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# Autonomic and Autogenic Crack Healing Approaches in Cementitious Materials

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## ABSTRACT

*Concrete is extensively used worldwide because of its low cost and feasibility. Cracking in early age concrete is the main obstacle in sustainability. Intrinsic and extrinsic crack healing are two fundamental approaches in concrete materials. Autogenic self-healing is understood as a chemical reaction of un-hydrated particles and the precipitation of $CaCO_3$ in cement-based composites. In contrast, autonomic self-healing is considered an artificial means of crack repair. The current review paper will show recent autonomic and autogenic approaches. The conclusion will summarize advantages and disadvantages, as well as future recommendations based on the literature review.*

**Keywords***: Autogenous, autogenic, autonomic, autonomous, self-healing, $CaCO_3$precipitation, concrete, cement.*

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## INTRODUCTION

Concrete is the most commonly used construction material throughout the world, as it is durable, robust, and rather inexpensive. Unfortunately, the brittle behavior of concrete under tensile loading is one of the adverse properties. Cracking at an early age is one of the great flaws or damage potentials in any phase of concrete structure. The main reasons cracks develop in concrete can refer to the following cases: volumetric change due to high temperatures, plastic settlement, creep, loading, shrinkage, or deterioration mechanisms such as freezing and thawing cycles, and alkali-silicate reaction. The formation of cracks allows aggressive liquids and gasses to penetrate the concrete layer and contact the reinforcement, finally leading to disastrous damage at low ultimate strain (around 0.01%) without warning due to the durability of concrete. Although safety and durability are critically important in any successful engineering project, concerns for infrastructure sustainability are growing due to greater recognition for the impact of the built environment on the natural environment.

Cracks found in early-age inspection and maintenance techniques for concrete structures are essential and difficult over time, especially in the case of large-scale concrete structures. The cost of continuous service and repair is drastically high in many infrastructures such as highways and tunnels. One third of the annual budget for enormous civil engineering construction is spent on inspection -- monitoring, maintenance, upgrade, and repair relyonthe cost and amount of labor required for diagnosis and repair work. The average annual maintenance cost for bridges in the USA is estimated at $5.2 billion and in Europe this cost comprises 50% of the annual budget. The implementation of certain protective strategies to prevent or retard steel corrosion can result in bridges with long-term durability, extended structural life, and significantly reduced maintenance and repair costs.

Various methods have been proposed to reduce maintenance and extend the service life of infrastructure according to material and structural engineering. Utilizing durable cementitious material may be an alternative strategy to control the development of single cracks, increase durability and reduce permeability of high-strength concrete. There have been many recent developments in the production of more durable concrete, and self-healing concrete. To date, self-healing cementitious composite approaches focus on two aspects: autonomic and autogenic crack healing in concrete. Autonomic crack healing is identified as man-made inclusions and autogenic crack healing is known as the natural hydration ability of un-hydrated cement to heal cracks over time.

Two main aspects to artificially improving fracture healing in concrete are the microcapsule and capillary tube methods. Microcapsules and capillary tubes filled with healing agents must have two outstanding characteristics including low viscosity and adequate adhesive strength. Due to diversity in manufacturing, different microcapsules are produced in terms of size, wall thickness and module of elasticity. Indeed, characteristics affect the amount of healing agents, resistance to failure in the mixing progress and the growth of cracks in a concrete matrix. Attention to microcapsule preparation and healing agents, also in addition to their compatibility with concrete, can improve the healing of concrete as a smart material.

Autogenic healing is understood as a chemical reaction of un-hydrated particles and $CaCO_3$precipitation in cement-base composites. The six following factors play an important role in autogenous healing: pervasiveness, stability, cost-effectiveness, reliability, quality and repeatability. To date, very little work has been carried out on reliability and repeatability. Three general, critical criteria conditions are necessary for reliable self-healing in concrete materials: the presence of specific chemical species, exposure to various environmental conditions, and small crack width (CW). To improve autogenic healing in concrete, various strategies are considered in terms of reliability and repeatability of healing. Engineered cementitious composites (ECC) exhibit healing of crack width intrinsically independent of steel reinforcing ratio and structural size under extreme loading.

In the current study, a survey is proposed of two major aspects associated with autonomic and autogenic crack healing techniques and requirement parameters of cementitious materials. In sequence, the advantages and disadvantages of each approach will be discussed based on the literature review. As a result, further studies will be recommended to enhance high self-healing efficiency in concrete materials.

### Autonomic Crack Healing Approach

The bio-inspired phenomena such as remediation of broken bones and regeneration of damaged skin inspire the re-design of materials to achieve new routes toward safer, longer-lasting products and components. The autonomic healing concept is described as follows: a microencapsulated healing agent is embedded in a structural epoxy matrix containing a catalyst (Grubb's) capable of polymerizing the healing fluid. (a) Cracks form in the matrix wherever damage occurs; (b) next, the crack ruptures the microcapsules, releasing the healing agent into the crack plane through capillary action; (c) finally, the healing fluid contacts the catalyst, which is randomly distributed in the matrix and triggers the polymerization reaction that helps repair the damage by bonding the crack surfaces closed.

In 1994, the first application of autonomic healing as man-made, self-healing ability of concrete was introduced by Dry (Dry 1994). Upon damage-induced cracking in the matrix, microcapsules are supposed to release their encapsulated liquid healing agent into the crack planes. All the involved materials must be carefully designed. For example, the encapsulation procedure must be chemically compatible with the reactive healing agent, and the liquid healing agent must not diffuse out of the capsule shell during its potentially long shelf life. At the same time, the microcapsule and tube walls must be resistant enough to the processing conditions of the host composite, while maintaining excellent adhesion with the cured matrix to ensure that the capsules rupture upon composite fracture. A self-healing mechanism or self-healing agent in concrete should ideally comply with the following items: ability to seal the cracks, compatibility with concrete ingredients, long-term potential activity, the ability to tend to multiple healing events, inexpensiveness and suitability to autonomous healing. Low viscosity, suitability to immigrate to crack faces and strength bonding are three critical criteria to enhancing suitable healing agents.

### Autonomic Crack Healing Techniques

Two main aspects are considered with regard to the autonomic healing concept, namely, the encapsulation method and the healing agent to be encapsulated. Two main methods have been proposed including the use of microcapsules and capillary tubes included healing agents, which are embedded in the concrete.

### Microcapsules as Carriers of Healing Agents

Microcapsules act as carriers which contain the healing agent. Furthermore, they are able to sense cracks and trigger the healing mechanism by releasing the healing agent (Figure2-1). In addition, the encapsulation material should exhibit good adhesion to the matrix and limited extension in order to rupture upon concrete cracking. Until now, the microencapsulation method has been improved steadily, modified and adapted for a variety of purposes and uses.

The initial development of microencapsulation began with the productionof pressure-sensitive copying papers containing dyes, at the end of the 1950s. Nano/microencapsulation has been defined as a technology of packaging solids, liquids, and protective walls that release their contents at controlled rates over prolonged periods under certain conditions. Microcapsules consist of two parts, the core and the shell. Compatibility of the core with the shell and host material is important for enhancing the high efficiency of microencapsulation. Nowadays, microencapsulation technology is eminent for using phase-change materials (PCM) in construction materials. PCMs can perform in gypsum (Noda Plywood Mfg. Co. 1985; Oliver 2011; Su, Wang et al. 2012), board, plaster, concrete, cement, paints and sealants (Tomiuchi and Nishihama 1986; Heinen and Babcock 1988; Origasa, Yoshida et al. 1988). Numerous researchers have reported investigation and analysis of thermal energy storage systems incorporating PCM for use in different construction materials (Regin, Solanki et al. 2008; Castell, Martorell et al. 2010; Castellón, Medrano et al. 2010; Zhang and Niu 2010; Cabeza, Castell et al. 2011; Chen and Fang 2011; Sadineni, Madala et al. 2011; Zhao and Zhang 2011).

