogenous healing. Among these reasons of autogenous healing in cementitious composites, it was clarified that crystallization of calcium carbonate within the crack fracture surface was the main mechanism for self-healing of matured concrete (9). Specifically, a calcite formation in the area of water-bearing cracks takes place in the material system $CaCO_3$-CO_2-H_2O according to the following reactions [1, 2] (9, 27)

$$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3 \ (pH_{water} > 8) \quad [1]$$

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

The water-insoluble $CaCO_3$ is evolved from a reaction between the calcium ions Ca^{2+}, derived from the concrete, and the in-water available bicarbonates HCO_3^-, or carbonates CO_3^{2-}. Furthermore, water temperature, pH value of the water and CO_2 partial pressure in the water favor the $CaCO_3$ precipitation in the crack.

Over recent years researchers have investigated the influence of autogenous healing on the durability of cementitious composites. Many experimental results and practical experiences have demonstrated that cracks in concrete have the ability to heal themselves and water flow through cracks was reduced with time. Self-healing of leaking cracks was extensively studied by Clear (32), Hearn (8, 23, 33) and Edvardsen (9). As shown in Figure 1, Otsuki (34) suggested that self-healing of microcracks could have been the reason for densification of the concrete cover, thus reducing the rate of migration of chloride ions into the concrete. In the study of water flow through cracked concrete under a hydraulic gradient, Edvardsen (9, 25) noted a gradual reduction of permeability over time, again suggesting the ability of the cracked concrete to self-seal itself and slow the rate of water flow. The main cause of self-healing was attributed to the formation of calcium carbonate, a result of reaction between unhydrated cement and carbon dioxide dissolved in water (9). Furthermore, Edvardsen (9) concluded that the formation of calcium carbonate responds to two different crystal growth processes under water exposure, i.e., the kinetics of surface controlled crystal growth in the initial phase and later a diffusion controlled crystal growth. The observations under ESEM and XEDS confirmed (35) that the microcracks in the specimens submerged in water were healed with significant amount of calcium carbonate, very like due to the continuous hydration of cementitious materials. Analyses of experimental results showed that there existed a damage threshold for self-healing both for high strength concrete and normal strength concrete (36). When the damage degree is less than the threshold, the self-healing ratio of concrete is increased with the increase in damage degree; while the threshold is exceeded, the self-healing ratio is decreased with the increasing of damage degree. Reinhardt (25) established the dependency of permeability and self-healing behavior of cracked concrete on temperature. For a cause of reduced chloride ingress, self-healing of microcracks has also been suggested by Fidjestol (37), Bakker (38), Sahmaran (39) and Li (40). Recently, Ismail (41) also confirmed that in the case of crack width below 60 µm, the self-healing potential of the mortar matrix can impede the effective chloride diffusion along a crack path.

Concrete exposed to high temperatures undergoes a reduction in performance, such as a decreased load-carrying capacity and durability due to thermo-mechanical and thermo-hydral processes, which result in cracking, loss of strength, and explosive spalling (42). Re-curing fire-damaged concrete in water can partly restore strength and durability performance (43–45). Moreover, high-strength concrete was found to have better recovery under re-curing due to its microstructure (46). Hence, the self-healing fire-damaged cementitious composite is becoming an attractive issue for researchers. Henry (42) investigated the loss and recovery of strength and the crack self-healing for normal-and high-strength mortars subjected to fire damage, and he proposed that recovery mechanism was contributed

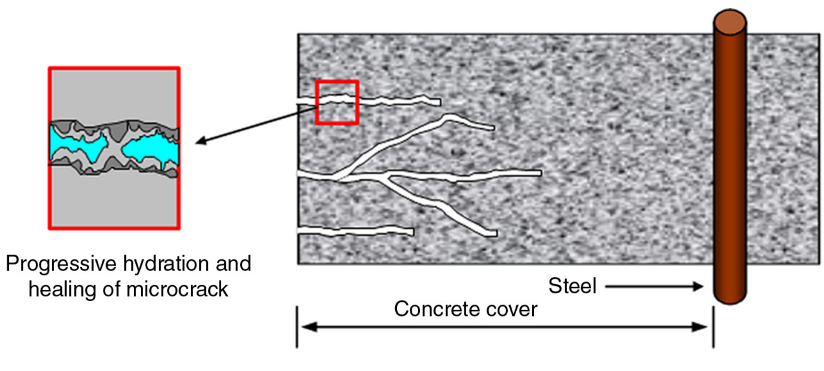

FIGURE 1. Healing of microcracks in concrete cover due to continuing hydration of unhydrated cement nuclei (34).

