SELF-HEALING PROPERTIES OF ENGINEERED CEMENTITIOUS COMPOSITES (ECC)

by

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DEDICATION

I dedicate this thesis to everyone who is trying to make the world a better place for others.

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ABSTRACT

Concrete is the most widely used construction material globally; however, its brittle behavior makes it prone to cracking, negatively impacting the structural durability and sustainability of concrete infrastructure. The introduction of self-healing mechanisms into concrete that can promote healing of cracks with the material produced by the concrete could solve many of the strength degradation and durability issues associated with cracking seen in current concrete structures. Even though many mechanisms have been used to induce self-healing in cementitious material, the self-healing of Engineered Cementitious Composites (ECC) has proven to be one of the most efficient mechanisms, as it has shown the ability to achieve recovery of transport and mechanical properties. The present study investigates the self-healing properties of ECC. In phase I of this research, the focus is on the repeatability of self-healing mechanism in ECC. The aim is to determine the positive/negative effect of applying a compression cycle on partially healed cracks. In this phase, the recovery of mechanical properties is measured to represent the self-healing efficiency rate. In phase II of the research, the extent of self-healing in a favorable condition is evaluated. Crystalline Admixture (CA) is used in this phase to improve ECC's self-healing properties, and self-healing is measured through the recovery of transport properties. Since the surrounding environment has a significant impact on ECC's self-healing process, three exposure conditions of air dry, tap water and sea water were studied in this experiment. Final results proved that applying a compression cycle on the partially healed cracks reduces the self-healing efficiency. Both results in Phase I and Phase II suggest that sea water is as a favorable condition for self-healing of ECC.

LIST OF ABBREVIATIONS AND SYMBOLS USED

ASTM	American Society for Testing and Materials
CA	Crystalline Admixtures
CH	Calcium Hydroxide
CSH	Calcium Silicate Hydrate
DIC	Digital Image Correlation
ECC	Engineered Cementitious Composites
CH	Calcium Hydroxide
CSH	Calcium Silicate Hydrate
FA	Fly Ash
FRC	Fiber-Reinforced Concrete
HPFRCC	High Performance Fiber-Reinforced Cementitious Composites
HRWRA	High Range Water Reducer Admixture
JCI	Japan Concrete Institute
MICP	Microbiologically Induced Calcite Precipitation
NDT	Non-Destructive Testing
OPC	Ordinary Portland Cement
PE	Polyethylene
PET	Polyethylene Terephthalate
PP	Polypropylene
PRAH	Permeability Reducing Admixture
PVA	Polyvinyl Alcohol
RCP	Rapid Chloride Permeability
RF	Resonant Frequency
SAP	Super Absorbent Polymers
SCM	Supplementary Cementitious Materials
SMA	Shape Memory Alloys
SMP	Shape Memory Polymers
UPV	Ultrasonic Pulse Velocity
XRD	X-Ray Diffraction

σ_0	Fiber bridging stress
σ_{cr}	Cracking stress
σ_{ss}	Steady-state stress
δ_0	Fiber rupture strain
δ_{ss}	Steady-state strain
E_c	Elastic modulus
J_{tip}	Crack tip toughness
J'_b	Complementary energy
K_m	Fracture toughness
R_S	Stiffness recovery ratio
R_U	UPV recovery ratio
U_f	Velocity factor
V_f	Fiber volume fraction
W_{max}	Maximum crack opening

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CHAPTER 1 INTRODUCTION

1.1 GENERAL

Concrete is a frequently used construction material worldwide due to its relatively low cost and design flexibility. Despite its proven advantages, concrete often exhibits cracks due to excessive tensile stresses or environmental conditions. These cracks are allowed to happen and are not considered a failure in reinforced concrete members, as long as their width does not exceed a specified criterion. However, via these cracks, aggressive substances enter into concrete, causing degradation and reinforcement corrosion. As a result of these phenomena, the concrete structure's durability and mechanical performance are compromised, and its service life will be reduced. Therefore, monitoring, maintenance, and repair of concrete cracks are of great importance. However, the inspection of cracks and repairing them is costly, especially for cracks in infrastructures such as bridges, highways, or tunnels. Even though cracks in infrastructure are not easily accessible and require a considerable amount of labor and budget, many of the infrastructure are in continuous service, making repairs even more difficult. Under such circumstances, one of the effective methods for repairing the cracks is to provide an automatic healing mechanism that triggers upon necessity and regains the concrete structure's functionality without human intervention.

Over the last two decades, the mechanisms introduced as self-healing methods into concrete support cracks to fill with the healing products formed through chemical reactions of substances coming from the cementitious matrix and the surrounding environment. Concrete has the inherent ability to heal the cracks with hydration of unhydrated binders and precipitation of calcite, which is referred as "autogenous self-healing”. However, this is a long process, and the amount of formed products depends on the surrounding environment's condition. The hydration process needs water to proceed, and the precipitation of calcite is a result of the reaction between calcium ions from concrete and carbonate ions dissolved in the surrounding environment, which vividly relies on the ion concentrations.

With understanding the mechanisms of autogenous self-healing, studies were carried out toward improving these mechanisms. Replacing cement with Supplementary Cementitious Material (SCM) that possess late hydration properties and could benefit the autogenous self-healing by providing more unhydrated binders is one of the methods. Another method is to include fibers in concrete that control crack width and provide nucleation sites for precipitation of healing products. In this regard, Engineered Cementitious Composite (ECC) has been noticed to show promising results of self-healing. A typical ECC mixture consists of both SCM (fly ash) and fibers (PVA).

The present investigation aims at evaluating the self-healing properties of ECC in different exposure conditions. The repeatability of self-healing in ECC is examined through a series of reverse flexural loadings, and the results are used to determine the possible effects of compression on the formation of healing products in the cracks. Also, the addition of Crystalline Admixture (CA) to the ECC mixture was studied in order to find the extent of self-healing in a favorable condition for ECC.

1.2 RESEARCH OBJECTIVES

The objectives of this research are:

- To determine the positive/negative impact of compression on the repeatability of self-healing in ECC
- To study the feasibility of improved autogenous self-healing in ECC exposed to marine environment
- To evaluate the extent of self-healing for ECC in a favorable condition

1.3 THESIS STRUCTURE

The present thesis is provided in a manuscript-based thesis format. Chapter 2 is submitted to a journal publication as a review paper. Original figures were created in this chapter to improve the authenticity of the work. Chapter 3 and 4 present Phase I and Phase II of the experimental research. Chapter 3 is also submitted to a journal publication, and it discusses the repeatability of self-healing in ECC specimens with the presence of a compression cycle. Chapter 4 discusses the effect of Crystalline Admixture (CA) on the self-healing of large cracks in ECC specimens, and it will be submitted to a publication in the future. Overall conclusions and recommendations are provided in chapter 5.

CHAPTER 2 A REVIEW ON AUTOGENOUS AND IMPROVED AUTOGENOUS SELF-HEALING IN CEMENTITIOUS MATERIALS: OUTLOOKS AND RESEARCH GAPS[1]

ABSTRACT

Self-healing of cracks in cementitious material has been extensively studied over the last two decades as a method of increasing durability in concrete infrastructure. Self-healing mechanisms are capable of recovering the mechanical and transport properties of concrete via filling the cracks after damage without manual interventions. If this recovery of cracks occurs as a function of late cement hydration or precipitation of calcite ($CaCO_3$) through contact with moisture, the mechanism is referred to as autogenous self-healing. Furthermore, these hydration/carbonation functions could be stimulated, which then generates improved autogenous self-healing technique. In this paper, a classification of major mechanisms is outlined, and from that, autogenous and improved autogenous self-healing mechanisms are defined and explained. Since a significant portion of this review paper focuses on improved autogenous self-healing methods, a separate section is dedicated to micromechanics and material properties of Engineered Cementitious Composite (ECC), as further discussed to be the pioneer of improved autogenous self-healing group. As effective as some of these mechanisms are, they have not reached to practical applications yet. To elaborate on research gaps in the literature, recent research and developments concerning the repeatability of self-healing mechanisms and the surrounding environment's effect on the self-healing process are discussed.

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[1] This chapter is submitted to a journal.

2.1. INTRODUCTION

Concrete due to its flexibility in design, availability of raw materials, excellent performance, and relatively low cost has been the most used human-made material worldwide for the last few decades and the consumption is still growing [1]. However, its main component, i.e., cement, is responsible for producing 7-8% of the global CO_2 emissions [2]. One approach to help minimize cement production is to build more durable structures. Durability of concrete is generally regarded as its resistance towards a particular environment to which it will be exposed during its service life [3]. By enhancing the durability, the number of years a concrete structure can safely function under service condition will increase, leading to less demand for new construction. Durability issues such as freezing and thawing, sulfate attacks, carbonation, and steel corrosion can be controlled because they are caused due to one reason, i.e., the cracks. Therefore, cracks should be monitored and repaired regularly in order to prevent ingression of harmful substances and deterioration of concrete structure. Nevertheless, providing continuous inspection and maintenance is challenging. The cost and amount of labor required for repairing, plus the indirect cost of pausing the serviceability of concrete structures such as bridges or tunnels for maintenance, could be substantially high [4]. Apart from the high cost of manual repair, the process may be difficult or even impossible due to the location of damage, e.g. cracks in underground concrete structures. Moreover, even though manual repair techniques have considerably improved through recent years, most of these repairs can only last ten to fifteen years [5, 6].

Self-healing of cracks in concrete has been introduced over the recent decades as an automatic mechanism to fill the cracks pathway and inhibit water ingress, also help regain the mechanical properties [7]. The concept of self-healing concrete could be considered as biomimicry, since the process exists in almost all living creatures, including human body. The research field of self-healing concrete is extensively broad and has grabbed the attention of multidisciplinary researchers, including civil engineers, chemical engineers, material engineers, bioengineers, etc. Fig. 2.1 clearly demonstrates the increasing trend of research on self-healing topic in the last decades.

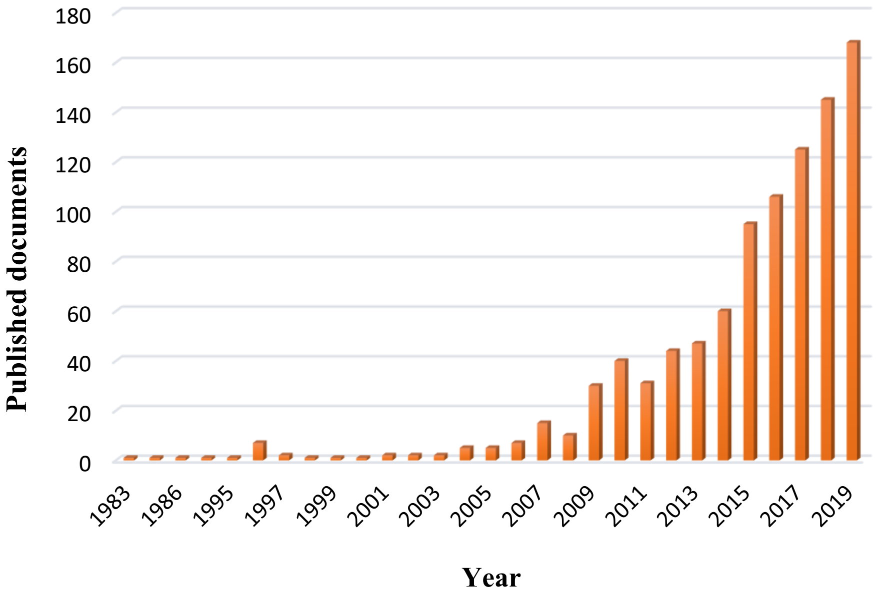


Fig. 2.1 Published documents in years including the phrase "self-healing concrete" – Data exported from Scopus [8]

The present paper suggests a new classification system of self-healing mechanisms based on previously published reports, and explores self-healing mechanisms that are associated with concrete's inherent properties of self-healing, i.e., autogenous and improved autogenous mechanisms. A comprehensive review of the techniques, processes, performances, and recent research achievements are provided. Even though research has been extensively carried out on concrete's self-healing properties, some aspects of this novel technology still require further investigation. To address a number of these research gaps, repeatability of self-healing and the effect of surrounding environment on self-healing are discussed in this review paper.

2.2. PRINCIPAL MECHANISMS OF SELF-HEALING

Over the last twenty years, that self-healing concrete has grabbed the attention of researchers in the field; the phenomenon remained without a reliable standard or guideline to accredit the methods and evaluation techniques; however, there have been two committee reports published so far. The first committee report, "TC-075B," was published in 2009 from the Japan Concrete Institute (JCI) on self-healing concrete [9]. The second committee report, "221-SHC," was published in 2013 in RILEM State-of-the-Art reports [7]. Although the representatives of JCI TC-075B are also members of RILEM TC-221, the terminologies adopted for the definitions and classification of self-healing techniques are not entirely aligned. In the following, a review of both perspectives is presented, and a new classification is established based on the self-healing mechanisms and processes.