Two basic techniques used in microcapsule manufacturing are physical and chemical, and include physical-chemical and physical-mechanical techniques. A summary of microcapsule method classification is shown in Table 2-1. A thorough description of these techniques is outside the scope of this review (Ghosh 2006; Boh and Šumiga 2008).

For self-healing materials, the most common encapsulation technique is in situ polymerization, which is a subset of the chemical method. Many papers have reported encapsulation fabrication by reacting urea-formaldehyde (UF)(White, Sottos et al. 2001; Asua 2002; Brown, Kessler et al. 2003; Yuan, Liang et al. 2006; Yuan 2008) (Figure 2-2), melamine-formaldehyde (Yuan, Liang et al. 2007), melamine-urea formaldehyde (MUF) (Liu, Sheng et al. 2009), polyurethane (PU) (Cho, Andersson et al. 2006; Yang, Keller et al. 2008), or boron trifluoride diethyl etherate (Xiao, Yuan et al. 2009; Xiao, Yuan et al. 2009) and the subsequent formation of a polymer shell wall at the interface of droplets in an oil-in-w

**Table 2-1:** Summary of microcapsulation preparation ater (o/w) emulsion.

| Chemical processes | Physical processes | |
|---|---|---|
| | Physical-chemical | Physical-mechanical |
| • interfacial polymerization<br>• in situ polymerization<br>• matrix polymerization | • Coacervation<br>• Layer-by-layer (L-B-L) assembly<br>• Sol-gel encapsulation<br>• Supercritical $CO^{2-}$ assisted microencapsulation | • Spray-drying<br>• Multiple nozzle spraying<br>• Fluid-bed coating<br>• Centrifugal techniques<br>• Vacuum encapsulation<br>• Electrostatic encapsulation |

Due to the development and specialization in microencapsulation technologies and applications, there are many variables to consider such as size, wall thickness, microcapsule toughness and matrix surrounding. As a result, microencapsulation products differ in structure and terminology (Yeom, Oh et al. 2000; Boh and Šumiga 2008).

Recently, Yang et al. have proposed a new system of carbon microfibers and microcapsules (PSMs) with an oil core and silica gel shell, consisting of methylmethacrylate (MMA) as the healing agent together with an initiator (catalyst) containing triethylborane (TEB). The overall preparation procedure of the PSMs is illustrated in Figure 2-3. The first step was to self-assemble the surface-sulfonated polystyrene particles at the water-oil droplet interface. The oil phase, either methylmethacrylate (MMA) monomer or triethylborane (TEB) solution (1.0M in hexane), was microencapsulated following the same procedure. The surface-sulfonated polystyrene particles of 0.7 ± 0.5μm in diameter were prepared as reported previously and the sulfonation time of polystyrene particles was 60h for this study. After some preliminary trials, 0.15g of the sulfonated polystyrene particles were dispersed into 45ml de-ionized water using a high-intensity ultrasonic vibracell processor operating at 20kHz and up to 10W for 2min to form a homogeneous system. Then 3g of oil phase (oil/TEOS = 17/3, mol/mol) was introduced and stirred continuously using a magnetic stirrer operating at 500rpm in a nitrogen atmosphere. The turbid mixture gradually evolved into a creamy-white emulsion in appearance after 20min. Finally, the sample was set aside for 24 hours (Yang, Hollar et al. 2011).

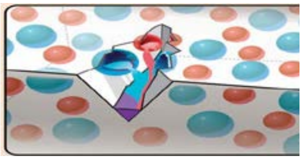

**Figure 2-1:** In capsule-based self-healing materials, the healing agent is stored in capsules until they are ruptured by damage or dissolved (White, Sottos et al. 2001)

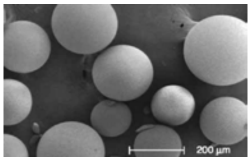

**Figure 2-2:** Urea-formaldehyde microcapsules containing dicyclopentadiene prepared by emulsion in situ microencapsulation. Reproduced from Brown, White and Sottos with permission (Brown, White et al. 2004)

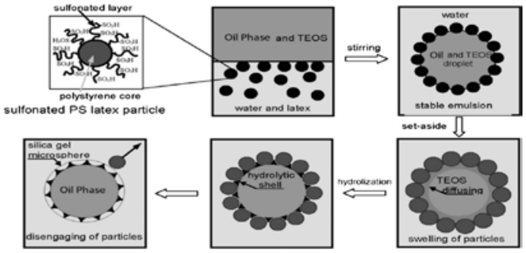

**Figure 2-3**: Schematic illustration of passive, smart microcapsule formation (Yang, Hollar et al. 2011)

### Capillary Tubes as Carriers of Healing Agents

A bio-mimetic method of obtaining self-healing functionality in composite materials is to embed hollow tubes with a reactive healing agent into polymers (Dry 1996), in polymeric composites at a millimeter length scale (Motuku, Vaidya et al. 1999), bulk concrete (Dry 1992; Dry 1994; Dry and McMillan 1996; Li, Lim et al. 1998; Dry 2000), and at a micrometer length scale (Bleay, Loader et al. 2001; Pang and Bond 2005a; Pang and Bond 2005b). These hollow fibers are very brittle. When cracking occurs, repair materials such as methyl methacrylate and ethyl cyanoacrylate liquid (Dry 1994; Lia, Limb et al. 1998; Dry 2000) are released from inside the cracks and subsequently heal the cracks like a host material. Future healing of the chemical agent streaming to the crack face plays an important role in crack elimination. This idea has been applied to cementitious materials to alter permeability, ductility, repair cracks, prevent corrosion and extend service life (Dry 1990).

In order to implement the hollow glass fiber repair mechanism, there are a number of logistical issues that must first be addressed. One of the initial challenges encountered when creating this type of self-healing system is the development of a practical technique for filling the hollow glass fibers with repair agent. When approaching this problem, the dimensions of the glass fiber itself must be considered, including diameter, wall thickness, and fiber hollowness, as well as the viscosity and healing kinetics of the repair agent (Hucker, Bond et al. 2003; Murphy and Wudl 2010). Hollow glass fibers with large internal volume have already been shown to improve structural performance of materials and maximize the storage capacity without creating sites of weakness within the composite (Hucker, Bond et al. 2002).

An experimental attempt of using adhesive-filled borosilicate capillary tubes embedded in fiber-reinforced ECC (Engineered Cementitious Composites) was carried out by Joseph et al. The trial beam is illustrated in Figure 2-4. They employed Cyanoacrylates (superglues) as one part of the healing agent due to acidic solutions, and quicker setting times into capillary tubes embedded in ECC material. Joseph et al. demonstrated that tubes with open ends would be better as this would eliminate the suction effect of closed ends after crack formation (Joseph, Jefferson et al. 2007). Indeed, the vacuum created between healing agents and wax plugs at the end of hollow tubes makes negative pressure, preventing the release of healing agents into crack faces.