to the chemical rehydration and full self-healing of cracks. Durability (air permeability and carbonation resistance) of fire-damaged concrete was recovered under water re-curing conditions, even if re-curing in air resulted in a lower durability performance than re-curing in water. The decreases of air permeability and the increases of carbonation resistance under water and air-water conditions were attributed to crack healing and porosity recovery of specimens. However, although porosity recovers to pre-fire levels after water and air-water re-curing and crack self-healing was observed, the pre-fire compressive strength, complete strength recovery, was not reached. In the meantime, the microcracks that were formed due to quenching were mostly healed within 7 days of water recurring and porosity was found to recover to pre-fire levels. Chemical analyses found that under water re-curing conditions, the crystalline structure and amounts of chemically bound water and $Ca(OH)_2$, one of the primary hydration products, returned to pre-fire levels. The instability of the healed cracks and rehydrated pore structure resulted in strength reduction even though the crystalline structure, amount of hydration product, and porosity were found to recover to pre-fire levels and crack self-healing was also observed. Henry concluded that weaknesses or flaws exist in the newly healed crack interface that could not be detected by visual observation but still produced an improvement in durability. Furthermore, water re-curing could not fully recover compressive strength due to this instability, the air permeability and carbonation rate were significantly reduced due to crack self-healing and a reduction in porosity which reduce mass transport ability. However, damage in the interface between the mortar and coarse aggregates and recovery properties in fire damaged concrete need to be solved.

3. MECHANICAL PROPERTY RECOVERY

Several experimental results have confirmed that the recovery of mechanical properties can be attained to some extents due to the self-healing in cementitious materials. For example, the recovery of flexural strength was observed in pre-cracked early age concrete beams while clamped and submerged in water (47). More recent work by Heide (48), as overviewed by Ghosh (20), has therefore focused on examining both the mechanical strength gain and reduction in permeability of early-age concrete which has been cracked and allowed to heal autogenously. Furthermore, it was observed that recovery of many mechanical related properties was possible after water immersion, e.g. the stiffness of pre-cracked specimens (49) and the compressive strength of pre-damaged cylindrical specimens (50). The self-healing observed from these investigations was associated with continued hydration of the unhydrated cement in cementitious materials. On the other hand, Granger (51) carried out an experimental program of mechanical test on ultra-high performance concrete and concluded that the self-healing of the pre-existing crack was mainly due to hydration of anhydrous clinker on the crack surface and that the stiffness of newly formed crystals is close to that of primary C-S-H. Joseph (22) concluded that the compressive stress applied to the crack faces was found to be very beneficial in respect to closing the initial crack, which was typically 50 μm wide. However, additional compressive forces above that required to cause crack closure and reinstate contact between the crack faces did little to improve the strength recovery following healing. As indicated above, the phenomenon of autogenous healing has been demonstrated to be effective for the recovery of mechanical properties.

The use of compressive forces to close cracks and to create contact between crack faces has been shown to be an effective approach to enhancing the natural autogenous healing process within cementitious materials (20, 48). Recently work undertaken at Cardiff University in UK has therefore examined the feasibility of low-level post-tensioning of cementitious materials using shrinkable polymer tendons to enhance autogenous healing behavior (22, 52). The system involves the incorporation of unbonded pre-oriented polymer tendons in cementitious beams. Post-tensioning is achieved by thermally activating the shrinkage mechanism of the restrained polymer tendons after the cement-based material has undergone initial curing. The concept has been investigated by using tendons formed from shrinkable polyethylene terephthalate (PET). The basic concept of material system is illustrated in Figure 2. Jefferson (52) has shown that the shrinkage activation of the PET tendon was sufficient to completely close the 0.3 mm crack created during the initial three-point loading on day 4. Furthermore, the reloading test data on day 8 indicated that not only had the restrained shrinkage of the tendon caused the crack within the mortar beam to completely close but it had also put the beam into compression. This new composite shape memory polymer cementitious system also had the potential to offer crack prevention in addition to crack healing, if the integral polymer tendons were activated prior to the occurrence of early-age cracking. However, crack closure through the external application of compressive forces in situ is impractical, and some improvement for this apparatus is necessary if active roles are expected to close the cracks in cementitious matrix.