The concept of self-healing is quite similar in both reports. It could be summarized as an event or process that is triggered inherently from concrete and results in the recovery of at least one function in concrete. TC 075-B then divides the self-healing mechanisms into three main groups of natural healing, autonomic healing, and activated repairing. Natural healing is characterized as pure autogenous healing, and it is defined as a phenomenon that inherently heals and seals the cracks by some chemical and physical reactions (late hydration, carbonation, crack clogging by loose particles, and swelling of concrete), without any special arrangement in the material design. Autonomic healing is then classified as autogenous-engineered healing, and it is described as a phenomenon in which cracks are healed in concrete with special material design, provided by Supplementary

Cementitious Material (SCM), special expansive minerals, fibers that suppress the widening of the crack widths, and interestingly, bacteria that precipitate calcite. It is stated that the additional materials are conventionally added to concrete not for self-healing purposes only, but to be an integral part of the structure constituting concrete. Also, the term "autonomic" was adopted to express concrete's own healing effect, because the structure of concrete itself accelerates the healing of cracks [9]. However, classifying bacteria-based healing in this group is not very well justified, since it has a unique process of biomineralization (Microbiologically Induced Calcite Precipitation (MICP)) that is separate from any form of autogenous healing [10]. Lastly, activated repairing, which is identified as pure engineered healing, is classified as every mechanism of devices embedded in the concrete beforehand to repair cracks autonomically. This category includes crack healing utilizing microencapsulation of healing agents, shape memory alloys, brittle pipes that vessel healing agents, and basically any technique that is engineered into concrete for only the purpose of active repairing upon cracking.

To overcome the complexities accompanied by TC 075-B definitions, the RILEM TC-221 committee proposed to classify the self-healing mechanisms into two main groups of autogenic and autonomic healing. Their taxonomy distinguishes the two techniques based on their purpose of presence in concrete. If materials components could otherwise also be present when not specifically designed for self-healing, it is categorized as an autogenic technique. On the other hand, if the recovery process uses materials components that would otherwise not be found in the concrete, then it is an autonomic healing technique (engineered condition) [7]. The RILEM TC-221 committee emphasizes on the simplicity of definitions and suggests that any technique can be categorized into these two groups by giving attention to the actual trigger mechanism of the self-healing process.

The present paper proposes another method of classification, trying to merge the two previous taxonomies. Simply dividing the self-healing techniques into two groups of autogenous and autonomous healing is acknowledged from the RILEM committee suggestion. Defining autogenous self-healing as any mechanism emerging intrinsically from a conventional concrete with a normal mix design to seal and heal the cracks. This includes late hydration, calcite precipitation, clogging by loose particles, and concrete swelling with moisture. Then, identifying autonomous self-healing as any engineered mechanism that (i) would otherwise not be found in a concrete mixture, and (ii) it is present to help heal the cracks. Adopting the TC-075B classification, the mutual area between autogenous and autonomous healing would be introduced as "improved autogenous self-healing," which could be described as any engineered condition inserted into concrete that helps improve the mechanisms of autogenous self-healing, as mentioned above. By doing so, any self-healing technique can be fit into these groups. The key is to understand the mechanism that is resulting in the self-healing process. For instance, using fibers could be categorized into the improved autogenous group because its function is to limit the crack widths so that autogenous healing could perform much more efficiently. Contrary to TC-075B, bacteria-based self-healing is not categorized in this group due to its unique biomineralization process and belongs to the autonomous healing group; however, the use of Super Absorbent Polymers (SAP) that provide water for late hydration belongs to the improved autogenous healing group. Use of SCMs that replace cement in the mixture and heal the cracks with late hydration is also considered to be part of improved autogenous self-healing; nevertheless, minerals that fill the cracks with their expansion and crystallization process are considered as autonomous techniques. A Venn diagram is illustrated in Fig. 2.2 to summarize the proposed taxonomy.

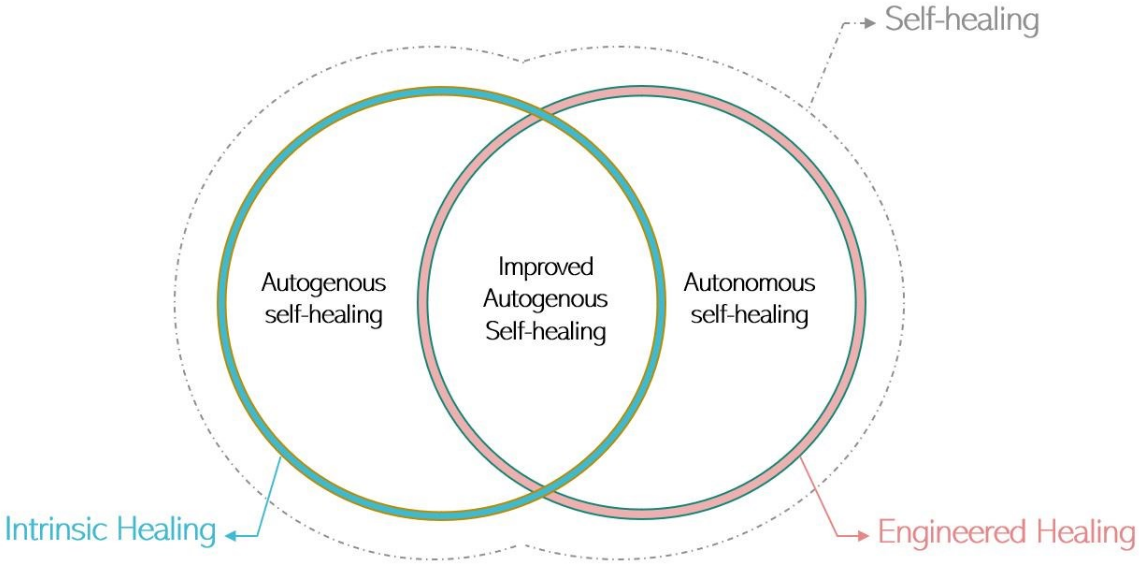


Fig. 2.2 Venn diagram explaining principal mechanisms of self-healing (the concept was adopted from JCI TC-075B [9])

2.3. AUTOGENOUS SELF-HEALING

The phenomenon was first observed in water retaining structures and pipes by the French Academy of Science in 1836 [7], then proved to be one of the main reasons for the long life-span of the ancient structures and buildings [11]. The process consists of a number of physical and chemical reactions that can happen simultaneously, with different rates and impacts on the healing mechanism. Fig. 2.3 summarizes the possible physic-chemical processes of autogenous self-healing in a crack exposed to water.

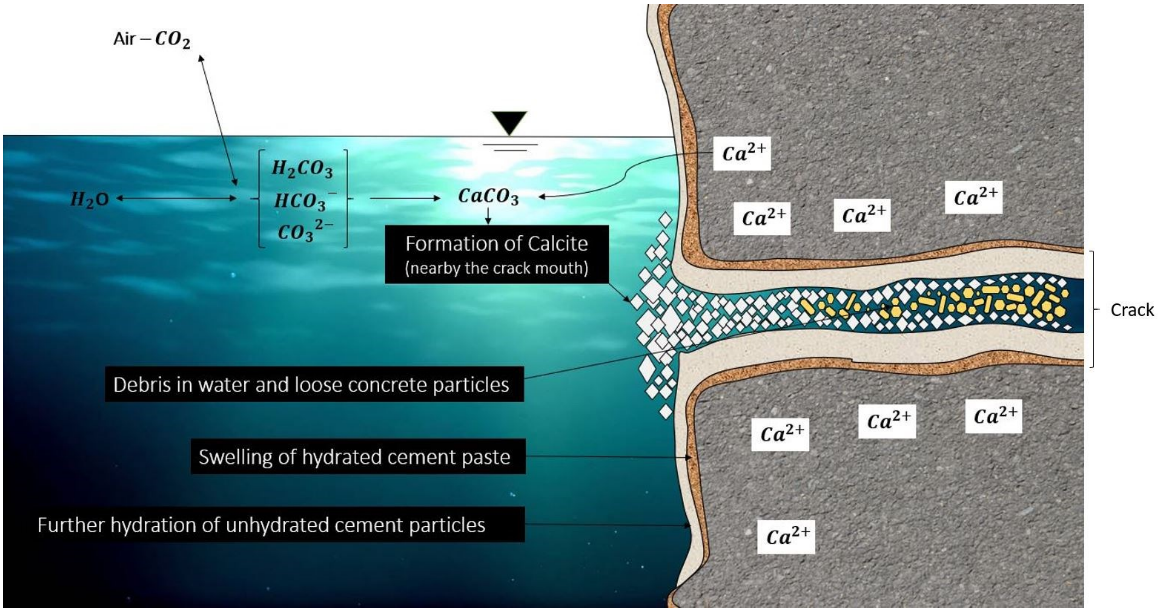


Fig. 2.3 Possible causes for autogenous self-healing.

Approximately 20-30% of the Portland cement used in the conventional concrete remains unhydrated inside the bulk paste [12]. The process gradually stops due to the consumption of all the mixing water, and lack of space for the hydration process to continue. When a crack occurs, both mentioned obstacles are lifted; therefore, there is a chance for further hydration. Since hydration of cement particles is started upon contact with water, this mechanism can take place immediately after water ingress into the crack. Early age concrete can benefit much more from the further hydration mechanism as there are more unhydrated cement grains available in the bulk paste [13]. Although autogenous healing produced by further hydration should technically present a strength similar to hydration products in the bulk paste, it has been proven that the components of the reaction products are different from the hydration products inside the bulk paste. Huang et al. [14] investigated the mineralogy of the healing products in a young Ordinary Portland Cement (OPC) by further hydration. They demonstrated that the hydration products consisted of almost 78% portlandite (CH) and 17% Calcium Silicate Hydrate (CSH), which is in contrast with the hydration products in the bulk paste. This contradiction in the nucleation and growth process can be attributed to the excessive availability of water from the outside environment (higher water/binder ratio) and the large space available for hydration inside a crack. Moreover, the leaching of portlandite from the bulk paste into the cracks and recrystallization of this product facilitates the process [15]. When the calcium ion concentration in the bulk paste is higher than the concentration in the water penetrated inside cracks, the ions can leach from the bulk cement paste into cracks [16]. This process can explain the high percentage of portlandite inside the cracks and also help with the calcite precipitation, which is the next important product of autogenous self-healing.

The leached calcium ions (Ca^{2+})from the bulk paste into the crack can react with the carbonate ions (CO_3^{2-}) diffused toward the cracks from the surrounding environment, leading to the precipitation of calcium carbonate crystals ($CaCO_3$) [17, 18]. The formation of calcium carbonate crystals is a slow process and highly depends on the availability of carbonate ions in the water or atmosphere; thus, it is the main source of autogenous healing in concrete at later stages [19-21]. The process consists of two phases; i) surface controlled crystal growth, in which calcium ions are directly available from the surface of the cracks and able to react with carbonate ions to form a calcite layer, and ii) diffusion controlled crystal growth, in which the calcium ions have to diffuse from the bulk paste and travel through the primary formed calcite layer to reach the carbonate ions and precipitate calcite crystals [19, 22]. The transformation of portlandite into calcite helps self-healing since the volume of calcite is 11% more than portlandite as a reaction product [23]. The process happens nearby the crack mouth due to a higher concentration of the ions at that location and the fact that with the formation of the first crystals nearby the crack mouth, the pathway for carbonate ion to travel through the crack would be blocked [17]. Fig. 2.3 simply demonstrates the process by which carbon dioxide (CO_2) present in the air transfers to water, and upon reaching to a supersaturation level with calcium ions, precipitates calcite. The process is described as follows [6, 24]

$$H_2O + CO_2 \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-} \qquad \text{Eq.2.1}$$

$$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3 \downarrow (pH_{water} > 8) \qquad \text{Eq.2.2}$$

$$Ca^{2+} + HCO_3^- \leftrightarrow CaCO_3 \downarrow + H^+ (7.5 < pH_{water} < 8) \qquad \text{Eq.2.3}$$

As illustrated in Fig. 2.3, the other possible causes of autogenous self-healing are swelling of hydrated cement paste due to water absorption and filling with loose concrete particles caused by the crack or debris in the water [7], which have minor impact on the autogenous healing process.

It is clear that all these physic-chemical reactions are not independent. The presence of water has been proven to be essential for all these reactions to proceed. It provides a suitable medium for the physical and chemical reactions and can help promote the formation of the reaction products with its pH, temperature, and pressure gradient. Recently, researchers have established that the wet-dry cycles have a greater influence on the autogenous healing efficiency than water submergence [22, 25]. The cement type has proven to be less impactful on the healing process [19], yet the cement clinker size that can controls the specific area to react with water, determines the unhydrated portions of cement available for further hydration [26, 27]. The amount of calcium ions in the concrete after initial hydration and the level of CO_2 concentration in the surrounding environment are critical for calcite precipitation. Furthermore, the size and geometry of crack can limit the nucleation sites for the formation of reaction products [28, 29]. As mentioned, these inconsistencies explain the wide range of healed cracks' widths reported via autogenous self-healing. Generally, it is accepted that autogenous self-healing is efficient in smaller cracks (~150 μm), but different ranges from 10 to less than 300 μm have been reported to be healed [7, 24, 30, 31].

2.4. IMPROVED AUTOGENOUS SELF-HEALING

Based on the described mechanisms for autogenous self-healing and the classifications presented previously, the new group of improved autogenous self-healing can be distinguished as any engineered device implemented into concrete that results in the improvement of any of the possible cause for autogenous healing. Fibers that bridge the cracks and control the crack width, Supplementary Cementitious Materials (SCM) that replace cement in the mixture, Shape Memory Alloys (SMA) that tend to compress and close the cracks, and Super-Absorbent Polymers (SAP) that provide water for further hydration are of the utmost techniques categorized in this group. In the following, a summary of each method and its contribution to autogenous self-healing is presented.