In a similar work, Tittelboom et al. conducted experimental studies on two-component polyurethane foam as healing agents, with glass and ceramic tubes as carriers. Healing agents have two eminent characteristics: low viscosity and the polymerization reaction. This means that the polymerization reaction does not rely on the mix ratio of both compounds. Expansion healing agents provide two benefits. First, in the expanding reaction, the additional volume created by the crack may be filled up with this healing agent without leaving too many gaps behind. Secondly, the expanding reaction acts as a driving force, pushing the healing agent out of the tubular capsules upon crack formation. Since the glass capsules used in most studies may have a negative effect on concrete durability (alkali-silica-reaction), in addition to glass, an alternative encapsulation material like ceramics was studied in this research. The advantage of encapsulating the healing agent is that multiple healing cycles may be obtained. Meanwhile, according to the average regain of strength and stiffness, the healing efficiency during the first cycle was comparable with the efficiency of manual crack healing. As cracking and crack healing occur internally, High Resolution X-ray Computed Tomography (HRXCT) was used as a non-destructive test method to evaluate the efficiency of crack healing (Figure 2-5) (Van Tittelboom, De Belie et al. 2011). More recently, acoustic emission analysis has been applied as a suitable technique for evaluating crack healing efficiency of concrete incorporated with encapsulated healing agents (Van Tittelboom, De Belie et al. 2012) (Figure 2-6).

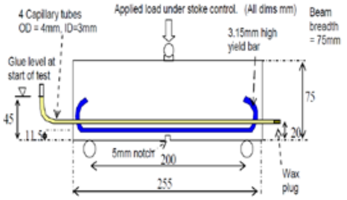

**Figure 2-4:** Testing arrangement (Joseph, Jefferson et al. 2007)

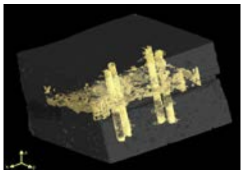

**Figure 2-5:** 3D visualization of the region in the mortar sample which contained the tubes and the crack (Van Tittelboom, De Belie et al. 2011)

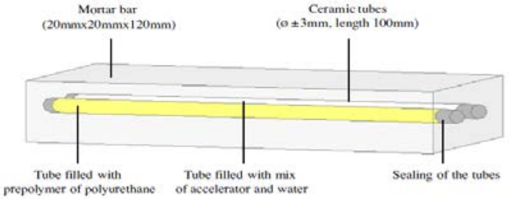

**Figure 2-6: Protection of the ceramic tubes by means of mortar bars (Van Tittelboom, De Belie et al. 2012)**

**Requirement parameters for Autonomic Crack Healing**

Autonomic repair is triggered by rupturing microcapsules in response to damage, followed by a release of healing agents into the crack plane where it is mixed with the catalyst and polymerizes. Four critical parameters in order to achieve effective self-healing exist. First, the thickness of the microcapsules' wall plays an important role in releasing healing agents. Very thick capsule walls will not rupture when the crack approaches, whereas capsules with very thin walls will break during mixing processes. Secondly, the healing liquid quantity that microcapsules deliver into the crack face is related to microcapsule diameter for a given weight fraction linearly (Rule, Sottos et al. 2007). Third, the elastic modulus of microcapsules and surrounding matrix as well as elastic modulus interactions determine how cracks will propagate in the matrix (Figure 2-2) (White, Sottos et al. 2001; Murphy and Wudl 2010). Finally, healing agent characteristics such as viscosity and bond strength are vital for autonomic healing.

Microcapsule walls must be sufficiently resistant to processing conditions of the host materials, while maintaining excellent adhesion with the cured concrete matrix to ensure that the capsules rupture upon composite fracture. The shell wall thickness largely relies on manufacturing factors and is typically between 160 and 220nm thick. In fact, the shell properties are critically depended upon kinetics of polymerization reactions, which are pH and temperature-dependent (Williams, Bond et al. 2009). The stability of urea-formaldehyde microcapsules prepared by in situ polymerization technique is mainly determined by the chemical structure and mechanical properties of the cross-linked shell material (Brown, Kessler et al. 2003).

Mean microcapsule size is affected by agitation rate or preparation conditions (Yeom, Oh et al. 2000). When the agitation rate is increased, the average microcapsule diameter decreases. Microcapsules with average diameters in the range of 10-1000mm were produced by varying the rate of agitation in the range of 200–2000rpm (Brown, Kessler et al. 2003). Extensive studies on controlling the size and surface morphology of microcapsules were conducted and the effects of three critical factors were examined, namely employing different pre-polymers, agitation rates and weight ratios of urea to formaldehyde (Cosco, Ambrogi et al. 2006; Yuan, Liang et al. 2006; Cosco, Ambrogi et al. 2007). On the other hand, microcapsules with a variety of diameters can carry certain volumes of self-healing agents to a crack face. The amount of healing agent stored in a microcapsule has a linear relation to the average microcapsule diameter for a given weight fraction of the capsules. Based on two relationships, to achieve optimum healing for a given crack size, microcapsule diameter and weight fraction are chosen logically (Rule, Sottos et al. 2007). Microcapsule diameter was found to have a significant effect on failure strength, with smaller capsules sustaining higher loads before failure. Capsules with smaller diameters, down to 220nm, were produced by utilizing sonication techniques and an ultrahydrophobe solution by Blaiszik et al. They demonstrated that it was possible to achieve optimum toughening at lower concentrations (Figure 2-3)(Brown, White et al. 2004; Brown, White et al. 2005; Blaiszik, Sottos et al. 2008; Blaiszik, Caruso et al. 2009). Microspheres with small diameter had higher self-healing efficiency than those used in previous polymer matrices (Wilson, Caruso et al. 2008). The stability of microcapsule diameter and shell wall thickness investigated under humid or wet environments are associated with mechanical properties (Yang, Keller et al. 2008).

The measurement of regained elastic modulus of healed cracked composites was found to be a critical factor in evaluating healing system efficiency (Lia, Limb et al. 1998). Investigating the mechanical properties of microcapsules such as elastic modulus illustrated that capsules with higher elastic modulus than polymer matrix material caused the development of a stress region surrounding due to the tendency to deflect cracks away from the capsule (Keller and Sottos 2006).

Many researchers have reported employing a variety of chemical additives as healing agents in cementitious materials. Regardless of the three mentioned critical causes -- size, wall thickness and modulus elasticity of microcapsules and matrix surrounding -- healing agents comprise one of the major, critical keys to achieving maximum self-healing efficiency in concrete or polymers (Lia, Limb et al. 1998; Blaiszik, Sottos et al. 2008; Wilson, Moore et al. 2008) in terms of regaining mechanical properties (Brown, Sottos et al. 2002; Liu, Lee et al. 2006). The most commonly used healing agents in concrete can be addressed to Superglue (ethyl cyanoacrylate) (Lia, Limb et al. 1998), cyanoacrylate (Dry 1992; Dry 1996), methylmethacrylateas (Carolyn 1994; Carolyn and William 1996) and alkali-silica solutions (MIHASHI and KANEKO 2000) as chemical healing agents to seal and re-heal the cracks in concrete. Recently, scientists and engineers have been focusing on utilizing bacteria as a self-healing agent in concrete (Jonkers and Schlangen 2009; Jonkers, Thijssen et al. 2010). Moreover, the low viscosity of healing agents is a critical factor in obtaining maximum recovery of mechanical strength between damage events. Low viscosity facilitates reaching the damaged site, and subsequently undergoing healing to fill the crack volumes. Another important parameter of adequate healing agents is having a sufficiently strong bond between the crack faces.