Based on the principle of autonomous healing in materials, an autonomous healing system that once breaking, the glass capillary tubes release cyanoacrylate into the crack plane which flows rapidly, under the influence of attractive capillary

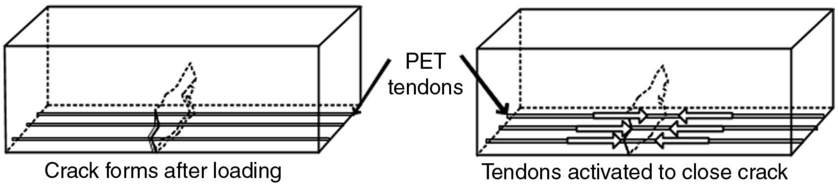

FIGURE 2. Schematic illustration of concept for new composite shape memory polymer cementitious material system (52).

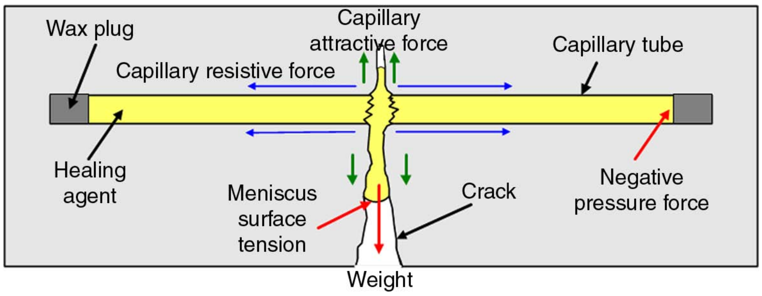

FIGURE 3. Schematic illustration of the main forces acting on an internally encapsulated healing agent (54).

forces, across the two crack faces was developed in concrete material by Joseph (53, 54), as demonstrated in Figure 3. The autonomous healing system offered a successful mechanism for restoring and in certain circumstances enhancing the mechanical properties of the composite. The infiltration of the cyanoacrylate reduced the permeability and therefore improved the durability of the new composite material. The rapid flow and curing ability of the low viscosity cyanoacrylate, which is evident in the primary healing strength gain, also suggests that this healing system might be applicable to healing damage created under dynamic situations, such as in earthquakes. Other recent work of autonomous healing in concrete can be referred in (12, 55–57).

4. INFLUENCE OF ADMIXTURES ON AUTOGENOUS HEALING

In the literature of self-healing, many different types of admixtures had been investigated to consider the healing efficiency of cracks in concrete. In these works, some of them focused on mechanical behavior, some focused on durability and others focus on microstructure. An interesting recent development has been the autogenous healing of expansive concretes by Hosoda et al. (58), Kishi et al. (31) and Yamada et al. (59). They have found that the inclusion of expansive agents in the concrete has allowed even large cracks of up 0.3–0.4 mm to heal (58). Furthermore, the addition of small amounts of various carbonates such as bicarbonate of soda also increased the self-healing ability of the concrete due to more calcium carbonate to be precipitated (59).

After the investigation of self-healing capability of cementitious composites with different admixtures such as chemical admixture, expansive agents and geo-materials, a self-healing concrete with normal water/binder ratio was developed and applied as a new method for crack control and enhanced the service life in concrete structure (60). Furthermore, this self-healing concrete was fabricated in factory and used for the construction of artificial water-retaining structures and actual tunnel structures. Crack-width of 0.15 mm was self-healed after re-curing for 3 days and the crack width decreased from 0.22 mm to 0.16 mm after re-curing for 7 days. Water permeability coefficient of self-healing concrete was significantly lower than that of conventional concrete. Meanwhile, the cracking sensitivity of developed self-healing concrete was similar to expansive concrete and has a better cracking resistance than normal concrete. Ahn (60) concluded that self-healing of the developed concrete occurred mainly due to the swelling effect, expansion effect and re-crystallization and the utilization of appropriate dosages of geo-materials allowed a high potential for the repairing of cracked concrete under the water leakage of underground civil infrastructure such as tunnels.