2.4.1. Fibers

Fibers have been extensively used in concrete over the years to control damage and improve structural properties [32-34]. Furthermore, their contribution to the improvement of autogenous self-healing is completely established by now, as incorporating dispersed fibers into concrete brings more than one improvement to autogenous self-healing mechanism [35]. They control and limit the crack width by bridging between the two faces of the crack, thereby less healing product is required to fill the cracks. Besides, they provide nucleation sites for crystallization of the healing products, also serve to help with clogging the cracks by attaching loose particles [36-38]. Studies on autogenous self-healing have proved that with keeping the crack width lower than 50 μm, a full closure of cracks could occur regardless of the exposure condition and duration, nevertheless, cracks up to 300 μm have been reported to be entirely healed, when favorable conditions are provided [19, 39]. This implies that with embedding only fibers into concrete, autogenous self-healing efficiency would be improved; therefore, it is classified as an improved autogenous self-healing technique.

Different types of fibers have been studied; among them, Polyvinyl alcohol (PVA), Polyethylene (PE), Polypropylene (PP), steel, and natural fiber were most investigated [35, 40]. PVA fibers have demonstrated to be more capable than other synthetics in terms of improving autogenous healing. It is through their polar nature that they can promote chemical precipitation of healing products with restoring water tightness [41, 42]. Natural fibers such as flax and sisal fibers also proved beneficial since they can absorb water during the wet periods and perform as a water reservoir that supplies for late hydration and carbonation during the dry periods [43, 44]. A combination of steel and synthetic fibers was reported to enhance the autogenous self-healing properties of concrete more than those used individually [36, 45]. Even though results reported high recovery rates in strength and water tightness when steel and synthetic fibers were incorporated jointly, there still remains the concern of steel fiber corrosion since the presence of water or moisture in the cracks is an essential element for the autogenous self-healing [40].

Fiber volume and dispersion in concrete can also affect autogenous self-healing by determining the cracking pattern and geometry. A more condensed cementitious composite with fibers results in multiple cracking with smaller crack sizes where less healing products are required; on the other hand, a lower fraction of fibers leads to a more localized fracture and damage growth with larger crack size [36]. Moreover, if the fibers' distribution in the cementitious composite is not almost homogenous, some initially induced cracks may lose tolerance and cause localized damage, which decreases autogenous self-healing efficiency. As previously discussed, younger specimens are more likely to heal through autogenous mechanism due to their higher fractions of unhydrated cement; however, studies have proved that old fiber-reinforced specimens have better fiber/matrix interfacial bond, therefore better distribution of cracks and accordingly more efficient healing was observed [38].

2.4.2. Supplementary Cementitious Materials (SCM)

Supplementary Cementitious Materials (SCM) are a group of industrial waste products, natural pozzolans, and activated minerals with relatively high portions of silica content that can replace clinker in cement production or replace cement content in the concrete mixture [46]. They are eco/environment-friendly materials with less required energy and $\mathrm{CO_2}$ emission compared to cement production, and their role is to supplement cement via two mechanisms; (i) Pozzolanic reaction: the silicate from SCM reacts with the calcium hydroxide ($\mathrm{CA(OH)_2}$)) formed through hydration of cement to form CSH, which is the main product of cement, (ii) Latent hydraulic reaction: SCM contains silica and calcium that can react chemically in an aqueous alkaline environment, with or without the presence of cement to form CSH [47, 48]. These chemical reactions of SCMs usually proceed slower than the reaction of the cement phase; therefore, they can provide late hydration, which favors autogenous self-healing [49]. It is worth mentioning that SCMs are categorized in the improved autogenous group because their chemical reaction and products are similar to cement, and also the fact that their main goal is to replace cement in concrete, thereby considered as cementitious material, not additives.

Fly ash, steel slag, and silica fume are primary sources of SCM that have been under investigation for cement replacement and proved beneficial for autogenous self-healing mechanisms [50-52]. Table 2.1 provides physical properties and chemical composition for a typical case of these materials and Portland cement for comparison. Their popularity of SCMs is directly related to their abundant resources since they are all considered as industrial waste products. Fly ash is a by-product of coal combustion, steel slag is a by-product of pig iron production, and silica fume is a by-product from silicon alloy production in electric arc furnaces [47]. However, recent investigations have claimed that these waste streams are declining, so to compensate for future demand, new sources of SCM should be identified [46, 53]. Natural pozzolans, including raw (e.g., pumice, perlite) and calcined minerals (e.g., metakaolin), are proposed as proper substitutes, which also have abundant resources around the world; nevertheless, their preparation price is still an issue compared with the mentioned waste products [54-56].

Table 2.1 A typical chemical composition and physical properties for fly ash, steel slag, silica fume and Portland cement [50, 57]

Material	Fly ash (Class F)	Fly ash (Class C)	Steel slag	Silica fume	Portland cement
$\mathbf{CaO}$	3.48	15.50	35.09	0.47	61.43
$\mathbf{SiO_2}$	60.78	46.97	37.55	95.6	20.77
$\mathbf{Al_2O_3}$	21.68	11.86	10.55	0.45	5.55
$\mathbf{Fe_2O_3}$	5.48	7.98	0.28	0.05	3.35
$\mathbf{MgO}$	1.71	6.51	7.92	-	2.49
$\mathbf{SO_3}$	0.34	3.47	2.95	-	2.49
Other	2.69	4.56	1.31	1.53	0.96
Specific gravity	2.10	2.27	2.79	2.22	3.06
Blaine fineness $(\frac{\mathbf{m^2}}{kg})$	290	306	425	-	325

As mentioned, significant portions of these SCMs remain unhydrated even at later ages; therefore, autogenous healing due to ongoing hydration is improved. Fly ash contains more unreacted binder materials than steel slag and is expected to demonstrate higher capacities of self-healing; however, it was found that steel slag performs better in terms of autogenous self-healing. This can be explained with the higher pH value of the pore solution and higher CaO content of steel slag that would favor the precipitation of calcite [50, 52]. There are two classes of fly ash, class F (low-calcium) and class C (high calcium), which both generally have less CaO content than steel slag; thus, their hydration process mainly relies on the consumption of $\mathrm{CA(OH)_2}$ from the cement paste to produce CSH and other hydration products (pozzolan reaction). Therefore, if a high percentage of cement is replaced with SCM, negative impacts on hydration could be observed [15, 52]. To compensate for low calcium availability, a few researchers have studied the effect of adding limestone powder and hydrated lime to high volume fly ash mixtures and reported promising results on the autogenous self-healing [58, 59].

2.4.3. Shape Memory Alloys (SMA)

Shape Memory Alloys (SMA) are smart materials that can be recognized with two characteristics, (i) Shape memory effect: the ability of the material to recover its pre-determined shape (length and diameter) upon temperature change (usually electrical currents), and (ii) Superelasticity: the ability to restore the material to its initial shape from the inelastic range upon unloading, which is obtained from stress changes [60-62]. SMA tendons/wires are usually made of nickel-titanium alloy (Nitinol) and can be fixed on the concrete member, or embedded as reinforcement in concrete [60, 63, 64]; nevertheless, the function remains the same. Over the years, Shape Memory Polymers (SMP) tendons were suggested to replace the SMA due to their lower cost. Polyethylene terephthalate (PET) is known as the pioneer in this group of materials [65].

The contribution of shape memory materials to autogenous self-healing is slightly similar to fibers, i.e., controlling the deflection and, subsequently, crack width, that demands less healing products [65]. However, they have the privilege of closing the cracks rapidly upon recovering their initial shape and, in some cases, apply a compression stress state on the crack faces, which is in favor of autogenous self-healing [66]. Both experimental and modeling results have confirmed that SMA can recover crack widths to a high degree, which can improve autogenous self-healing [60, 67, 68]. For example, it was reported that cracks up to 3mm were more than 90% recovered [63] (see Fig. 2.4). However, studies regarding SMA's application mostly concern the recovery of mechanical properties of the concrete member (e.g., strength, deflection, Young's modulus, etc.) and crack closing capacity, rather than the efficiency of autogenous self-healing. Further research is required to understand the effect of SMAs on the improvement of autogenous self-healing.

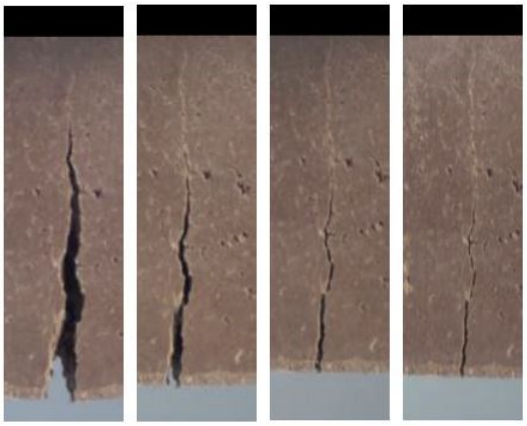


Fig. 2.4 Crack closure of beams with internally embedded SMA wires; from left to right shows the progress of SMA effect on crack [63]

2.4.4. Super-Absorbent Polymers (SAP)

Super-Absorbent Polymers (SAP) are natural or synthetic water-insoluble cross-linked polymers that absorb, swell, and retain large amounts of liquid (up to 500 times their own weight) from their surrounding environment [69, 70]. Hydrogel is another term often used for SAPs when the surrounding aqueous environment is water. The swelling capacity of SAP follows the osmotic pressure, which is proportional to the concentration of ions in the aqueous solution. While in the dry state, the ions in SAPs are bound close together by the polymer network, and there is high osmotic pressure inside, upon absorption of water (or any liquid), the osmotic pressure is reduced by diluting the charges [69, 71, 72] (see Fig. 2.5.a). The swelling capacity has also been related to the nature of monomers and the cross-linking density [73].

With regard to improving autogenous self-healing, SAPs are multifunctional. When added to concrete during mixing, they take up water and swell, then shrink upon subsequent hardening of concrete and leave macropores in the matrix. These macropores act as initial flaws and promote multiple cracking, which encourages autogenous self-healing [74, 75]. Then upon cracking, water ingress into the cracks, and SAPs absorb moisture and swell again, filling the crack space immediately. This feature not only provides a rapid sealing of cracks, but is also helpful when SAPs are used in water retaining structures where there is water flow, and by reducing that, there is a higher chance for precipitation of healing products (e.g., calcite) [72, 76, 77]. Lastly, the water that has been absorbed by the SAPs during the wet period will gradually be released during dry cycles to promote further hydration (see Fig. 2.5.b) [78, 79]. Moreover, since the pore solution in concrete is a calcium-rich medium, the SAPs swollen in the cracks often contain calcium ions, which helps with calcite precipitation [80]. However, a recent study has reported that calcium ion complexation suppresses swelling of SAP [81].

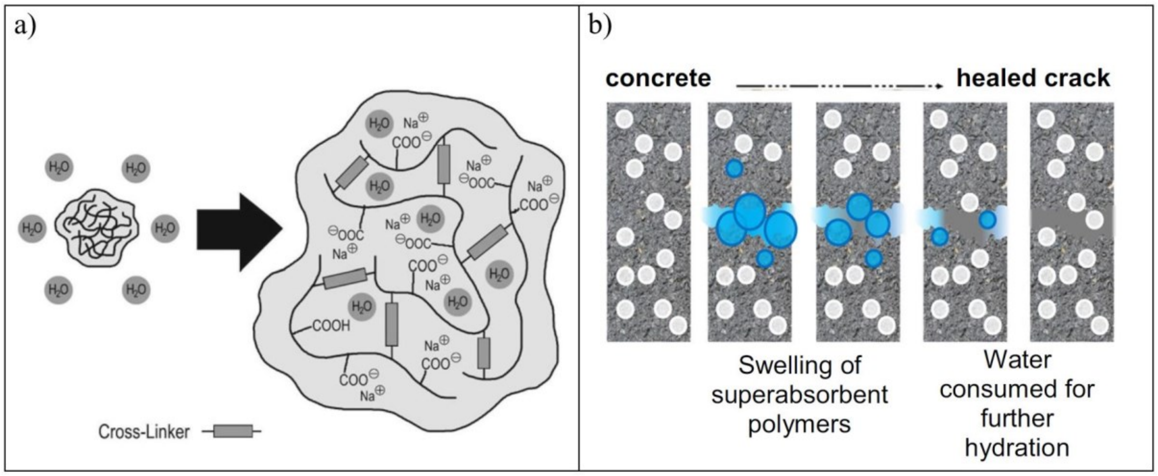


Fig. 2.5 a) The process of absorbing water and swelling of a typical SAP [69] and, b) the improvement of autogenous healing in cementitious materials with SAP [79]

Despite the improvements that SAPs provide for autogenous self-healing, the porous network structured due to the swelling of SAPs raises noticeable concerns regarding the mechanical properties of concrete (e.g., strength) [82]. Recent investigations proposed the coating of SAPs with primer and barrier layers to delay their swelling in fresh concrete and reduce macropore network formation [83]. Moreover, the introduction of pH-sensitive SAPs that keep a low swelling rate in high alkalinity (during the mixing of concrete) and demonstrate high absorption capacity in a more neutral pH (water ingress through cracks) has reported effective in terms of controlling porous network formation and improving autogenous self-healing [84, 85].

2.5. ENGINEERED CEMENTITIOUS COMPOSITES (ECC)

ECC is a class of High Performance Fiber-Reinforced Cementitious Composites (HPFRCC) that has been developed based on the idea of applying fracture mechanics into fiber-reinforced composite systems [86], and it was first established as a new product in the early 1990s by Li at the University of Michigan [87]. Unlike conventional FRC, ECC exhibits metal-like strain hardening behavior after matrix first cracking. The unique material properties of ECC is driven by its micromechanics and constituents, which results in controlled multiple cracking and high tensile strain of over 3% (See Fig. 2.6) [88]. In the following sections, the micromechanics is explained, and it is revealed how the unique microstructural properties and constituents of ECC result in a self-healing attribute for this material.