**Bacteria as Healing Agent in Autonomic Healing**

A wide array of bacteria live on or in materials, which exist in the earth's environment from natural soils to alkaline lakes (Nielsen, Rainey et al. 1994; Clegg 2001; Belkova 2005) to air, and from the human body to the Arctic ice to the Sahara Desert (Dorn and Oberlander 1981; Douglas and Beveridge 1998; Rodriguez-Navarro, Rodriguez-Gallego et al. 2003; Sakai and Fukuta 2003; Pedersen, Nilsson et al. 2004; Sleep, Meibom et al. 2004; Fajardo-Cavazos and Nicholson 2006; Ghosh, Chattopadhyay et al. 2008; Jonkers and Thijssen 2010). The suitability of bacteria and their ability to participate in calcite precipitation, the ability to react with low-metabolic activity for extended periods of time, to the ability to withstand high mechanical strength and the characterization of long-term viability under dry conditions have been demonstrated by several researchers (Schlegel 1993; Sagripanti and Bonifacino 1996; Stocks-Fischer, Galinat et al. 1999; Ramakrishnan 2007).

Four critical criteria for the microbial precipitation of calcium carbonate ($CaCO_3$) are determined as follows: the concentration of dissolved inorganic carbon (DIC), the calcium concentration, pH and the presence of nucleation sites (areas of extremely localized budding or reaction) (Hammes and Verstraete 2002). The concentration of carbonate ions relies on the concentration of DIC and the pH of a given aquatic system. Several environmental factors, such as temperature and the partial pressure of carbon dioxide, can affect DIC concentration. Consequently, the equilibrium reaction and constant governing the dissolution of $CO_2$ in aqueous media are given in the following equations:

| | | |
|---|---|---|
| $Ca^{2+} + CO_3^{2-} CaCO_3$ | | (1) |
| $CO_{2(g)} \leftrightarrow CO_{2(aq)}$ | ($pK_H = 1.468$) | (2) |
| $CO_{2(aq)}+H_2OH_2CO_3^*$ | ($pK = 2.84$) | (3) |
| $H_2CO_3^* \leftrightarrow H^+ HCO_3^-$ | ($pK_1 = 6.352$) | (4) |
| $HCO_3^- \leftrightarrow CO_3^{2-} + H^+$ | ($pK_2 = 10.329$) | (5) |

The influence of urea on microbial carbonate precipitation (MCP), mechanical properties (Sadegzadeh, Page et al. 1993; Mwaiuwinga, Ayano et al. 1997; De Muynck, De Belie et al. 2007; Siddique and Chahal 2011) and permeability (De Muynck, Cox et al. 2008; Chunxiang, Jianyun et al. 2009) have been investigated by numerous researchers. Urea is degraded to carbonate ($CO_3^{2-}$) and ammonium ($NH_4^+$), resulting in an increase of pH and carbonate concentration in the bacterial environment. The chemical process is given in Eqs (6) to (10). The last two reactions give rise to a pH increase, shifting the bicarbonate equilibrium, resulting in the formation of carbonate ions (Eqs. (9) and (10)). Because the cell walls of bacteria are negatively charged, the bacteria are able to draw cations from the environment, including positively charged calcium ions, which deposit on their cell wall surface. The $Ca^{2+}$ ions then react with the $CO_2^{3-}$ions leading to the precipitation of calcium carbonate ($CaCO_3$) at the cell surface. This precipitation serves as the nucleation site (Eqs. (11) and (12)) (Figure 2-7) (Dick, De Windt et al. 2006; Chunxiang, Jianyun et al. 2009; Van Tittelboom, De Belie et al. 2010) .

| | |
|---|---|
| $CO(NH_2)_2 + H_2O \rightarrow NH_2COOH + NH_3$ | (6) |
| $NH_2COOH + H_2O \rightarrow NH_3 + H_2CO_3$ | (7) |
| $H_2CO_3 + H_2O \leftrightarrow HCO^{3-} + H^+$ | (8) |
| $2NH_3 + 2H_2O \leftrightarrow 2NH_4^+ + 2OH^-$ | (9) |
| $HCO_3^- + H^+ + 2NH_4^+ + 2OH^- \leftrightarrow CO_3^{2-} + 2NH_4^+ + 2H_2O$ | (10) |
| $Ca^{2+} + Cell \rightarrow Cell\text{-}Ca^{2+}$ | (11) |
| $Cell\text{-}Ca^{2+} + CO_3^{2-} \rightarrow Cell\text{-}CaCO_3\downarrow$ | (12) |

George et al. conducted factorial experiments to determine the optimum conditions for significant impact on microbial carbonate precipitation (MCP) based on bacterial cell concentration, and initial urea and $Ca^{2+}$ concentrations. They found that the optimum conditions for MCP were 666mM urea and 250mM $Ca^{2+}$ at $2.3\times10^8$ cells/$mL^{-1}$ bacterial cell concentration (Okwadha and Li 2010). $Ca^{2+}$ ions are necessary for bacterial growth and metabolisation (Yang, Wang et al. 2007).

Bacterial cells cannot be added to cement specimens directly and do not survive due to the decreasing pore diameters during cement material hydration. In terms of increasing viability and the time-related functionality of bacteria (Bang, Galinat et al. 2001; Soltmann, Raff et al. 2003; Soltmann and Böttcher 2008; Wang, Van Tittelboom et al. 2012) and urease enzyme (Bachmeier, Williams et al. 2002) as self-healing agents, a variety of studies employ Polyurethane (PU) (Bang, Galinat et al. 2001; Bachmeier, Williams et al. 2002; Wang, Tittelboom et al. 2010; Wang, Van Tittelboom et al. 2012), silica sol-gels (Soltmann, Raff et al. 2003; Soltmann and Böttcher 2008; Wang, Tittelboom et al. 2010; Wang, Van Tittelboom et al. 2012) and expanded clay particles (Jonkers and Schlangen 2009) as carriers and protection for remediation of cracks in concrete. Earlier reports have shown that bacteria reduced porosity and permeability by up to 50% and 90% (Kantzas, Stehmeier et al. 1992; Gollapudi, Knutson et al. 1995; Stocks-Fischer, Galinat et al. 1999; Muynck, Jan et al. 2005) and also increased compressive strength up to 17% and 25% after 7 and 28 days, respectively (Ghosh, Mandal et al. 2005; Ghosh, Mandal et al. 2006). This novel bio-chemical self-healing agent illustrated good potential for increasing durability, compressive strength and decreasing the water absorption aspects of concrete constructions in wet conditions (Bang, Galinat et al. 2001; Wang, Tittelboom et al. 2010; Wiktor and Jonkers 2011; Chahal, Siddique et al. 2012; Wang, Van Tittelboom et al. 2012).

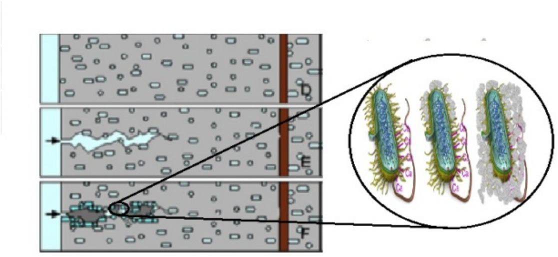

**Figure 2-7:** Scenario of crack healing by concrete immobilized bacteria. Bacteria on fresh crack surfaces become active due to water ingression, they start to multiply and precipitate minerals such as calcite ($CaCO_3$), which eventually seal the crack and protect the steel reinforcement from further external chemical attacks

### Autogenic Crack Healing Approach

Autogenic healing is understood as a chemical reaction of unhydrated particles and precipitating $CaCO_3$ in cement-based composites. Three general, critical criteria conditions are necessary for autogenous healing events in concrete materials: the presence of specific chemical species, exposure to various environmental conditions, and small crack width. To improve autogenic healing in concrete, various strategies and requirements are considered in terms of reliability and repeatability of healing.