Additional water is essential for the mechanism of autogenous healing, but in some cases this is a problem when the availability of water is limited. Meanwhile, fly ash is a pozzolanic material that reacts with $Ca(OH)_2$ from cement hydration and produces C-S-H gel. Significantly, this reaction is less influenced by the availability of free water than the hydration reaction of cement. Termkhajornkit (61) investigated the self-healing ability of fly ash–cement paste due to the autogenous shrinkage cracking in a sealed curing condition after 28 days. Experimental results showed that the fly ash–cement system had the self-healing ability for shrinkage cracks. The self-healing ability of fly ash–cement paste increased as the replacement ratio of fly ash increased from 0% to 50% by volume. Hence, hydrated products from fly ash might seal the cracks and prolong the service life of materials. However, the self-healing ability, the efficiency and the mechanical property recovery of ordinary concrete added fly ash require to be further explored.

5. SELF-HEALING OF FIBER REINFORCED CEMENTITIOUS COMPOSITE

Self-healing capability of fiber reinforced cementitious composites was also attractive and investigated by many researchers, such as Li (10) and Homma (62–64). Especially, ECC has been fast developed in recent years as an extremely durable and environmentally friendly material. Given the well-controlled crack width, Li and coworkers (4, 65) have investigated the self-healing behavior of ECC under a number of exposure conditions. In their experiments, deliberately pre-cracked ECC specimens were exposed to various commonly encountered environments, including water permeation and submersion, wetting and drying cycles, and chloride ponding. The mechanical and transport properties can be largely recovered, especially for ECC specimens preloaded to below 1% tensile strain. Besides the small crack width, the low water/binder ratio in addition to the large amount of fly ash in their mixture also helps promote self-healing via continued hydration and pozzolanic activities. Based on experimental results, Şahmaran (39) proposed that micro-cracks of ECC can be easily closed by autogenous healing process even after exposure for 30 days to NaCl solution. The observed autogenous healing in ECC added fly ash can be attributed primarily to the large fly ash content and the relatively low water to binder ratio within the ECC mixture (39, 50, 66–68). Both transport properties, permeability, and chloride diffusion, showed a decrease over time not only due to the tight crack width but also the presence of self-healing of the micro-cracks. From these studies, it was apparent that self-healing both in the mechanical and transport sense was present in ECC. Recent work (64) showed that many fine fibers of polyethylene (PE) were bridging over the crack and crystallization products became easy to be attached due to the PE fibers, even though crack width reached 100 μm. However, in the place of steel cord bridging of cementitious composite, the deposition of crystallization products was not seen. Similarly, when crack width was too wide, little attachments of the crystallization products could be confirmed. Therefore amount of the PE fibers per volume has a great influence on the self-healing if the crack width was well-controlled. Also, polyvinyl alcohol (PVA) fibers in ECC provide nucleation sites for healing products that may aid in the self-healing of ECCs.

Self-healing of ECC has been concerned by many researchers in recent years (16, 35, 69–72). The resonant frequency measurements and the permeability measurements together suggested that autogenous healing within cementitious materials can be achieved, provided that damage must be restricted to very tight crack widths, below 150 μm and preferably below 50 μm, at least under 10 wet–dry cycles exposure regime (69). The microstructures of ECC specimens before and after self-healing are shown in Figure 4 (a) and (b). Further, the majority of autogenous healing products are characteristic of calcium carbonate crystals from image analysis results. Specifically, C-S-H is the main self-healing product for crack widths of 15 μm, and C-S-H and $CaCO_3$ are the main self-healing products for crack widths of 30 μm. Less self-healing product is seen at crack widths of 50 μm; however, below this width, cracks can be almost completely healed (71). It is believed that rehydration and the formation of