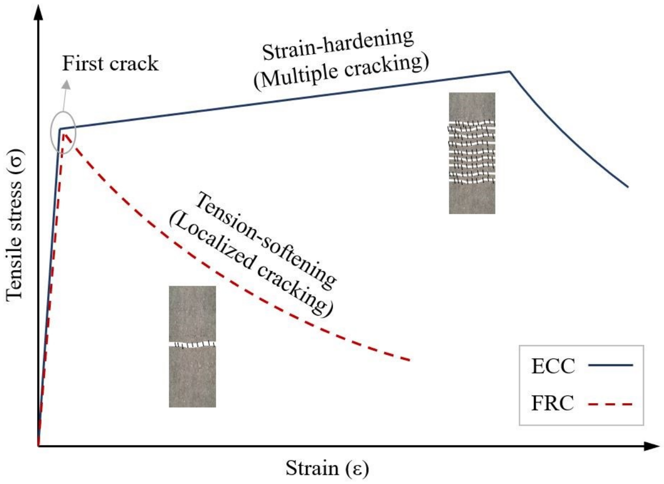


Fig. 2.6 Tensile stress-strain behavior of ECC vs. FRC

2.5.1. Micromechanics of ECC

ECC derives its high tensile ductility by controlling the growth of the cracks from pre-existing flaws with two complementary criteria. The first criterion is regarded as the strength criterion, which relates to the most fundamental property of fiber-reinforced cementitious material, the fiber bridging property across a crack, generally referred to as the σ-δ curve (Fig. 2.7) [89]. The strength criterion asserts that the tensile stress to initiate a crack (σ_{cr}) from a pre-existing flaw must be less than the maximum fiber bridging stress (σ_0), written as Eq. 2.4:

$$\sigma_{cr} < \sigma_0 \qquad \text{Eq.2.4}$$

The first cracking stress (σ_{cr}) is dependent on the maximum pre-existing matrix flaw size and matrix fracture toughness (K_m). These are properties of matrix material and are influenced by the binder and aggregate type and size, w/c ratio, etc. [90]. The maximum fiber bridging capacity (σ_0), varies from one crack plane to another due to the inevitable spatial non-uniformity in fiber dispersion. If Eq. 2.4 is not satisfied on any of the crack planes, a localized cracking system will be generated that cancels the multiple cracking properties of ECC, which results in a tension-softening post-peak behavior. [91]. Therefore, in order to maintain Eq. 2.4, a high (σ_0/σ_{cr}) ratio is desired, which can be obtained with a high fiber volume fraction (V_f), a strong fiber and/or strong fiber-matrix bond [92].

The second criterion for multiple cracking in ECC is concerned with the crack propagation mechanism, which in turn is governed by the energetics of the crack extension. This criterion is known as the energy criterion and employs the complementary energy concept (J'_b). The complementary energy depends on the crack propagation pattern, that is influenced by the fiber and fiber-matrix interface. If the fiber-matrix interface is weak, pull out of fibers occurs, resulting in a small peak strength (σ_0). On the other hand, if the interface is strong, the fibers will fail in rupture and a small value for (δ_0) is obtained. In either case, the complementary energy illustrated as the hatched area in Fig. 2.7 will be small [89].

The steady-state crack analysis reveals that in order to achieve a multi-cracking strain-hardening behavior in ECC, the complementary energy (J'_b) should be greater than the crack tip toughness (J_{tip}, i.e., the energy required to break down the crack tip material to extend the bridged crack) [93]. The steady-state flat crack propagation mode states that the crack opening is uniform at (δ_{ss}), except for a small region behind the crack tip. A balance of energy needs to be maintained so that the work done due to the ambient tensile stress (σ_{ss}) should be equal to the crack tip breaking energy (J_{tip}) and the energy required to open the crack against fiber bridging from 0 to δ_{ss} [94], written as:

$$\sigma_{ss}\delta_{ss} - \int_0^{\delta_{ss}} \sigma(\delta)d\delta = J_{tip} \qquad \text{Eq.2.5}$$

Where,

$$J_{tip} = \frac{{K_m}^2}{E_c} \qquad \text{Eq.2.6}$$

E_c is the matrix elastic modulus and K_m is the matrix fracture toughness. The concept of complementary energy (J'_b) can also be written as,

$$J'_b \equiv \sigma_0\delta_0 - \int_0^{\delta_0} \sigma(\delta)d\delta \qquad \text{Eq.2.7}$$

The energy criterion is satisfied when,

$$J'_b > J_{tip} \qquad \text{Eq.2.8}$$

Eq. 2.4 and Eq. 2.8 are the two criteria that indicate strain hardening is a material property and is generated when they both are satisfied. It is vividly clear that the σ-δ curve plays the dominant role in determining whether a composite will show a strain hardening behavior with multiple cracking or is going to fail in localized cracking under uniaxial tensile load. Therefore, it is critical to maintain a balance between fiber volume fraction, diameter, length, strength, and modulus, in addition to the interfacial chemical and frictional bond properties, when tailoring an ECC mixture [94].

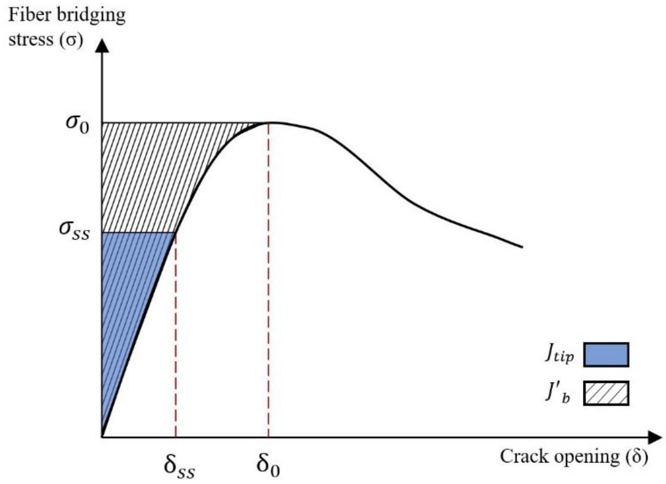


Fig. 2.7 Typical σ-δ curve for a strain-hardening composite reproduced from [95]

2.5.2. Self-healing of ECC

A standard ECC mixture (known as M45) consists of cement (C), fly ash (FA), silica sand (S), water (W), High-range Water Reducer Admixture (HRWRA), and polyvinyl-alcohol (PVA) fiber, however, alternate compositions with different types of SCM and fiber have been developed and studied [36, 50, 96]. The suggested portions for standard ECC are tabulated in Table 2.2 (all ingredients proportions by weight, except for fiber, which is presented in volume fraction) [97].

Table 2.2 ECC mix portions

Ingredients	C	FA	S	W	HRWRA	PVA (%)
Weight	1.00	1.20	0.80	0.58	0.013	2.00

ECC could claim to be the rightful representative of the improved autogenous self-healing group. Applied micromechanics that results in multiple-cracking pattern with controlled crack widths (less than 100 μm) and dens fractions of fibers inside the cracks, plus adding high portions of SCM, develop a multifunctional approach toward improving autogenous self-healing. Both hydration of unreacted cement/SCMs at early age and calcite precipitation at later periods play essential roles in ECC's self-healing process [37, 98, 99]. Since ECC presents unique mechanical properties in terms of deflection capacity and subsequently damage control, research has also been extensively carried out over the years to address ECC's efficiency in improving autogenous self-healing [50, 100-103]. Improved autogenous self-healing has demonstrated to be pervasive and reliable in ECC when specimens are cured under controlled laboratory conditions. Durability, transport, and mechanical properties were also recovered to a high degree under different exposure conditions, including chloride and highly alkaline environments [31, 101, 104, 105]. In addition, promising self-healing results have been reported in large scale applications of ECC [106, 107].

2.6. MINERAL-BASED SELF-HEALING

The present paper distinguishes between mineral-based self-healing techniques, which belong to the autonomous healing group, and self-healing performed using SCMs, categorized as improved autogenous self-healing. The former is considered an additive with expansive, swelling, or crystallization properties, but the latter is a cement replacement with pozzolanic or latent hydraulic reactions that produce similar hydration products to cement, as discussed in section 2.4.2. To establish a better understanding of the differences, two types of expansive and crystalline admixtures and their mechanism of self-healing in concrete are explained in the following.

2.6.1. Expansive Admixtures

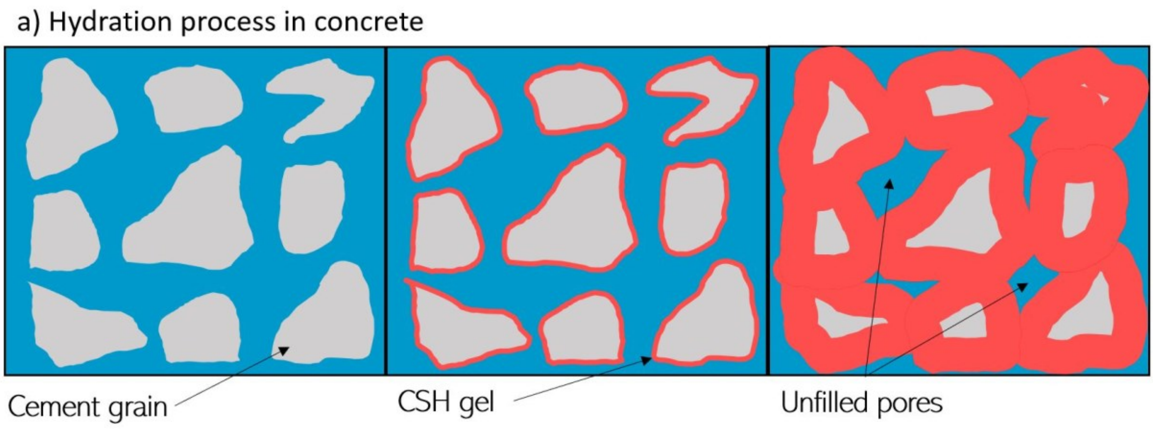
Self-healing of cracks can be achieved through the expansion of mineral additives implemented into concrete during mixing. Upon cracking and water ingress, the unreacted portions of these minerals start to react with water and expand, leading to crack healing [108]. Calcium sulfoaluminate ($Ca_4(AlO_2)_6SO_4$), free lime (CaO), Magnesia (MgO), and anhydrite ($CaSO_4$) are of the common expansive minerals that have been studied (separately or combined) to induce self-healing mechanism into concrete [109, 110]. Their main reaction products, which have larger volumes than the reactant, are usually ettringite, magnesium hydrate, magnesium carbonate, and calcium hydroxide [111, 112]. It is worth mentioning that the original purpose of introducing these minerals into concrete was to compensate for drying shrinkage using their expansion properties [113]. The reported healed crack widths using expansive additives are between 100 μm to 400 μm, depending on the type of mineral and its fraction in the mixture, the healing exposure condition, and duration [17, 110, 114]. An important issue regarding the use of expansive minerals is that if not protected, a considerable portion of these additive minerals react with water during concrete initial mixing and be consumed; therefore, proper techniques such as encapsulation and coating have been proposed to protect the healing agents from undesirable reactions [114, 115].

2.6.2. Crystalline Admixtures (CA)

Crystalline Admixture is a market name used to label a group of hydrophilic admixtures containing active chemicals that form water-insoluble pore-blocking precipitates upon reaction with water, leading to densification of CSH and resisting water penetration. Every manufacturer has a unique formula for crystalline admixtures; therefore, the chemicals' reactions and products vary depending on the ingredients. Active chemicals used in crystalline admixtures are types of carbonates ($Na_2CO_3, NaHCO_3, Li_2CO_3$), active silicates (sodium silicate, ethyl silicate), Talcum powder, etc. [28, 111, 116, 117], usually mixed with crystalline promoter/catalyst, cement and sand. ACI TC212 categorizes CA as type of permeability reducing admixture with the capability to function under hydrostatic pressure (PRAH) [118]. The report states that tricalcium silicate (C_3S) in cement is the reacting component with CA and the reaction is described as follows:

$$3CaO - SiO_2 + M_xR_x + H_2O \rightarrow Ca_xSi_xO_xR - (H_2O) + M_xCaR_x - (H_2O) \qquad \text{Eq.2.9}$$

Where tricalcium silicate reacts with the crystalline catalyst/promoter (M_xR_x) in the presence of water to form modified CSH ($Ca_xSi_xO_xR$) and pore-blocking precipitate (M_xCaR_x). The carbonate ions (CO_3^{2-}) from some active chemicals can also react with calcium hydroxide ($CA(OH)_2$) formed during the hydration process and produces calcite. Furthermore, the Ca^{2+} ions leaching from the admixture can react with the carbonate ions (CO_3^{2-}) and precipitate calcite [17, 117]. Altogether, the reactions lead to matrix densification as they fill the pores in between cement grains, minimizing drying shrinkage and chloride ion penetration [118]. The unreacted portions of CA will be present in the matrix for late crystallization and filling the cracks when activated by moisture (see Fig. 2.8).