### Autogenic Crack Healing Techniques

Effective autogenous healing in cementitious materials can occur when the six following especially important factors are considered: pervasiveness, stability, economy, reliability, quality and repeatability. Attempts to finding composites engineered to control extremely tight crack width and precipitating $CaCO_3$ have led to autogenous Cementitious Composites. Autogenous Cementitious Composites are classified into three: Engineered Cementitious Composite (ECC), chemical additives and shape memory alloys to improve autogenous healing.

### Engineered Cementitious Composite (ECC)

Engineered Cementitious Composite (ECC) was identified as an ultra-ductile, fiber-reinforced, cementitious composite which emerged in the early 1990s (Li 1993; FISCHER, WANG et al. 2003). ECC exhibited heal crack widths intrinsically independent from steel reinforcing ratio and structural size under extreme loading. The tight crack widths in ECC are possible by using micromechanics as an effective tool for designing low permeability ECC composites which lead to two critical criteria of forming multiple cracks and the maximum fiber bridging stress versus crack opening relationship ($\sigma$-$\partial$) for the composite (Li and Yang 2008) (Figure3-1). The micromechanics concept allows optimization of the composite for attaining high tensile ductility and tight micro-crack widths while minimizing the amount of reinforcing fibers (generally less than 2-3%). The maximum fiber bridging stress versus crack opening relationship can also be used as a guide for tailoring the fiber, matrix, and fiber/matrix interface within the composite to meet the low permeability criteria. Experimental permeability tests exhibited low permeability and significant amounts of self-healing in the cracked state (Lepech and Li 2009). Apart from the mix design, fiber distribution is another crucial factor for the mechanical properties of ECC. The influence of different mixing sequences outcome increases the tensile strain capacity, the ultimate tensile strength and improves fiber distribution in ECC (Zhou, Qian et al. 2012).

Based on experimental outcomes, there was a close relationship between the durability performance and average or maximum crack widths of the structure. It was believed that cracks with a width below 0.1mm could be easily closed (Edvardsen 1999; Reinhardt and Jooss 2003) and self-healing behavior could be promoted when ECC specimens were exposed to various commonly encountered environments, consisting of water permeation and submersion, wetting and drying cycles, chloride ponding and deicing salts (Sahmaran, Li et al. 2007; Şahmaran and Li 2007; Li 2008; Yang, Lepech et al. 2009). The tensile stress-strain curve of ECC shown in Figure 3-1 demonstrates that ECC is able to control tight crack widths as an intrinsic property of ECC materials (Weimann and Li 2003).

Engineered Cementitious Composites (ECC) containing fly ash (FA), high volume fly ash (HFA), limestone powder, blast-furnace slag (BFS) and poly-vinyl-alcohol (PVA) as a replacement of cement remained durable in terms of mechanical performance and exhibited a tensile strain capacity of approximately 3%. Putting above additives to the ECC matrix modified the ECC microstructure and decreased the residual crack width from a 60μm level to a 10-30μm level or sometimes even lower than 10μm (Kim, Kim et al. 2007; Şahmaran and Li 2007; Şahmaran and Li 2009; Zhou, Qian et al. 2010; Kan and Shi 2012; Şahmaran, Özbay et al. 2012). In contrast, the partial replacement of 10% and 20% of normal-weight silica sand with equal weights of pre-soaked saturated lightweight fine aggregate (LWA) has a negative effect on the ductility and strength properties of ECC (Şahmaran, Lachemi et al. 2009). By applying the new type of cementitious matrix with the characteristic of low drying shrinkage, drying shrinkage at an early age could be decreased remarkably. Meanwhile, the average ultimate tensile strain achieved was still 2.5% and individual crack width in the strain-hardening stage was much smaller than that in traditional ECC (Zhang, Gong et al. 2009). Recently, a possible solution to obtaining better ductility and strain-hardening behavior has been to employ superabsorbent polymer (SAP) particles with 0.2% and 0.4% by weight of total binder materials in the ECC matrix with 50% and 70% FA. Introducing SAP in the matrix could reduce crack width and drying shrinkage, particularly in SAP particles in the matrix with 50% FA. However, SAP particles adversely affect the strength properties of ECC mixtures, such as tensile strength and compressive strength (Yao, Zhu et al. 2012).

Besides the introduction of external chemicals as healing agents, Li et al. and coworkers investigated the self-healing phenomena as an intrinsic property of cementitious matrices, relying on a continuous dispersion of self-healing compounds (i.e., free calcium ions or unhydrated cement particles) intrinsic to the concrete matrix. The latter, often referred to as autogenous healing, has various advantages over encapsulation self-healing (Yang, Lepech et al. 2005). Differences and similarities in healing behavior of early-age (3-day) ECC and that of more mature ECC were investigated under a broader set of environmental exposure conditions. Experimental analysis was conducted to determine the rate and extent of autogenous healing in terms of resonant frequency and uniaxial tensile tests of the healed ECC materials. Re-healing was found to be less at 3 days of early-age specimens than in more mature specimens of 90 daysor older, something associated with stiffness recovery. Although, self-healing for these early-age ECCs exhibited significant robustness when the preloading strain was limited to 0.3% (Yang, Yang et al. 2011). The self-healing behavior of ECC specimens incorporating nanoclay as internal water reservoirs was investigated according to four different curing conditions (air curing, carbon dioxide curing, wet/dry curing and water curing) and pre-cracking time at 14 days, 28 days and 56 days. Experimental findings on deflection capacity, flexural strength, stiffness and crack pattern revealed reasonable recovery of deflection capacity with different pre-cracking times in the air curing condition, pointing to the fact that nanoclay could be used as internal water supply for further hydration to occur. However, final crack location showed that healing efficiency had relatively weak strengthening under air curing, even in the presence of nanoclay (Qian, Zhou et al. 2010).

### Expansive Admixtures as Additives to Cementitious Composites

Chemical admixtures have been classified according to the specific function they perform, typically: water reduction, set retardation or acceleration, fluidification, air entrainment, corrosion inhibition, washout prevention, impermeabilization, shrinkage control, freeze-thaw resistance, etc. (Jolicoeur and Simard 1998). Expansive admixtures as chemical additive includes iron powder, alumina powder, magnesia, calcium sulfo aluminate ($CaO\text{-}A1_30_2\text{-}S0_3$) and calcium oxide (CaO). However, the main groups are the calcium sulfo aluminate series. Several expansion mechanisms of expansive additives have been proposed as follows: increasing volume, the spreading out of surrounding and forming, coexisting pores. The mechanism of expansive admixtures as cement replacements is attributed to the hydration of unhydrated cement grains leading to carbonation, since the bonding material thus formed contains crystals of calcium carbonate and calcium hydroxide. Evaluating the morphology, shape and size of precipitated particles (Figure 3-2) in the cracks indicated that using different carbonates, $NaHCO_3$, $Na_2CO_3$ and $Li_2CO_3$ and expansive agents in concrete as partial cement replacement, had much higher self-healing behavior than in cracked, normal concrete (Kishi, Ahn et al. 2007; Ahn 2008). In another investigation, the agents studied included expansive agents, geo-materials and chemical admixtures as well as some combinations of them. An expansive agent was added to an alkaline geo-material with a $SiO_2$ content of 71.3% and an $Al_2O_3$ content of 15.4%. The expansive agent comprised three mineral admixtures: $C_4A_3S$ (hauyne), $CaSO_4$ (anhydrite) and CaO (free lime). In the case of the chemical agent, various types of carbonates such as $NaHCO_3$, $Na_2CO_3$ and $Li_2CO_3$ were chosen to supply the effect of cementitious re-crystallization with expansive agent in air voids in cracked concrete. Experimental reports demonstrated that most of the modified geo-polymeric gel was structured by dense phases as opposed to hydro-garnet phases. These geo-polymeric gels were small in size as they formed in the cracking zones and also as they formed through the polymerization of individual aluminate and silicate species. The self-healing ability was dramatically affected by alumino silicate materials and different modified calcium composite materials. According to the results, the crack width of concrete was significantly self-healed up to 33 days after re-curing (Ahn and Kishi 2009; Ahn and Kishi 2010).