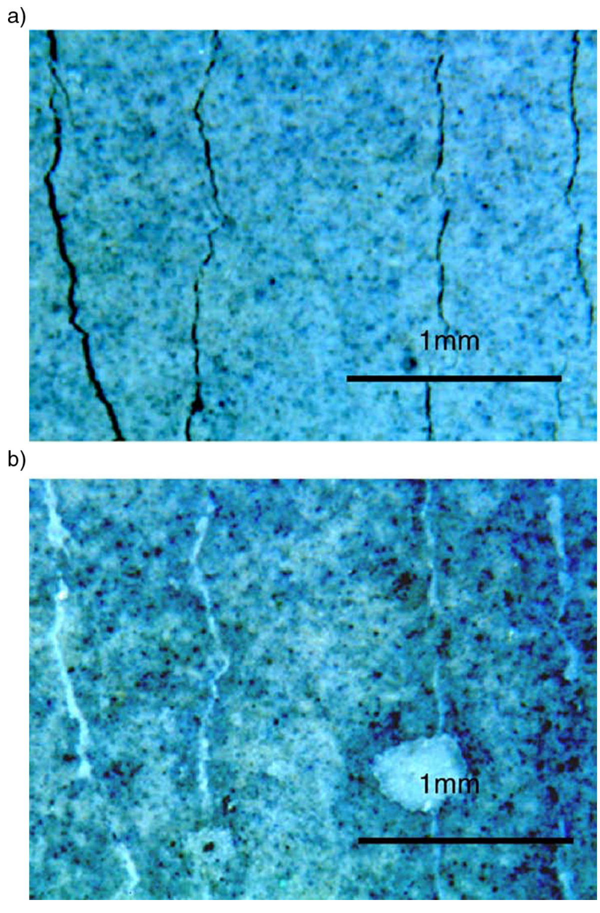

FIGURE 4. Microcracks in ECC before and after self-healing, (a) Before self-healing, (b) After self-healing (69).

$CaCO_3$ crystals are the main reasons for the self-healing phenomena and exposure of crack damaged specimens to wet-dry cycles was the most effective promoter of self-healing.

Autogenous healing of early ages (3 days) ECC damaged by tensile preloading was investigated by Yang (16). Comparison of the self-healing characteristics of the early age (3 days) specimens with those of more mature specimens at 90-day age or older, it found that higher stiffness recovery magnitude was attained in mature specimens than in young specimens. Figure 5 shows the percentage stiffness recovery for the 3-day age specimens as well as those for 6-month old specimens, after pre-damage to different levels, and then allowed to undergo re-healing with identical cycles of wetting and drying. The recovery decreased with increasing damage level for the young specimens, dropping from 100% at 0.3% pre-damage to about 10% recovery at 3% pre-damage. For the more mature specimens the recovery was remarkably maintained at approximately 80% for all four levels of pre-damage (0.5%, 1.0%, 2%, 3%). The author has pointed out that, for the same imposed (pre-damage) strain, the younger specimens tended to develop a smaller number of cracks of a larger averaged width compared to mature specimens, while the mature ECC accommodated a larger number of cracks and maintained a tight crack width on average. Regardless of age, a common trend was also observed that smaller cracks (less than 20 μm width before healing took place) tended to be more completely filled with C-S-H gels, while the larger cracks (50 μm or larger) tended to be partially filled with a mixture of C-S-H gels and calcite particles after the same exposure condition resulting in incomplete healing.

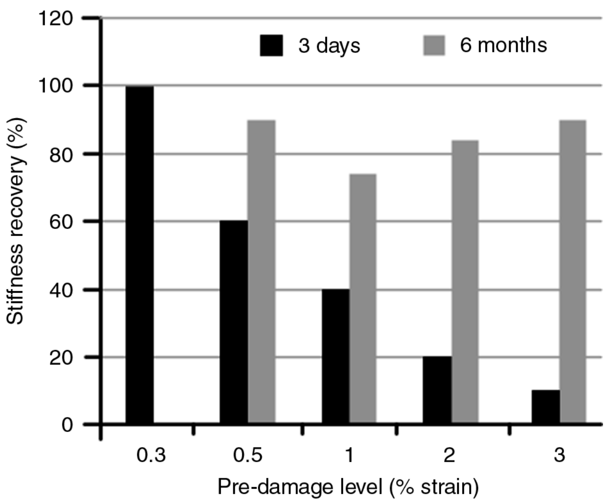

Figure 5. Stiffness recovery on autogenous healing for 3-day and 6-month age ECC specimens, subjected to various pre-damage levels (16).

An interesting approach on self-healing capability of ECC was proposed by Qian (70). Inspired the concept of nanoclay proposed, nanoclay was added in the mixtures to investigate its feasibility to act as internal water reservoirs to promote self-healing behavior of ECC, eliminating the dependence on the external water supply. Due to the water retaining capacity of nanoclay to internally cure and heal the damage along the microcracks, the air cured sample showed reasonable recovery of deflection capacity and the flexural strength increased at the age of 14 days and 28 days. So it was promising to utilize nanoclay as distributed internal water reservoirs to promote self-healing behavior within ECC without relying on external water supply. According to the procedure and thoughts of their work, it seems that nanoclay can be considered as a catalyst in the embedded capsule self-healing strategy and unhydrated cement particle as self-healing agent (73–76). In some sense of methodology, there exists a consistence between autogenous healing and autonomous healing.