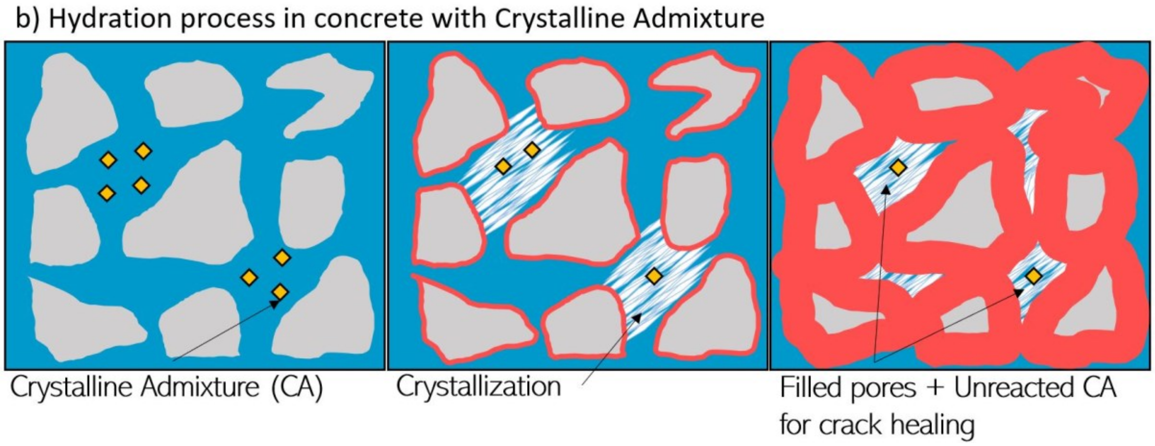


Fig. 2.8 Schematic demonstration of hydration process in concrete a) without CA leading to unfilled pores, and b) with CA leading to filled pores and unreacted portions of CA left in the matrix for promoting crack healing

The researchers have reported promising self-healing results using CA. When mixed with concrete at 1-4% of cement weight, it has proven to improve the self-healing capability considerably [28, 116]. The best results are reported when combined with other expansive and swelling minerals in the mixture [119]. If there are fibers in the matrix, CA's crystallization process could apply a prestressing force on the fibers, helping with regaining the mechanical properties [120]. Also, since the sea water is an ion-rich medium, studies have shown that self-healing process by using CA can be improved when sea water is selected as the surrounding environment [121].

2.7. RESEARCH GAPS

2.7.1. Repeatability of Self-healing Mechanisms

Almost all of the self-healing mechanisms in the literature have demonstrated to be feasible to some extent in lab condition, however, if used in practice, there should be adequate criteria that determine their effectiveness and limitations in different applications. In this regard, researchers proposed implementing "robustness criteria" to accredit different self-healing mechanisms and address their merits and demerits [12, 122, 123]. To ensure that a self-healing mechanism is robust, it needs to meet six robustness criteria, including shelf life, pervasiveness, quality, reliability, versatility, and repeatability. Among six, the repeatability criterion raises significant challenges into the healing mechanisms due to the inevitable repeating nature of external loads/harsh environmental conditions that induce damage over the lifetime of infrastructure. Also, concrete tends to show localized cracking behavior, threatening the healed cracks upon repetitive damages. Moreover, studying the life-cycle cost of implementing self-healing mechanisms into concrete structures proves that the healing function must be repeatable in order to justify the extra initial cost caused by the self-healing mechanism (see Fig. 2.9). Therefore, a robust self-healing technique is required to function not just once, but to trigger upon multiple cracking over the lifetime of the infrastructure.

With ECC's development in the last few years, the repeatability of improved autogenous self-healing has brought attention to the researchers. Fibers that bridge the cracks to control the damage and provide nucleation sites, plus high pozzolanic ingredients and unhydrated cement that promote C-S-H formation, are suggested to be effective for a repeatable autogenous self-healing mechanism [124]. A thorough study carried out by Sahmaran et al. [125] on the repeatability of self-healing in ECC proved that under certain conditions (i.e., the presence of water and limiting crack with to 190 μm), the healing method demonstrates acceptable results even after nine cycles of loading and unloading. Herbert et al. [98] also claimed that improved autogenous healing in ECC is repeatable in the natural environment but highly dependent on the amount of damage and weather conditions. To overcome the water-supplying problem for repeatable autogenous self-healing in ECC, Snoeck et al. [80]

implemented SAPs in strain-hardening cementitious composites. He compared the results for two consecutive loading cycles and found out that SAP can play a significant role in regaining the mechanical properties of the damaged concrete under repeated loads. Stimulating CSH formation in ECC through adding hydrated lime was also reported beneficial for repeated self-healing [58]. Cuenca et al. [126] studied the repeatability of self-healing under three different exposure conditions of water immersion, open-air, and wet/dry cycles for a year for a typical Fiber Reinforced Concrete (FRC) with Crystalline Admixtures (CA). They concluded that effects of CA persist after repeated cracking-healing cycles, but highly depended on its surrounding environment, as almost no healing was observed in the open air. In another attempt, Cuenca and Ferrara [127] tried to correlate fracture toughness parameters from mechanical recovery to the crack sealing capacity index of FRC with CA under repeated cracking-healing cycles. They stated that the exposure condition and the crack width play a dominant role in the healing efficiency under repeated loading.

Nevertheless, it is difficult to define a single load pattern in the lab that perfectly simulates the external repeating loads condition and timeline. Since majority of the research conducted on assessing the repeatability of self-healing mechanisms employed a simple series of loading and unloading, it is possible that with a more precise loading approach, different results be achieved not only for the repeatability index but also for the whole robustness criteria. Different magnitudes, frequencies, and directions of loading should be tested for this purpose. Unfortunately, the lack of field studies, in this case, expands the existing research gap.

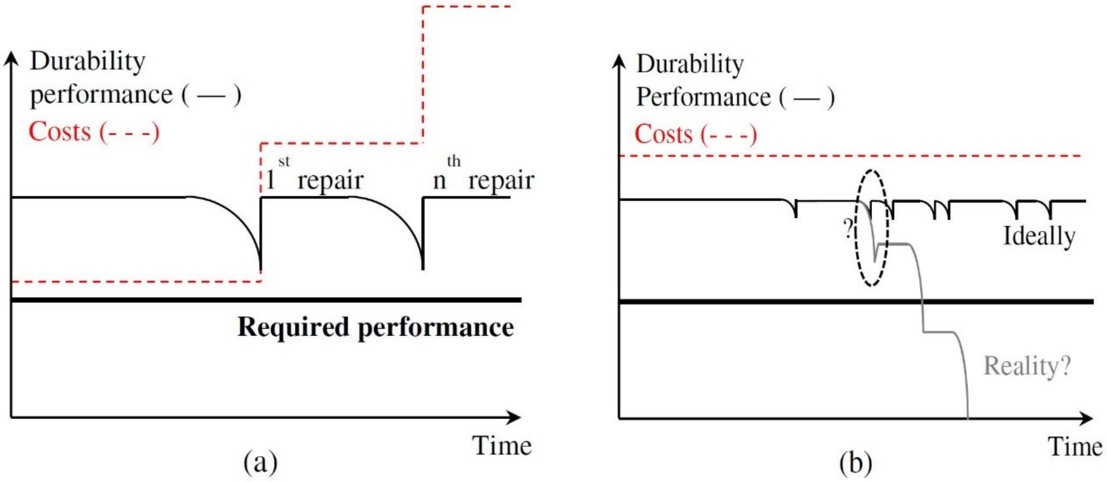


Fig. 2.9 Durability performance vs. time diagrams demonstrating conceptual life-cycle cost of a structure made with a) conventional concrete and, b) ideal self-healing concrete [80].

2.7.2. Effect of the Surrounding Environment

Concrete members serve under different environmental exposure conditions based on their role in the structure. Through extensive investigations carried out in the last decades, the fact that the effect of the surrounding environment is inevitable on almost all of the self-healing mechanisms has been well established [15, 128]. Therefore, adopting a unique and effective self-healing method for a concrete structure highly depends on the exposure condition that the structure is expected to face throughout its service life.

Usually, the curing conditions employed in the lab for assessing the effectiveness of a self-healing method are either based on their potential positive effects on the self-healing process or representing the anticipated field of application of the structure. Exposure to local climate, submerging in water, applying freeze/thaw and wet/dry cycles, controlled temperature, and relative humidity are the most common curing conditions investigated by the researchers [102, 119, 128]. By collecting more in-depth knowledge of the surrounding environment and its effects on self-healing, the favorable self-healing mechanism can be adopted; plus, in some cases, the surrounding environment can be tailored or promoted in a way that enhances the self-healing function. The studies carried out by Yildirim et al. [129] proved that increasing the concentration of dissolved (CO_3^{2-}) ions in the water surrounding ECC specimens promotes the precipitation of calcite, which is the primary source of autogenous healing at later ages, even for crack widths more than 200 μm (see Fig. 2.10).

However, the effects of different soil types as the surrounding environment of a concrete member have been missing in the literature. Concrete pipes, tunnels, and foundations of concrete and steel structures are the main structural members with soil as their surrounding environment through their lifetime. Since soil is full of chemical substances (e.g. Ca^{2+}, Mg^{2+}, Na^{+}, etc.) and these substances may transfer into cracks by dissolving in the groundwater or rainfall run-off, there is a high possibility that by examining soil as the surrounding environment, different soil types demonstrate different results for self-healing of cracks (see Fig. 2.11). To cover the research gap here, a thorough study must be carried out to identify the proper types of soil that exhibit the most remarkable improvements in the self-healing results of cracks.

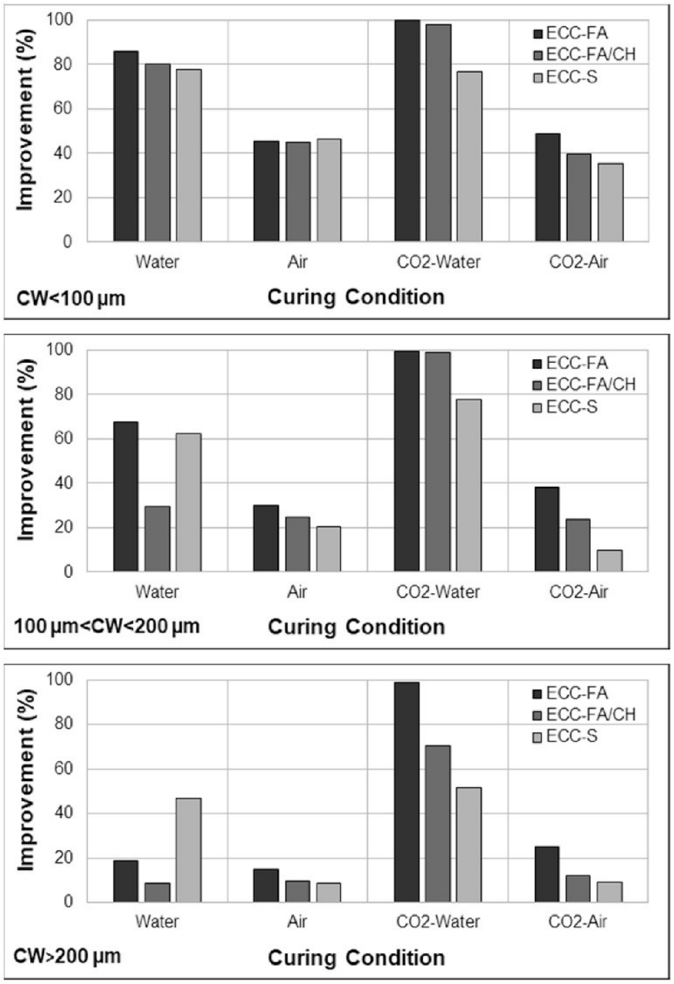


Fig. 2.10 Self-healing improvement in ECC specimens under multiple curing conditions and different crack widths [129]

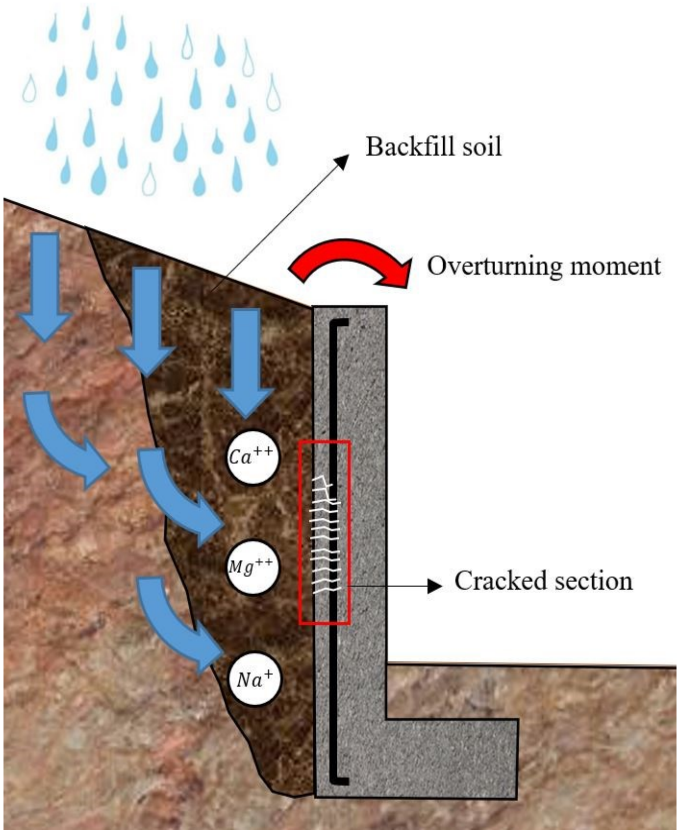


Fig. 2.11 Schematic demonstration of backfill soil acting as the surrounding environment of a typical retaining wall with the possibility to promote self-healing of cracks

2.8. CONCLUSION AND OUTLOOKS

The present review paper presents the fundamentals and recent research developments of autogenous and improved autogenous self-healing mechanisms. The possible causes for autogenous self-healing are identified, and improved autogenous self-healing mechanism is further defined as any mechanism that can improve any of those possible causes. Fibers that bridge between the cracks and provide nucleation sites for precipitation of autogenous healing products, and also limit the crack width, Supplementary Cementitious Materials (SCM) that replace cement in the mixture and add a late hydration mechanism into the concrete matrix, Shape Memory Alloys (SMA) that tend to compress and close the cracks, and Super-Absorbent Polymers (SAP) that supply water for further hydration are of the discussed methods categorized in this class.