### Shape Memory Polymer Cementitious Composite

The first experimental record of the shape memory alloys was reported by Chang and Read in 1932. The unique properties are the result of reversible phase transformations of SMAs. Two major properties of SMA, the shape memory effect (SME) and super-elasticity, are associated with the thermal-induced or stress-induced reversible hysteretic phase transformation between austenite and martensite. Austenite and martensite have two different crystal phases in SMAs. SME refers to the phenomenon that SMAs return back to their predetermined shapes upon heating, while super-elasticity refers to that the ability of SMAs to undergo large amounts of inelastic deformations and recover their shapes after unloading. Nitinol shape memory alloy (SMA) is the most commonly used, where SMAs can be used as actuators as well as in active, semi-active controls of civil structures and self-healing concrete. Investigation indicates that the critical stresses are temperature dependent, and the temperature at the unloading process determines the residual strain (Duerig, Melton et al. 1990; Song, Ma et al. 2006).

The basic concept of incorporating shrinkable, shape memory polymer (SMP) materials into a cementitious matrix consist of two stages. First, shrinkage at an early age, with external and internal stress, caused cracks in the cementitious material. Second, activation of the shape memory polymer tendon due to heating resulted in decreased crack width and increased compressive stresses across the closed crack faces as shown in Figure 3-3. It was also shown in the respective work that the effect of heating combined with additional curing helped increase the mortar's strength by approximately 25% and also that this system had the potential to increase the natural autogenous crack healing process and generally improved the durability of concrete structures (Jefferson, Joseph et al. 2010). Experimental investigation revealed that incorporating SMA wire into mortar increased the range of deflection and also should be able to close cracks (Sakai and Fukuta 2003). Another attempt at using shape memory alloy (SMA) tendons demonstrated that significant pre-stressing was achieved (El-Tawil and Ortega-Rosales 2004).

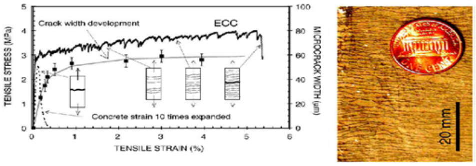

Figure 3-1: Typical tensile stress–strain curve and crack width development of ECC (Li and Yang 2008)

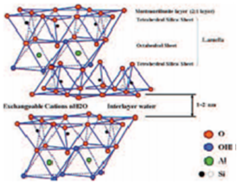

Figure 3-2: Chemical structure of geo-material (Ahn and Kishi 2009)

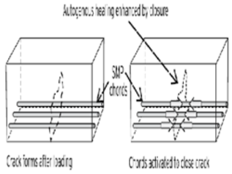

Figure 3-3: Shape memory polymer-cementitious composites (Jefferson, Joseph et al. 2010)

### Requirement Parameters for Autogenic Crack Healing

Effective autogenous healing in cementitious material can occur when the six following factors are considered especially important: pervasiveness, stability, economy, reliability, quality and repeatability. However, this relies on three criteria vital to improving self-healing efficiency: the Essential Chemical Species, Essential Environmental Exposure, and Small Crack Width.

Acceptable concentrations of special chemical species, which are satisfied with concrete ingredients, are essential for displaying the self-healing method. Environmental elements like carbon dioxide, calcium chloride in seawater and deicing salt are factors that support self-healing. Second, many infrastructure types are exposed to different conditions, from underwater immersion to cyclic wet-dry exposure that helps to heighten self-healing. Finally, the major challenge in designing and performing self-healing is controlling the tight cracks' width in concrete. Keeping tight crack width below 150μm and possibly less than 50μm is difficult to achieve consistently.

## Comparison and discussion

Two novel areas of self-healing cementitious composites focus on the natural ability of hydrates to heal cracks over time (autogenic) and artificial means of crack repair that are man-made inclusions (autonomic). Limitations of autogenic healing in nature and healing benefits have led to extensive studies of autonomic healing in concrete by a variety of authors. Encapsulation technique and the chemical healing agent are the two main aspects to be considered with relation to the autonomic healing concept, while autogenic healing is involved in unhydrated cement and calcite precipitation in a concrete crack. The progress in this area of research will be discussed, including the advantages and disadvantages of the various extrinsically and intrinsically self-healing approaches.

## Autonomic Crack Healing

The first benefit of the microencapsulation self-healing approach, both in internal or external cases, is that there is additional high healing efficiency due to larger amounts of healing agent that can be handled. However, in internal encapsulation, the rate of releasing healing agent and the effectiveness of self-healing is lower than the external reservoir due to limited amounts of healing agent. In fact, the number of healing cycles decreases with a decline in healing liquid. Secondly, multiple healing is only feasible when excess healing agent is available in the concrete matrix after the first healing has occurred. The third advantage is the easy connection to the external reservoir, making it one of the strongest points of utilizing hollow glass/ceramic tubes in concrete compared with the microencapsulation approach. In this state, an abundance of healing agent is always available when cracks occur in the position of fiber. In addition, other advantages that the hollow fiber self-healing concept has included that it is possible to minimize Poisson ratio effects on the presence of hollow fiber associated with location and orientation of the surrounding reinforcing fibers. The ease of using microencapsulation within bulk material is yet another advantage of this approach.

Paying attention to reservoir manual assembly and healing liquid rate are the first disadvantages of implementing the microencapsulation approach (Dry 2000; MIHASHI and KANEKO 2000; Joseph, Jefferson et al. 2007). The negative effects on the mechanical properties of concrete or cement based materials are the second drawback of employing this system. On the other hand, the reciprocating nature of this structure under lateral load and the presence of macro cracks cause a discontinuity in the hollow fibers. Thirdly, utilizing this method can affect the friability of hollow glass and ceramic tubes in the mixing process, a factor that brings out problems with casting concrete in vivo. Next, the vacuum created between the healing agent and wax plugs at either end creates a reverse pressure force. This negative pressure force causes a decline in glue or ink into the crack face. The fifth point is that the effectiveness of a healing system depends on capillary attractive force and gravity force. Thus, the microencapsulation approach also needs micro mechanical design because fractures rely on size, wall thickness, weight fraction and elasticity modules of capsules in comparison with elasticity modules of the host material. Seventh, resin as a healing agent needs to meet the catalyst prior to any repair occurring as well as it needs low viscosity to reach the crack face. Additionally, clumping of microcapsules due to weak dispersion causes the creation of weak regions in the material after consumption of the healing resin. However due to these factors healing liquid does not reach far enough areas of the crack faces and fluid masses are insufficient to overcome the capillary resistive force of the glass tube (Joseph, Lark et al. 2010).

Four keys to improving calcium carbonate precipitation are summarized as follows (Kishi, Ahn et al.): the calcium concentration (Wang, Tittelboom et al.), the concentration of dissolved inorganic carbon (DIC), the pH and the availability of nucleation sites. The biggest prerequisites of $CaCO_3$ precipitation are adequate carbonate ions and calcium so that the ion activity product (IAP) oversteps the soluble constant (Hammes and Verstraete 2002). An alkaline environment in concrete (pH) is one of the main factors preventing the survival of bacteria in the mixture; hence, bacteria cannot be directly added to concrete ingredients. The optimum pH range recommended for better bacterial growth in concrete is between 7 and 9. To overcome this problem, some scientists are focusing on the microencapsulation method to immobilize bacteria with and without nutrients. Another obstacle to the recovery of mechanical behavior is that the addition of bacteria and organic materials to concrete can result in undesirable strength loss.