6. MODELLING AND SIMULATION CONTRIBUTING TO SELF-HEALING

Experimental research has revealed the feasibility and the recovery of mechanical properties for self-healing concrete. However, it is generally not difficult to directly extract the quantitative measurements such as the autogenous healing efficiency of unhydrated cement nuclei and the exact dosage of healing agent for autonomous healing approach in terms of experimental methods. Simulation and modeling tools as well as various analytical approaches provide a powerful extension of traditional experimental investigations and offer an alternative to at least partly overcome these deficiencies.

Using an advanced history dependent contact model for DEM simulations, Herbst (77) proposed a model for local self-healing that allows damage to heal during loading such that the material strength of the sample increases and failure/softening is delayed to larger strains. By a concurrent algorithm-based computer simulation system with the acronym SPACE (Software Package for the Assessment of Compositional Evolution), He (78, 79) investigated the influences of water/cement ratio and cement fineness on the structure of unhydrated cement nuclei that is underlying concrete's self-healing capacity in hardened cement paste. Compared to fineness of cement, water/cement ratio is the dominating factor for the self-healing capacity of concrete. Based on the concept of autonomous healing and elementary principles from probability theory, Zemskov and Jonkers (80, 81) have recently developed analytical models for computation of the probability that a crack hits an encapsulated particle. The analytical models (random placement mode of capsules in a layered structure and fully random placement mode of capsules in bulk material) allowed to estimating combinations of crack lengths, capsule size, and mean intercapsule distance in order to analyze the efficiency of a self-healing material. However, their models are restricted in two-dimensional case. For three-dimensional case, further work need to do.

For investigation of the self-healing phenomenon on healing the cracks of matrix, it is necessary to consider the self-healing efficiency or amount of the rehydration product of unhydrated cement nuclei. Based on two practical different cracking modes of unhydrated cement nuclei, i.e., splitting crack mode and dome-like crack mode as respectively illustrated in Figure 6 and Figure 7, theoretical models on the self-healing efficiency of rehydration reaction of the unhydrated cement nuclei were developed by Lv (82–84). Recurring to a generalized hydration reaction model of cement particles and the particle size distribution of cement approximated by Rosin-Rammler function (85, 86), the self-healing efficiency model quantitatively considered the influence of the volume fraction, particle size distribution and cracking modes of unhydrated cement nuclei randomly distributed in hardened cement paste. Generally speaking, for unhydrated cement particles on a specific crack surface, splitting crack mode and dome-like crack mode may occur together. Hence, for considering the efficiency due to rehydration of unhydrated cement nuclei, the total self-healing efficiency should was commonly developed based on the two different cracking modes. Furthermore, the reliability of these theoretical models was verified via computer simulation technology and the simplified self-healing process was also simulated. It showed that based on the different cracking mode of unhydrated cement nuclei randomly distributed in the matrix, the self-healing efficiency had a distinction even for the same particles size distribution. However, the specific rehydration reaction of unhydrated cement particles left in matrix should be well considered to determine the healing efficiency of autogenous healing.