ECC has been introduced as the pioneer branch of improved autogenous self-healing group. ECC's micromechanics and constituents are explained, and it could be claimed that self-healing in ECC is reliable to a great extent if favorable conditions are provided, i.e. controlled crack width (less than 50μm) and moisture in the surrounding environment. In this conditions, even repeatable crack healing could be considered as a feasible action. To further improve ECC’s self-healing behavior, a combination of ECC and other compatible healing techniques such as addition of mineral based additives could be investigated.

A new classification of the principal self-healing mechanisms is introduced based on JCI TC-075B and RILEM TC-221 recommendations. The latter, provided in 2013, presents a good summary of the concept of self-healing, terminologies, methods of evaluation, and results of the research. Future recommendations/guidelines prepared for self-healing concrete could suggest standard limits of efficiency for different self-healing techniques. A good step in evaluating the efficiencies of different self-healing methods and filtering the proper ones would be implementing "Robustness criteria" to accredit the self-healing mechanisms. With regard to these criteria, repeatability raises a significant challenge for self-healing mechanisms, due to the inevitable repetitive nature of external loads or harsh environments that induce cracking over the life-time of concrete structures. Moreover, to justify the higher initial cost of concrete created while implementing self-healing mechanisms, a repeatable self-healing mechanism which is capable of filling the cracks upon multiple crack re-openings must be selected. Fibers and super-absorbent polymers are proved to be compatible additives that help promote the repeatability of improved autogenous self-healing. Further research needs to be carried out on the repeatability of self-healing techniques, with considering a more accurate loading plan, based on the real-life application of structures.

Furthermore, the processes of autogenous and improved autogenous self-healing are greatly dependent on the surrounding environment. Availability of moisture and reactive ions can affect both processes substantially. Soil as the surrounding environment of concrete that can retain moisture and different types of ions, should be investigated for possible chances of improvement in autogenous self-healing.

CO_2 sequestration into mineral forms of carbonates (e.g., calcite) has been introduced as an emerging branch of research on concrete materials. The study aims at developing techniques to insert CO_2 (gaseous or liquid form) into concrete during mixing or curing process, establishing a sustainable mineral form of the greenhouse gas. Since autogenous self-healing is partially achieved via calcite precipitation in the cracks (which occurs through the sequestration of CO_2 from the surrounding environment), it seems that there is a link between these two fields of research. A mutual research interest could lead to exploring technologies to improve CO_2 sequestration in the self-healing process.

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CHAPTER 3 REPEATABILITY OF SELF-HEALING IN ENGINEERED CEMENTITIOUS COMPOSITES (ECC) UNDER REVERSE LOADING CYCLE[2]

ABSTRACT

The present study investigates the effects of reverse flexural loading cycles on the repeatability of self-healing in Engineered Cementitious Composites (ECC). The experimental work is designed to test two cases of instant and sustained loading and three different exposure conditions of tap water, sea water, and air dry. A total of 27 prism specimens (100×100×350 mm) were fabricated, and a four-point bending test was used for flexural load application at different stages and to further measure the recovery in mechanical properties. Ultrasonic Pulse Velocity (UPV) test was carried out before and after every loading stage and the wave travel time was compared as an indicator of healing efficiency. To monitor crack propagation patterns and crack widths, Digital Image Correlation (DIC) technique was used. To further analyze the mineralogy and microstructure of the healing products, X-ray Diffraction (XRD) test was conducted on two groups of tap water and sea water exposures. Concluding results proved that sea water and tap water are suitable environments for autogenous self-healing process. Furthermore, reverse loading cycles were demonstrated to impact the self-healing results and should be considered for repeatable self-healing purposes.

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[2] This chapter is submitted to a journal.

3.1. INTRODUCTION

Self-healing mechanisms have been introduced into cementitious materials over the last twenty years to enhance the durability and increase the lifetime of the infrastructure while diminishing the repair cost and labor [1-3]. Autogenous and Autonomous mechanisms are the two major methods of self-healing in cementitious materials [4]. While autogenous method is mainly focused on the further hydration of unhydrated particles and crystallization of calcium carbonate [5, 6], autonomous healing is more versatile with representing encapsulation techniques of adhesive agents [7-9] and bacteria [10-12]. The existing literature on self-healing concrete is broad, and the results are promising, however, the application of self-healing mechanisms has yet remained in the academic stage [13-16]. To establish a better connection with industry, some researchers suggested implementing "Robustness criteria" as a filter to identify and accredit the practical methods to be used in sustainable infrastructure [17-20]. The robustness criteria implies that every mechanism needs to meet at least six criteria including shelf life, pervasiveness, quality, reliability, versatility, and repeatability to be justified for application in sustainable infrastructure. Among them, the repeatability i.e. the ability of the mechanism to be able to trigger not only once, but upon multiple cracking over the estimated lifetime raises a significant challenge. Due to the inevitable repetition of external loads/harsh environments that induce cracking over the lifetime of the infrastructure, accompanied by the localized cracking behavior of cementitious composites, the repeatability of the mechanisms that mainly rely on the formation of low-strength and low-toughness healing products (e.g. $CaCO_3$) is threatened. It also questions the micro and macro encapsulation techniques when the healing agents are consumed and hardened during the first cracking, ending the healing process [17, 21]. Moreover, the repeatability of self-healing mechanism is a crucial asset for justifying the life cycle cost of self-healing mechanisms for industry [22]. To help obtain a repeatable self-healing mechanism in concrete, a set of physical, chemical and environmental conditions are suggested [23]. Fibers that bridge the cracks to control the damage, high unreacted ingredients that promote the formation of strong materials such as Calcium Silicate Hydrate (C-S-H) or crystals, and presence of moisture in the surrounding environment are suggested to be most effective [24-29].

Engineered Cementitious Composite (ECC) that possesses two-third of the aforementioned properties, has been of high interest to researchers for its repeatability properties. ECC is a special category of High-Performance Fiber-Reinforced Cementitious Composites (HPFRCC), introduced by Li [30]. The main characteristic of ECC that distinguishes it from other fiber-reinforced cementitious composites is its strain-hardening behavior that is the result of a synergetic interaction between fibers, cementitious matrix and the interface [31]. Adding to its unique structural behavior, the high fractional volume of micro-fibers that limits the crack widths, plus the high portions of Supplementary Cementitious Material (SCM) such as fly ash that remain unreacted during the initial hydration, not only promotes self-healing, but suggests the fact that it can introduce repeatable self-healing into the infrastructure [17, 24, 26, 32].

Sahmaran et al. [24] studied the repeatability of self-healing in ECC through the Resonant Frequency (RF) and Rapid Chloride Permeability (RCP) tests. He concluded that ECC specimens could recover up to 85% of their initial RF measurements, even after six repetitive preloadings. However, it should be considered that the crack widths in his test were limited to 190 μm, and wet/dry cycles were provided during curing periods. Snoeck and De Belie [29] suggested implementing Super Absorbent Polymers (SAP) in ECC to help with the water supply during the curing time under repeated loads, however, Herbert and Li [32] claimed that ECC is capable of maintaining its self-healing functionality after multiple damage in the natural environment. To see the effect of different loading conditions, Yildirim et al. [26] assessed the self-healing behavior of ECC under increasing sustained loading cycles. After 180 days of initial curing, the prism specimens were subjected to 40% of their ultimate flexural capacity, and 10% increase was applied every 30 days for 5 cycles. Ultrasonic Pulse Velocity (UPV) test and recovery of mechanical properties were used to measure the healing efficiency over the test period. It was stated that the deflection results were more adversely affected by progressive sustained loading than the healing process, indicating the influence of loading condition on the healing process. To study a more conventional case of concrete, Cuenca et. al [27] replaced ECC with a normal Fiber Reinforced Concrete (FRC) to keep the fibers in action, and changed the fly ash as the source of late hydration with Crystalline Admixtures (CA) which are water soluble additives that produce crystals during the fresh and hardened state. They studied the repeatability of self-healing under three different exposure conditions of water immersion, open air, and wet/dry cycles for a year and concluded that effects of CA persists after repeated cracking-healing cycles, but it highly depended on its surrounding environment, as almost no healing was observed in the open air. In another attempt, Cuenca and Ferrara [28] tried to correlate fracture toughness parameters from mechanical recovery to crack sealing capacity index of FRC with CA under repeated cracking-healing cycles. They concluded that the exposure condition and the crack width play a dominant role in the healing efficiency under repeated loading.

The present experimental study is designed to investigate the repeatability of the self-healing mechanism in ECC with addressing two decisive parameters, namely: loading condition and exposure condition. As it was concluded in the previous studies, different loading conditions can have a significant impact on the healing process. To further investigate that, a set of reverse loading cycles were used in this study. Along, cases of sustained loading were carried out to assess the crack stability effects on the repeatability of self-healing. Furthermore, since the surrounding environment has been reported numerous times as a determinant factor on the repeatability of self-healing, and also due to direct contact of many of our infrastructure with the ocean, it is essential to study the effects of sea water on the repeatability of the healing process. Therefore, exposure to tap water, sea water and air dry is considered in this study to investigate the effect of exposure condition on the healing process.

3.2. RESEARCH SIGNIFICANCE

The magnitude and direction of external forces that are transferred into a structural concrete member varies, depending on the member's role and position in the structure. Moreover, some external forces act at multiple directions (e.g., wind load), while some are hardly predictable (e.g., seismic load). That implies different events for a partially healed crack. Almost all of the available literature on the repeatability of self-healing has considered the repetitive external cycles as loading cycles that open up the partially healed cracks to the pre-cracking level or higher. However, there is a chance that the partially healed cracks undergo a compression state where they are forced to close due to the external forces. This applies a new condition to the healing process that has not been studied yet. The main scope of this study is to investigate the positive/negative impacts of this new condition on the functionality of the healing process in ECC during multiple damaging. The results will determine the necessity of considering reverse cycles while the repeatability of a self-healing mechanism is under investigation.

3.3. EXPERIMENTAL PROGRAM

The experimental program implemented in this study aims to measure the repeatability of self-healing mechanism in ECC under reverse loading cycles. For this purpose, 27 ECC prism specimens with a single mix design were fabricated and afterward, tested under tension and compression cycles. Four-point bending test was selected for loading cycles and also to measure the self-healing through regaining of mechanical properties. Digital Image Correlation (DIC) technique was used to monitor the loading stages and to measure Crack Mouth Opening Displacement (CMOD), and Ultrasonic Pulse Velocity (UPV) test was employed to assess the healing efficiency of cracks during the test period. To study the mineralogy of the formed healing products, X-Ray Diffraction (XRD) test was conducted on the healing products scratched from the face of the cracks after final loading.

3.3.1. Material Properties and Specimen Fabrication

A single ECC mix design incorporating Class-F fly ash (FA), type GU Portland cement (C), micro-silica sand (S) with an average aggregate size of 225 μm, water (W), high-range water-reducing admixture (HRWRA) and polyvinyl alcohol (PVA) fibers with a nominal tensile strength of 1100-1400 MPa, diameter of 38 μm, length of 8 mm and specific gravity of 1.3 was used in this study. Table 1. provides details on the portions of the mix design. Water to cementitious material ratio (W/FA+C) was 0.27. The compressive strength of the adopted mix design was measured by means of compression test on three standard cylindrical specimens at the age of 7-day and 28-day and the results were 28.5 MPa and

40.0 MPa, respectively. The relatively high FA/C ratio of 2.2 was selected to promote the healing efficiency of ECC by late hydration [25, 32, 33]; also, it reduces the cement portion in the mixture.

Table 3.1 ECC mix design for 1 m^3

Ingredients	FA	C	S	W	PVA	HRWRA
Weight (kg)	823	375	435	318	26	3

3.3.2. Test plan and Exposure conditions

The objective of this study is to investigate the repeatability of self-healing in ECC after a series of loading cycles. The novelty is to use a reverse loading cycle as the repeating cycle between pre-cracking and final loading cycles to determine the effect of compression stress on the healing process of partially healed cracks. Also, since the sustained state of loading keeps the crack width wider and disturbs the healing process by making the cracks unstable, the effects of applying a set of sustained loading conditions on the healing efficiency was studied in parallel to repeatability.

For this purpose, three groups of Reference (REF), Reverse (REV), and Reverse-Sustained (RES) were planned to be tested. A summary of the test plan and studied exposure conditions is presented in Table 3.2 The first loading cycle applied to all three groups was pre-cracking. This step was conducted using the four-point bending test after the initial curing period was completed. Generally, pre-cracking is applied as a force/displacement-controlled test in which the specimen is damaged up to a specific percentage of its ultimate force/displacement capacity. However, for the case of ECC, it was difficult to determine a certain ultimate force/displacement capacity. After testing 6 dummy specimens under four-point bending test, it was observed that the continuation of post-linear behavior (strain-hardening stage) is highly dependent on the fiber orientation and dispersion at the crack locations and also the crack propagation pattern [23, 34]. Therefore, in this study the specimens were pre-cracked up to a point where a visually distinguishable crack (~400-500μm) was observed on the tension side. For a few ECC prisms, reaching this point was also accompanied by a small load reduction, indicating that the specimen is now experiencing post-peak behavior (tension softening stage). However, for most of other specimens, the load was increasing when a distinct crack was observed. This provided an excellent set of data to evaluate the healing efficiency of ECC in terms of regaining the mechanical properties during both strain hardening and tension softening stages.