## Autogenic Crack Healing

The first serious challenge which is not easy to overcome is identified in tight crack widths (CW) of probably less than 50μm. Secondly, the quality of the created calcite due to the second hydration of unhydrated cement is unknown in terms of the reliability of autogenous self-healing in concrete. In contrast, autogenous self-healing is available due to the presence of intrinsically-contained micro-reservoirs of unhydrated cement particles. Compared with four autonomic, self-healing approaches, employing autogenous self-healing is more economical.

Expansive admixture incorporation with cement and water start to create Ettringite ($3CaO.A1_20_3CaS0_4.32H_20$) or calcium hydroxide Ca(OH) by hydration reaction to expand the concrete. Many researchers showed that combining expansive admixture with other mineral additions can heighten the self-healing efficiency of cement based materials. A disadvantage of this approach may be addressed to the concentration of $Ca^{2+}$ ions at the cracking lips. The concentration of $Ca^{2+}$ ions gradually increases due to the cement being exposed to water, and therefore the amount of carbonate ions is reduced because of water dilution. On the other hand, incoming water consists of hydrogen carbonate ($HCO^{-3}$) and carbonates ($CO_2^{-3}$). This causes an increase in the concentration of carbonate ions in nearby crack surfaces in water. Finally, there is a higher amount of calcium carbonate precipitation in the crack mouth than in other states. Calcium carbonate precipitation in the crack mouth benefits the recovery of mechanical properties in concrete. In addition, the reactive ingredients react with $Ca(OH)_2$ to produce a crystalline product when water is available. Third, unexpected expansion is another drawback since hydration is more than in cement. Unexpected expansion in concrete at an early age causes premature failure from the inside if there are no restrains, leading to low strength or no strength. A further disadvantage of expansion agents is that they can hydrate in unnecessary spaces at an early age even if no cracks are present. Basically, expansion agents are unavailable when cracks occur in the matrix because the expansive agents hydrated in an unforeseen disruption.

The fundamental idea behind the activation of shape memory polymer is heating, which leads to crack closure and improved flexural stress during cracking. Direct heating or electrical currents can be applied to raise temperatures in shape memory alloys. Increasing material temperature causes increased tensile force due to inherent properties and transfer to crack faces. Therefore, tensile forces in shape-memory polymers will create compressive force in split crack lips. The first disadvantage is that realizing heat in a cement-based material incorporated in shape-memory alloys increases the complexity of the self-healing system. Secondly, it is important to beware of concrete hydration because high heating may have a negative impact on

Ettringite production. Finally, it is not easy to perform this method for large buildings and infrastructures because of some environmental conditions.

## CONCLUDING REMARKS

Concrete is the most commonly used construction material in the world because it is long-lasting, robust, and quite cheap. In contrast with concrete's high compression strength, it has low tension strength leading to cracks due to loading and ambient conditions. Because of cracking, the cost of inspection and maintenance increases over time. To overcome these challenges, scientists and engineers are focusing on the aforementioned strategies, the autogenic and autonomic approaches in self-healing. Over two decades, autogenic healing has been known as a natural ability while autonomic healing has been understood as the artificial capacity of crack repair in concrete. Table 5-1 shows a summary of the self-healing approach in cementitious materials.

1) According to Table 5-1, many research works have been conducted on the experimental strategies. Meanwhile, only few studies have been performed on other areas such as math modeling, simulation and the theoretical concept. The most impressive reasons for employing laboratory studies can be the latency in chemical reactions. In fact, self-healing phenomena are identified as chemical reactions that lead to improved physical and transport properties of cementitious composites. Therefore, future works need to consider comparisons between simulation and experimental studies, particularly on the autogenous self-healing method.
2) Fewer research works utilize different encapsulation techniques such as silica gel, polyurethane, porous expanded clay particles and glass, or ceramic tubes to survive bacterial spores and calcium lactate against alkali environments in the concrete matrix (Van Tittelboom, De Belie et al. 2011; Wang, Van Tittelboom et al. 2012). Hence, it is possible to capsulate expansive agents for preventing unwanted expansion in concrete. Employing autogenous and autonomous strategies simultaneously seems to be a promising approach to improve repeatability and reliability of self-healing cementitious materials.
3) Incorporating nanomaterial with concrete ingredients as a novel trend to retrieving mechanical properties has been considered, especially in ECC composite materials (Sakulich and Li 2011). It is possible to improve self-healing efficiency in concrete, and CNTs have the potential to be successfully used to realize the next generation of stronger, lighter, self-healing materials. The numerical analysis of the possibility of using carbon nanotubes as a reinforcing self-healing device that has the ability to slow down split propagation in a hasting matrix and automatically heal the crack, has been found by Lanzara at el. (Lanzara, Yoon et al. 2009) (Figure 5-1). However, future experimental and simulation studies are necessary to study concrete incorporation with carbon nanotubes and nanoclays as internal reservoirs. The self-healing efficiency of nanomaterial in concrete compounding with or without different approaches may be an exciting tendency to examine.
4) Self-repair of material damage such as cracks in a material or coating applied to a building or bridge, has relied on capillary force for transporting the healing agents. On the other hand, to overcome the vacuum created between healing agent and wax plugs at the end of hollow fiber, an active pumping capability for pressurized delivery or circulation of liquid healing agents in micro-channel systems significantly improves the degree of healing compared with capillary force methods (Hamilton, Sottos et al. 2012) (Figure 5-2).

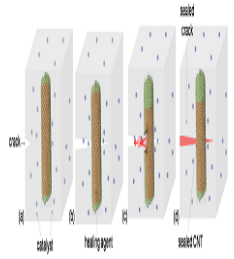

**Figure 5-1: Concept of the self-healing process using carbon nanotubes (Lanzara, Yoon et al. 2009)**

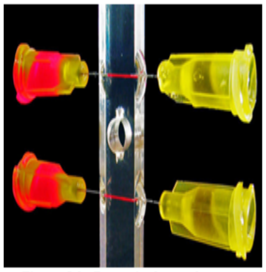
**Figure 5-2: Pressurized vascular systems for self-healing materials (Hamilton, Sottos et al. 2012)**

5) Introducing superabsorbent polymer (SAP) in the matrix could reduce crack width and drying shrinkage. Utilizing a new type of cementitious matrix with the characteristic of low drying shrinkage also decreases individual crack width in engineered cementitious composites. On the other hand, experimental findings indicate that the distribution of fibers alters the integrity of ECC materials. Therefore, experimental work will need to be conducted to find self-healing efficiency over time related to the replacement of binder materials or cements and the mixture method.
6) According to Table 5-1, all experimental findings report the self-healing behavior of concrete or cementitious composites when samples are exposed to several environmental conditions including wet-dry, immersion and lab conditions with moderate humidity. Therefore, subsequent work will be essential to evaluate the quantity and quality of self-healing when specimens are exposed to air-dry or low humidity. As such, concrete fabrication with some additives and expansive agents which consume less water should be considered.