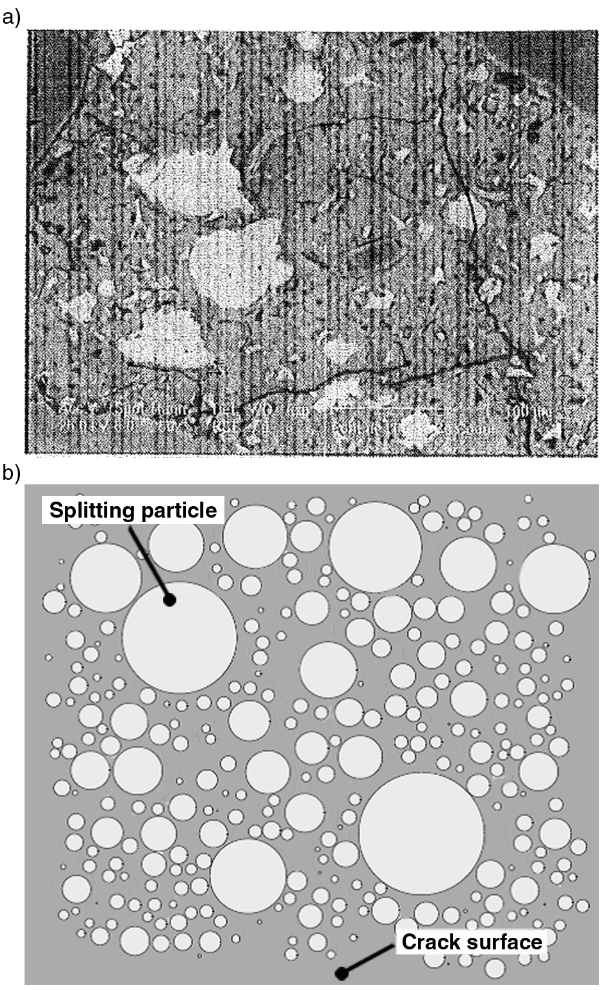

FIGURE 6. Self-healing efficiency of unhydrated cement nuclei for splitting crack mode (83), (a) A practical cracking surface zone for unhydrated cement nuclei were splitting in cementitious materials due to different mechanisms and its induction (87), (b) Splitting crack mode.

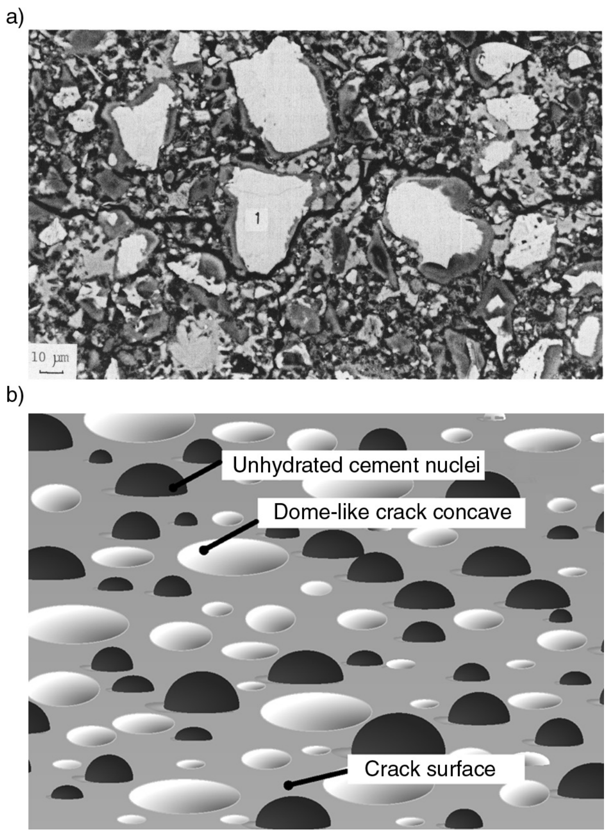

FIGURE 7. Self-healing efficiency of unhydrated cement nuclei for dome-like crack mode (82), (a) The tendency of cracks to follow the external surface of the unhydrated cement nuclei due to the unhydrated cement nuclei as strong inclusions in hardened cement paste (88), (b) Crack surface of dome-like crack mode.

For determining the exact dosage of capsules incorporated via autonomous healing, several intersecting models of cracks and capsules had been presented for regularly distributed crack patterns in cementitious composite. Before loading or at the initial stage of service, both the number and the size of cracks generally are small. In other words, the crack spacing could be larger than the size of capsule. Of course, the crack may propagate with the increase of loading or the service time. However, it is expected to heal the defects in matrix before micro-cracks become macro-cracks. Consequently, based on the assumption that the crack spacing is larger than the length of capsule embedded, short capsules model were developed by Lv (89, 90) to determine the exact dosage. Meanwhile, the long capsules model for dosage of capsules required was also presented to investigate the autonomous healing in cementitious composite (91, 92). Based on a general assumption that the capsules are randomly dispersed in the matrix and the cracks of matrix appear to be certain layout or special orientation, Lv (89, 90) developed the analytical model on determining the dosage of capsules embedded to heal the cracks of cementitious composites. Specifically, the outer/inner cracks in materials caused by different type of mechanisms were simplified to linear cracks in a two dimensional surface model, or planar cracks in Figure 8(a) and zonal cracks in Figure 8(b) in a three dimensional model. Then, by combining the geometrical probability theory with binomial probability distribution, the theoretical solutions on the exact dosage of capsules required to completely repair the cracks for specific crack patterns were developed. For example, considering the crack pattern as shown in