After pre-cracking, the specimens in group RES were put inside a sustained loading fixture to continue experiencing the final mid-span deflection that they have been subjected to under the pre-cracking stage. Hence, the amount of mid-span relaxation after unloading the pre-cracking force was measured for these specimens by means of DIC and then applied to them using the sustained fixture as shown in Fig. 3.1.c. A digital displacement gauge was fixed perpendicular to the bottom of the specimens at the mid-span to measure the mentioned displacement. The load was applied with an ACDelco digital torque wrench shown in Fig 3.1.b, which was calibrated three times with a pancake load cell before the tests and compatible results were obtained (Fig 3.1.a). In this step of the test, the specimens in group RES undergo a tension (T) state, where cracks are being opened up (see Fig. 3.1.d).

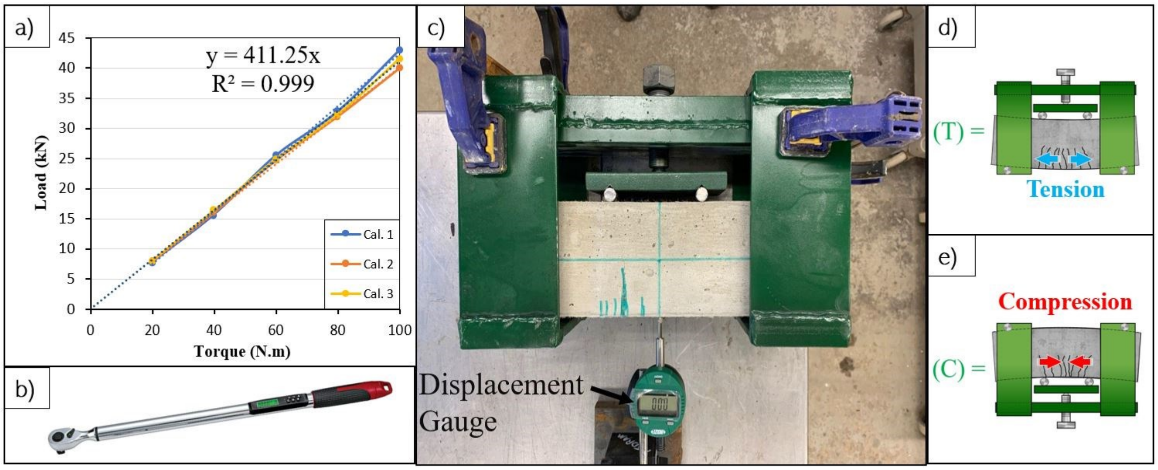


Fig. 3.1 Sustained loading fixture setup tools and test conditions, a) Torque vs. load calibration of the torque wrench, b) ACDelco digital torque wrench, c) sustained loading fixture clamped to the table and displacement gauge fixed at the mid-span, d) cracks under sustained tension and, e) cracks under sustained compression

To study the effects of different exposure conditions on the healing process, specimens were exposed to three different curing conditions, including tap water, sea water, and air dry for four months afterwards, which provided the cracks with enough time to partially or entirely heal. Upon completing the first curing period, the repeating cycle which was selected to be a reverse cycle in this study, was applied through a force-controlled four-point bending process to groups REV and RES. The specimens in group REV were placed upside down in the Instron setup and were subjected to bending loading. The purpose of this loading cycle was to apply compression stress on the partially healed cracks, and the criteria for selecting its loading limit was to have the least impact on the mechanical properties of the other side of the cracked prisms. Therefore, based on the pre-cracking results of specimens, 10 kN was selected as the compression cycle loading limit to be applied in this stage, which as demonstrated in Fig. 3.2, will predict to affect the other side of the prisms linearly, therefore minor impact on the mechanical properties is generated.

For group RES, the specimens were put upside down in the sustained fixtures and the compression (C) cycle was applied with the torque wrench (see Fig. 3.1.e). As mentioned, the torque wrench was calibrated using a pancake load cell and the equivalent torque for 10 kN load was obtained to be 25 N.m.

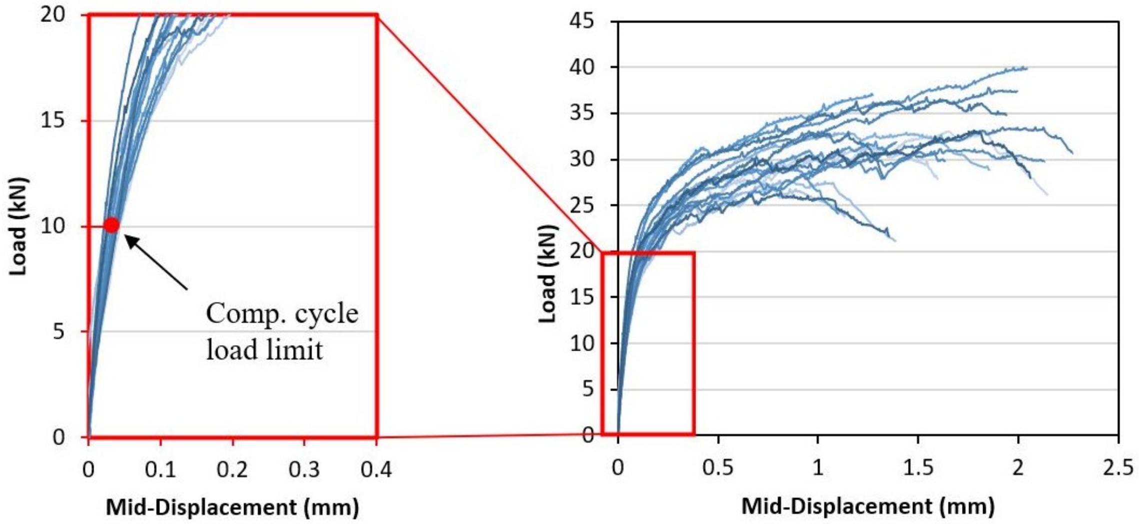
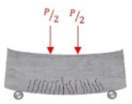
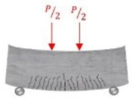
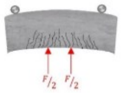
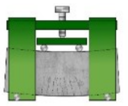
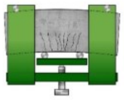


Fig. 3.2 Using pre-cracking results of ECC prisms to determine the compression cycle load limit

Table 3.2 ECC test plan and exposure conditions

Group name	UPV	Pre-cracking	UPV	Exposure (4 months)	UPV	Reverse loading	UPV	Exposure (2 months)	UPV	Final loading
REF				Tap water		N/A		Tap water		
				Sea water				Sea water		
				Air dry				Air dry		
REV				Tap water				Tap water		
				Sea water				Sea water		
				Air dry				Air dry		
RES				Tap water (T)				Tap water (C)		
				Sea water (T)				Sea water (C)		
				Air dry (T)				Air dry (C)		
Note: Three specimens were tested for each case of study, making a total number of 27 specimens.										

Next, the specimens were exposed again to the same curing conditions that they experienced for the first four months. After another two months of curing period, all groups were taken out and tested under four-point bending until failure. The self-healing process for each specimen was studied individually and also as a group, and results were obtained and compared as relative values. To validate the results and also to have different ECC behaviors studied in each case, three specimens were tested for each case of study, making a total number of 27 specimens.

3.3.2.1. Four-point Bending Test

In order to induce controlled flexural cracks on ECC prisms and also to evaluate healing efficiency through the recovery of mechanical properties, four-point bending test was carried out for all loading stages of this test. It is the nature of the four-point bending system to provide a maximum moment region between the middle loads, promoting the ECC multi-cracking behavior in this region; hence real ECC behavior is investigated. An Instron 8501 load cell with a 100 kN capacity was used to apply a loading rate of 0.5mm/min, and one data was recorded per 0.5 seconds. Mid-span deflection was measured via an LVDT placed in the middle of the test setup. The specimen's dimensions and apparatus configuration were in accordance with ASTM C78 [35] (See Fig. 3.3). It is worth noting that the test setup was placed upside down in the actual tests due to the upward load exertion of the Instron.

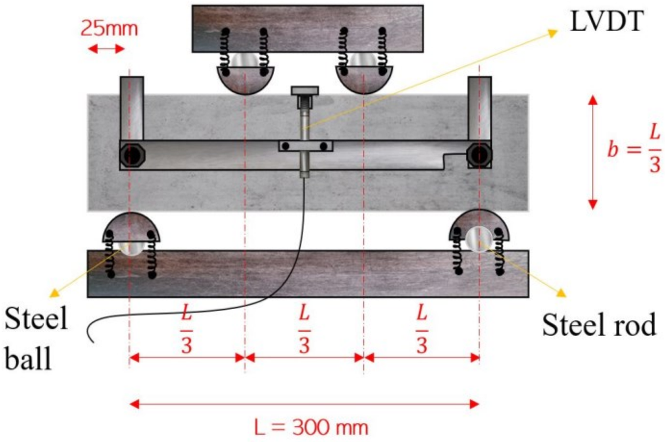


Fig. 3.3 Four-point bending test apparatus and dimensions

3.3.2.2. DIC Analysis

Digital Image Correlation (DIC) is an optical measuring technique that determines the displacement field of the surface of an object under loading. The method tracks the movement of a grey value patterns (speckle pattern) on the surface of the specimen at any point of time with regards to a desired reference pattern. The test requires a camera to record the test process and software to further analyze the results (See Fig. 3.4). In this study, DIC analysis was conducted using the software GOM Correlate 2018. A Canon 750D equipped with a 35 mm lens was adopted to record the test for all stages of loading. The surfaces that were supposed to be recorded were first sprayed with a white paint and after drying, painted with a black speckle spray. The camera was placed at a distance of approximately 500 mm from the specimen and at a perpendicular angle to the front side. The technique was used to determine crack propagation patterns, measure the crack mouth opening and also to measure the mid-span relaxation after unloading which was used in applying sustained load with the fixture.

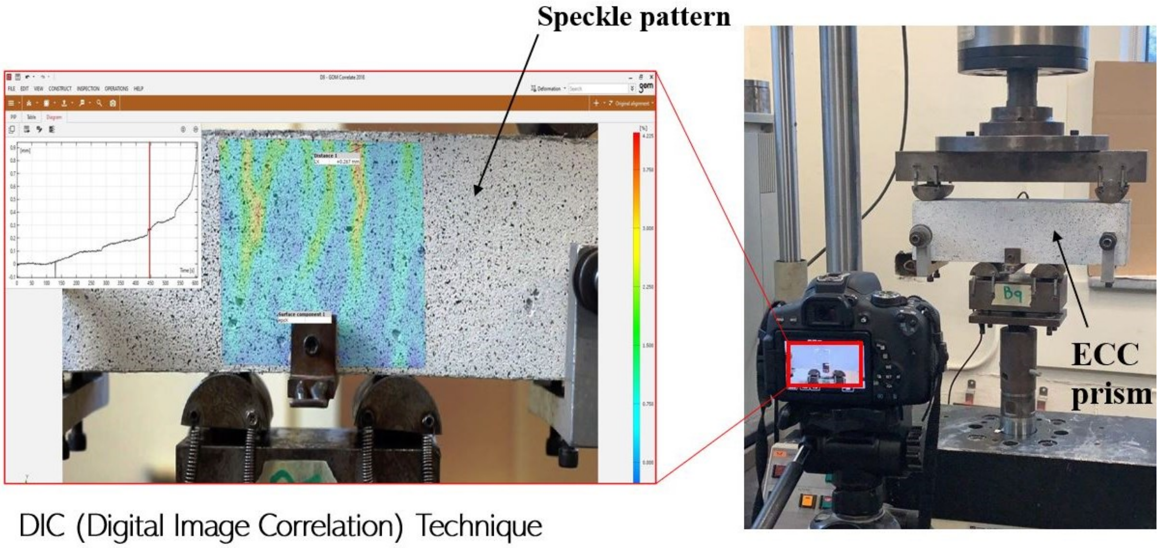


Fig. 3.4 Recording four-point bending test to use in DIC analysis

3.3.2.3. UPV Test

Ultrasonic Pulse Velocity (UPV) method is a simple Non-Destructive Testing (NDT) technique used to assess the mechanical properties of concrete, such as strength and also to detect defects such as cracks. The test measures the travel time of a compressional ultrasonic wave over a known path length through concrete. As shown in Fig. 3.5, the presence of a crack would increase the travel time of the wave, yet filling that crack with healing products would cause the time to decrease ($T_2 > T_3 \geq T_1$). This change in transmission time, which is a result of pre-cracking and crack healing, is used as an evaluation parameter to measure the healing efficiency over the test period.

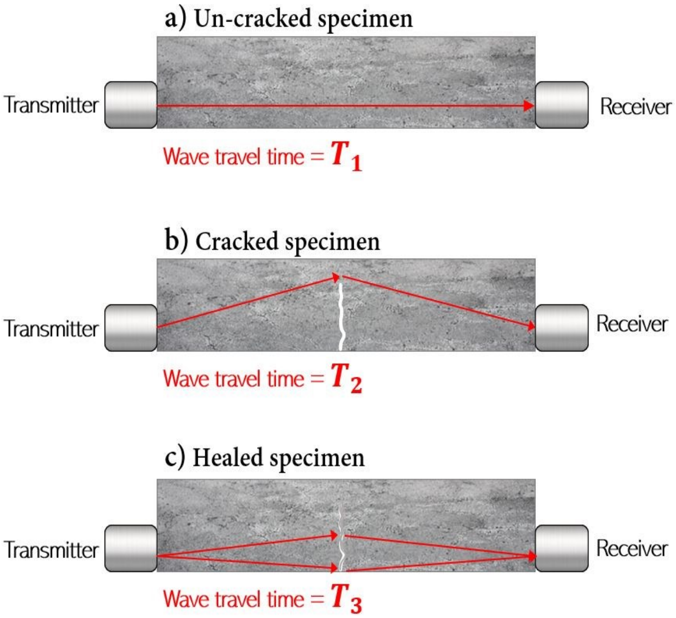


Fig. 3.5 Wave travel path through concrete prisms; a) un-cracked specimen, b) cracked specimen and, c) healed specimen.