**Table 5-2: Summary of healing cementitious composites**

| source information | | | Research Methodology | | | | | | Subject | | healing Approach | | | | | | material research | | | | healing evolution | | | | | | | | | another object | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | Autonomic | | | Autogenous | | | | | | | | | | | | | | | | | | | | | |
| NO | Authors | year | Experimental | Math Modelling | Simulation | Theory concept | Review | Framwork | self-healing | cement | Microcapsulation | capillary tubes | bacteria | Expansive agents | Shape Memory | ECC | Host material * | healing agent * | carrier material * | chemical edditive * | Unxial tension | resonant frequency | permeability | Chloride ingression | compressive strength | SEM INVESTIGATION | X-ray microanalysis (E | MPN numbers | Acoustic emission | casting condition | CaCO3 precipitation | cristization structure | curing condition | cracking | precracking time |
| 1 | van der ZWAAG | 2010 | | | | | √ | | √ | √ | √ | √ | √ | √ | √ | | | | | | | | | | | | | | | | | √ | | √ | |
| 2 | Ramakrishnan et al. | 1999 | √ | | | | | | | √ | | | √ | | | | C | | | | | | | | | √ | | | | | √ | | | √ | |
| 3 | Henk M Jonkers | 2008 | | | | | | √ | √ | √ | | | √ | | | | C | | | | | | | | | | | | | | √ | | | | |
| 4 | Jonkers and Schlangen | 2009 | √ | | | | | | √ | √ | | | √ | | | | C | | | | | | | | | | √ | | | | √ | | | | |
| 5 | Jonkers and Thijssen | 2010 | √ | | | | | | √ | √ | | | √ | | | | C | | | | | | | | √ | | √ | √ | | | | | | | |
| 6 | Edvardsen | 1999 | | | | √ | | | √ | √ | | | | | | √ | C | | | | | | √ | | | | | | | | √ | | | √ | |
| 7 | Ramakrishnan et al. | 2001 | √ | | | | | | | √ | | | √ | | | | C | | | | | | | | √ | √ | | | | | √ | | | √ | |
| 8 | De Muynck, De Belie et al. | 2007 | √ | | | | | | | √ | | | √ | | | | C | | | | | | √ | √ | | √ | √ | | | | √ | | | | |
| 9 | Ramakrishnan, Panchalan. et al. | 2001 | √ | | | | | | | √ | | | √ | | | | C | | | | | | | | √ | | | | | | √ | | | | |
| 10 | Wang, Tittelboom et al. | 2010 | √ | | | | | | √ | √ | | √ | √ | | | | C | | | | | | | | √ | √ | √ | | | | √ | | | | |
| 11 | Van Tittelboom, De Belie et al. | 2011 | √ | | | | | | √ | √ | | √ | | | | | C | | | | √ | | √ | | √ | | √ | | | | | | | √ | |
| 12 | Wang, Van Tittelboom et al. | 2012 | √ | | | | | | √ | √ | | √ | √ | | | | C | B. s | S.G/P | | | | √ | | √ | √ | √ | | | | √ | | | | |
| 13 | Siddique and Chahal | 2011 | | | | | √ | | | √ | | | √ | | | | C | | | | | | √ | | √ | | | | | | | | | | |
| 14 | Wiktor and Jonkers | 2011 | √ | | | | | | √ | √ | | | √ | | | | C | B. a/C.l | PECP | | | | | | | | | | | | | | | | |
| 15 | De Muynck, Cox et al. | 2008 | √ | | | | | | | √ | | | √ | | | | C | B. s | | | | | √ | | | √ | √ | | | | | | | | |
| 16 | Siddique and Chahal | 2011 | √ | | | | | | | √ | | | √ | | | | C | S. p | | | | | √ | √ | √ | | | | | | | | | | |
| 17 | Okwadha and Li | 2010 | | | | √ | | | | √ | | | √ | | | | C | S. p | | | | | | | | √ | √ | | | | √ | | | | |
| 18 | Van Tittelboom, De Belie et al. | 2010 | √ | | | | | | | √ | | | √ | | | | C | B. s | S.G | | | | √ | | √ | | √ | | √ | | √ | | | √ | |
| 19 | Yang et al. | 2011 | √ | | | | | | √ | √ | √ | | | | | | C | M.m/T.m | S.G | | | | √ | | √ | √ | √ | | | | | | | | |
| 20 | Van Tittelboom, De Belie et al. | 2012 | √ | | | | | | √ | √ | | √ | | | | | C | P | C.t | | | √ | | | | | | | | | | | | | |
| 21 | Yang, Z., J. Hollar, et al | 2011 | √ | | | | | | √ | √ | √ | | | | | | C | MMA/TEB | S.G | | | | √ | | √ | √ | √ | | | | | | | | |
| 22 | Lv, Z. and H. Chen | 2012 | | √ | | | | | √ | √ | | | | | | √ | | | | | | | | | | | | | | | | | | | |
| 23 | Huang, H. and G. Ye | 2012 | | | √ | | | | √ | √ | √ | | | | | | | | | | | | | | | | | | | | | | | | |
| 24 | Ahn and Kishi | 2010 | √ | | | | | | √ | √ | | | | √ | | | | | | | | | | | | √ | √ | | | | √ | | | | |
| 25 | Kishi, Ahn et al. | 2007 | √ | | | | | | √ | √ | | | | √ | | | | | | CO3 | | | | | | √ | √ | | | | √ | | | | |
| 26 | Sisomphon, K., O. Copuroglu, et al. | 2012 | √ | | | | | | √ | √ | | | | √ | | | | | | | | | √ | | | √ | √ | | | | √ | | | √ | |
| 27 | Jefferson, Joseph et al. | 2010 | | | | | | √ | √ | √ | | | | | √ | | | | | | | | | | | | | | | | | | | √ | |
| 28 | Simon Dunn | 2010 | √ | √ | | | | | √ | √ | | | | | √ | | | | | | | | | | | | | | | | | | | | |
| 29 | Joseph, Jefferson et al. | 2007 | √ | | | | | | √ | √ | | √ | | | | | C | Cy | | | | | | | | | | | | | | | | | |
| 30 | Yang, Yang et al. | 2011 | √ | | | | | | √ | √ | | | | | | √ | ECC | | | | √ | √ | | | | | | | | √ | | | √ | | |
| 31 | Yang, Lepech et al. | 2009 | √ | | | | | | √ | √ | | | | | | √ | ECC | | | | √ | √ | √ | | | √ | √ | | | √ | | | √ | | |
| 32 | Qian, Zhou et al. | 2010 | √ | | | | | | √ | √ | | | | | | √ | ECC | | | | | | | | √ | √ | | | | √ | | | √ | √ | √ |
| 33 | Kan and Shi | 2012 | √ | | | | | | √ | √ | | | | | | √ | ECC | | | | √ | √ | | | | √ | | | | √ | | | √ | √ | |
| 34 | Li and Yang | 2008 | | | | | | √ | √ | √ | | | | | | √ | ECC | | | | √ | √ | √ | | | √ | √ | | | √ | | | √ | √ | |
| 35 | Qian, S., J. Zhou, et al. | 2009 | √ | | | | | | √ | √ | | | | | | √ | ECC | | | | | √ | | | √ | √ | √ | | | | | | | | |
| 36 | Ghosh, Mandal et al. | 2006 | √ | | | | | | | √ | | | √ | | | | | | | | | | | | √ | √ | | | | | √ | | | | |

C = Cement or Concrete methylmethacrylate (MMA)/triethylborane(TEB) Cyanoacrylates (superglues) = Cy

B. s = B. sphaericus calcium sulfoaluminate additive (CSA) and crystalline additive (CA) porous expanded clay particles = PECP

S.G/P = silica gel/Polyurethane Methylmethacrylate monomer = M.m Ceramic tubes = C.t

Sporoscarcina pasteurii = S. p B. a/C.l = Bacillus alkalinitrilicus/calcium lactate NaHCO3, Na2CO3 and Li2CO3 = CO3

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