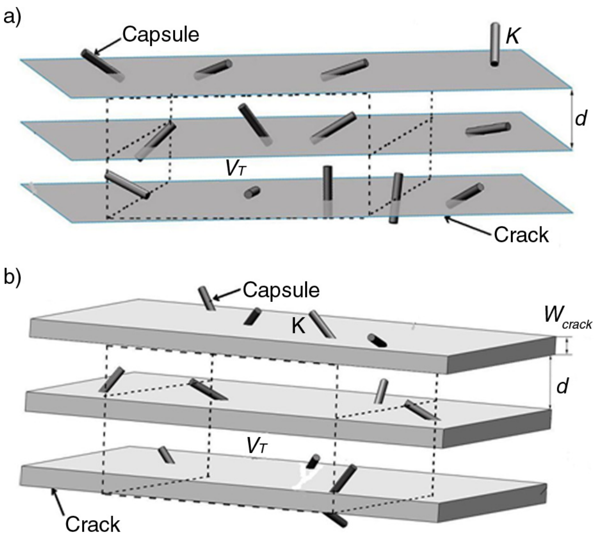

FIGURE 8. Schematic illustration of simplified pre-oriental cracks pattern in cementitious material based on different cracking mechanisms, (a) Planar cracks pattern, (b) Zonal cracks pattern.

Figure 8(b), assume that there are parallel planar cracks with a width of w_{crack} and the crack space is d, and capsules K containing repair-agent are randomly dispersed in cementitious matrix. Moreover, let l_{cap}, r_{cap} be the length and the radius of the cylindrical capsule K and a capsule K can repair the crack with a fixed volume V_{heal} in matrix. Concerning to this crack pattern, how to determine the number of capsules completely repairing those zonal cracks in sampling region was investigated by authors from the viewpoint of geometrical probability (90). After a series of computation and transformation, it was expected that the lowest volume fraction V_V of capsules required in per unit volume of cementitious matrix is expressed as [3]

$$V_V \geq \frac{2w_{crack}}{l_{cap} + \pi r_{cap} + 2w_{crack}} \cdot \frac{\pi r_{cap}^2 l_{cap}}{V_{heal}} \qquad [3]$$

At the same time, the reliability of those proposed theoretical solutions was verified via computer modeling technology. The authors also presented the hitting probability model of a crack intersecting with capsules when cracks randomly occurred and capsules with healing agent were disorderly dispersed in the matrix (93). These theoretical models and analytical solutions were expected to quantitatively characterize the self-healing efficiency of unhydrated cement nuclei or dosage of healing agent required and to be facilitating the experimental research.

7. CONCLUSIONS

A review of current work in the arena of self-healing cementitious materials including autogenous healing and autonomous healing was presented. Attentions were paid to autogenous healing capability of an innovative concrete added geo-materials, self-healing of engineered cementitious composites and fire-damaged concrete, modeling and simulation of self-healing phenomenon, effect of mineral and admixtures on mechanism and efficiency of self-healing concrete. Self-healing cementitious material is promising to improve their long-term performance, service life and durability problems due to cracking. The development of self-healing concrete potentially offers great benefit to the construction industry and potentially massive savings to the annual amount of cost on repair and maintenance of concrete structures in the future.

Compared to autogenous healing, much more issues for autonomous healing want to be solved. First, it is difficult to determine the critical dosage of capsules in practical experiments and applications based on various actual conditions in cementitious composite. Second, how to select the self-healing agent, optimize a critical size and geometrical shape of capsules and guarantee the compatibility of agent used in cementitious materials. The long term durability of concrete materials healed by autonomous healing is also vacant. However, the methodology of computer simulation and modeling method are recommended for these problems from recent work of autonomous healing in cementitious composites.

To improve the efficiency of autogenous healing and mechanical properties, some novel techniques were developed such as the post-tensioning of cementitious materials using shrinkable polymers, incorporating the nanoclay and PVA fibers. Those approaches have deed facilitated the occurrence of self-healing behavior and have improved the efficiency. Meanwhile, autogenous healing concrete could be optimized if free water (i.e. nanoclay), a critical crack width, fibers control the cracks and good curing environment are available in the mixture. Of course, the intrinsic or natural character of cementitious materials has to be taken into account in designing autogenous healing concrete, such as a relatively high water-binder ratio and the low efficiency of rehydration of unhydrated cement nuclei. The autogenous healing of cementitious materials not only offers a immediately promising solution to crack repair and improves the long-term durability and service life, but also consumes the anthropogenic CO_2 emissions, which jeopardize the conditions of earth and are harm for humans' life.

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