The testing scheme is illustrated in Fig. 3.6 Based on ACI 228.2R [36] and ASTM C597 [37] recommendations, two transducers with a natural frequency of 54 kHz and 50 mm diameter were employed to transmit and receive compression wave signals. A Pundit UPV tester with the time-sensitivity range of (μs) and a pulse voltage of 110 V was used in this study. The transducers were placed on the smaller facet of the ECC prisms such that the top of them were at the center of the facet and the bottoms were leveled. Concrete surface was cleaned and sanded before attaching the sensors and honey was used for smoother connection. The test was started from the virgin state of the specimens onwards and the travel times were recorded before and after every loading cycle and compared as a relative parameter indicating the healing efficiency.

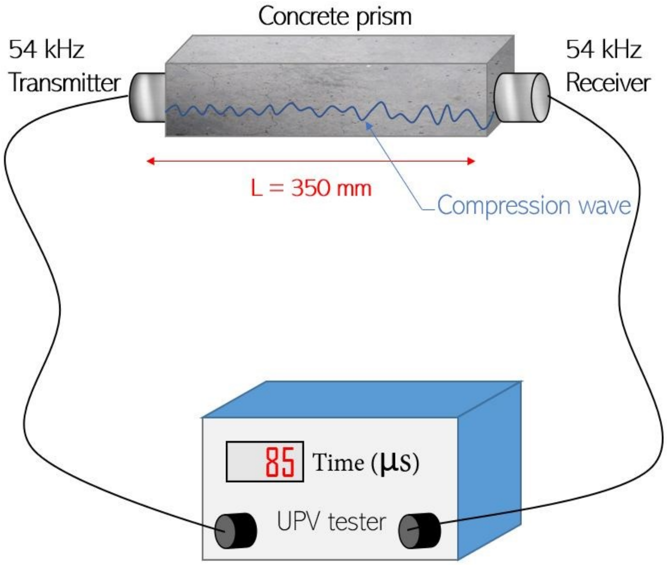


Fig. 3.6 UPV test setup

3.4. RESULTS AND DISCUSSION

3.4.1. Recovery of Mechanical Properties

After testing 27 ECC prism specimens under four-point bending, it was observed that different mechanical behavior is likely to be achieved after that first cracking occurs. As shown in Fig. 3.7, the specimens demonstrate different strain-hardening and tension-softening properties in pre-cracking stage, which can be related to the location and size of the initial flaw that usually generates the main crack and also the orientation and dispersion of fibers at the flaws in each ECC specimen [38]. This issue caused a relatively wide range of peak strengths and deflections that if used for self-healing evaluation purposes, then there was a high chance of self-healing results being manipulated by the pre-cracking loading process. On the other hand, the initial stiffness showed consistency in the pre-cracking step, furthermore, it deals more directly with crack opening stage. As autogenous self-healing progresses, the newly generated healing products start to fill the cracks, which mostly happens at the nucleation sites provided by the dense pack of PVA fibers at crack locations [39]. It is reasonable to believe that the formation of new products around the fibers increases the initial stiffness of the section via increasing fibers' bond with the cementitious matrix [40]. Therefore, Stiffness recovery ratio ($\mathrm{R_S}$) was selected in this study as the representative of recovery in mechanical properties, and is defined as follows:

$$\mathrm{R_S} = \frac{\text{Initial stiffness of final loading}}{\text{Initial stiffness of precracking}} \leq 1 \qquad \text{Eq.3.1}$$

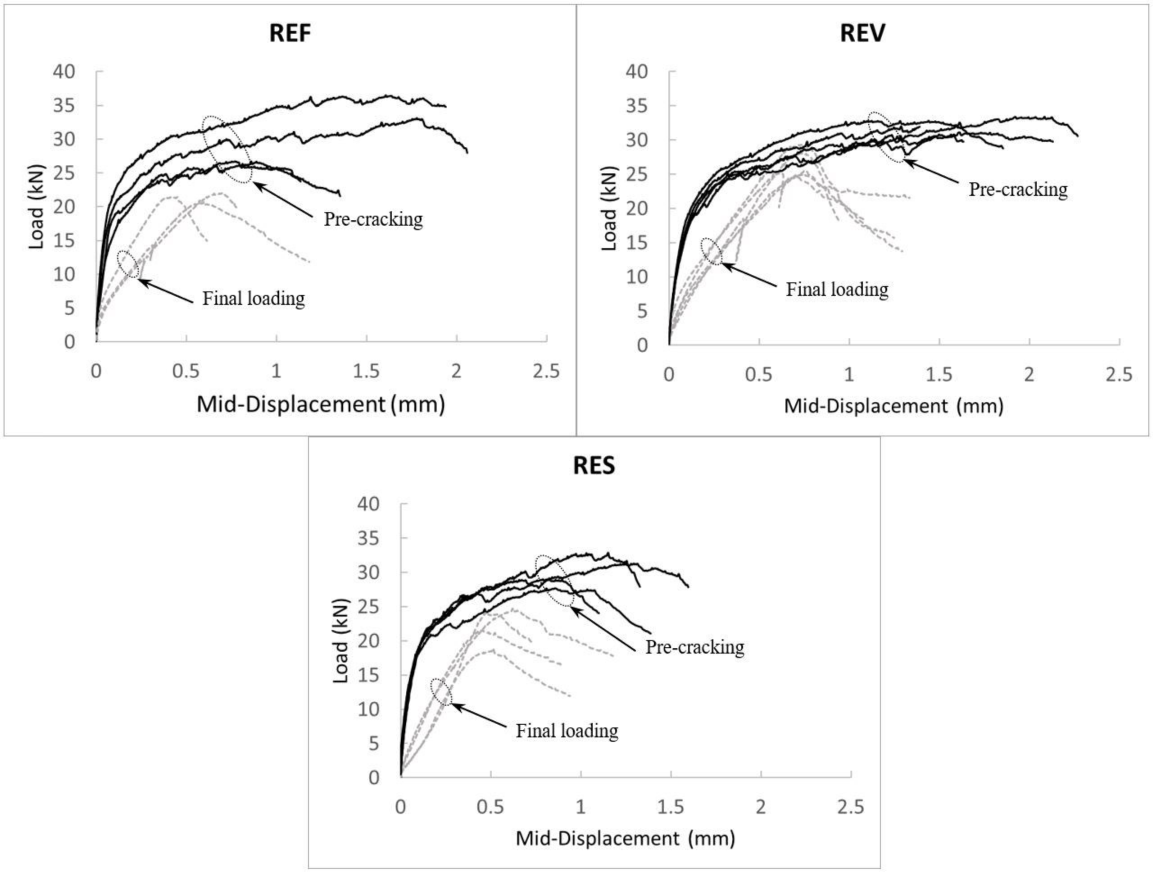


Fig. 3.7 Load vs. Midspan deflection of pre-cracking and final loading for groups REF, REV, and RES

By comparing the results of the stiffness recovery ratio ($\mathrm{R_S}$) for REF and REV groups shown in Fig.3.8, it can be stated that applying a compression cycle to the cracks that have already undergone some healing process decreases the recovery of stiffness. This trend was observed in all exposure conditions, more significantly in tap water and sea water with a

%39 and 8% decrease, respectively. This contradicts the idea that applying a compression cycle to a crack will help the autogenous healing process by closing the crack and reducing the space required for healing production. That could be the case if the compression cycle was applied before the healing process initiated, but apparently, applying forces that compress the partially healed crack (such as a series of reverse loading cycles) destroys the brittle structure of newly formed healing products (e.g. $CaCO_3$), and reduces the amount of stiffness that could be recovered over time.

The trend was more adversely affected by the sustained loading condition in RES group. Results in Fig. 3.8 show that a series of reverse loading cycles where the loading condition is sustained and accordingly, cracks are larger and more unstable minimizes the chances of improved autogenous self-healing process. With applying a sustained condition to the reverse loading cycles, the stiffness recovery ratio decreased to 13%, 49% and 55%, for sea water, tap water and air dry conditions, respectively. It is worth mentioning that in this investigation, the cracks widths for the selected specimens in sustained condition of tension were around 800~1000μm, which is an extremely high value for ECC.

Generally, sea water proved to be a better medium for autogenous self-healing, rather than tap water or air dry. Presence of different ions dissolved in sea water, such as Mg^{2+}, helps with formation of new healing products such as brucite ($Mg(OH)_2$) that can promote crack healing efficiency of ECC in addition to portlandite ($Ca(OH)_2$) and calcite ($CaCO_3$). According to Fig. 3.8 ECC specimens cured in sea water, reached to 80% of their initial stiffness in REF group, where there was one pre-loading and one final loading, and no reverse cycle. In addition, a comparison of results between REF and RES groups shows that loading condition is less impactful on sea water exposure with %21 decrease, however there was a %69 and %57 decrease in specimens exposed to tap water and air dry.

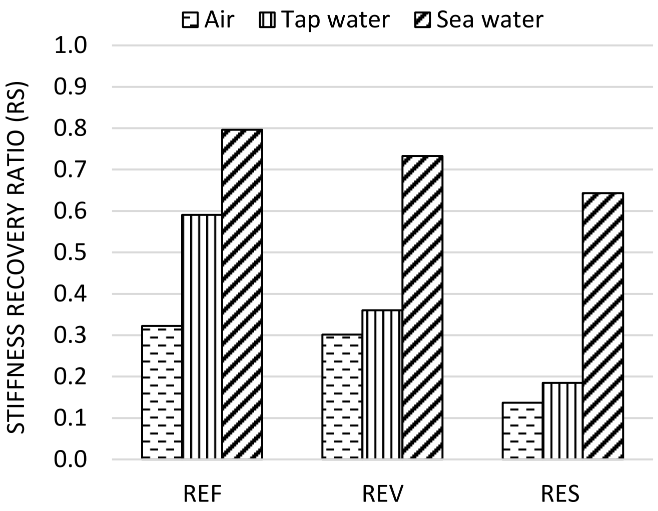


Fig. 3.8 Stiffness recovery ratio (R_S) of groups REF, REV, and RES exposed to different environmental conditions

3.4.2. UPV Results

Ultrasonic Pulse Velocity test was carried out for all ECC specimens throughout the test plan. Table. 3.3 summarizes the travel times of the compression waves measured at different stages of cracking and healing. To verify the results, three specimens were examined for each case, and the average of the results is presented. As predicted, the time values for the intact ECC prisms are almost the same (84-85 μs), showing a constant velocity of ~4.2 km/s that is generally considered in the range of good quality concrete [41, 42]. After the initial pre-cracking, the travel time for all cases increased, indicating the presence of the cracks in the specimens. The results for the two cases of REF and REV are quite similar since the pre-cracking stage is identical for both conditions. However, the specimens in group RES demonstrated higher travel times due to the sustained loading that eliminated the relaxation after unloading.

Table 3.3 UPV test results

Group name	Exposure conditions	UPV results (μs)						
		Intact ECC specimens	After pre-cracking		After finishing the 1st curing period	After applying compression cycle to REV and RES		After finishing the 2nd curing period
REF	Tap water	84	95	1st exposure condition (4 months)	90	N/A	2nd exposure condition (2 months)	88
	Sea water	85	96		90			88
	Air dry	84	96		94			93
REV	Tap water	84	95		90	91		89
	Sea water	84	95		90	90		88
	Air dry	84	96		92	92		94
RES	Tap water	85	98		91	89		89
	Sea water	84	99		90	89		89
	Air dry	84	98		93	96		95

With the first exposure condition of four months finished, all specimens were taken out of their curing condition and tested for UPV measurement. At this stage, the UPV values showed improvement in the wave travel time in all specimens, indicating that cracks are being filled with healing products. This improvement in wave travel time was more obvious in specimens exposed to tap water and sea water as expected. Even though, it should be mentioned that another cause for the improvement of UPV values in the specimens cured in tap water and sea water at this stage could be the densification and continuous hydration of the concrete matrix due to the penetration of the moisture from the surrounding environment. After applying the reverse compression cycle to the specimens in groups REV and RES, the UPV test was conducted again to determine the compression state's effect on partially healed cracks. Results tabulated in Table. 3 prove that in group REV, where tension cracks are relatively small (300~400 µm), compressing the cracks will not significantly impact wave travel time. Although cracks are being closed by the compression force, yet the applied force will affect negatively on the structure of the healing products formed during the first curing period. Since cracks are wider in group RES (800~1000 µm) and there is a less chance for the formation of autogenous healing products, the compression cycle's effect is more significant on closing the cracks, rather than the destruction of newly formed products.

To investigate the overall effect of different loading conditions on the self-healing efficiency, UPV Recovery ratio (R_U) was defined as follows:

$$R_U = 1 - \left(\frac{\text{Final UPV} - \text{Intact UPV}}{\text{Intact UPV}}\right) \leq 1 \qquad \text{Eq.3.2}$$

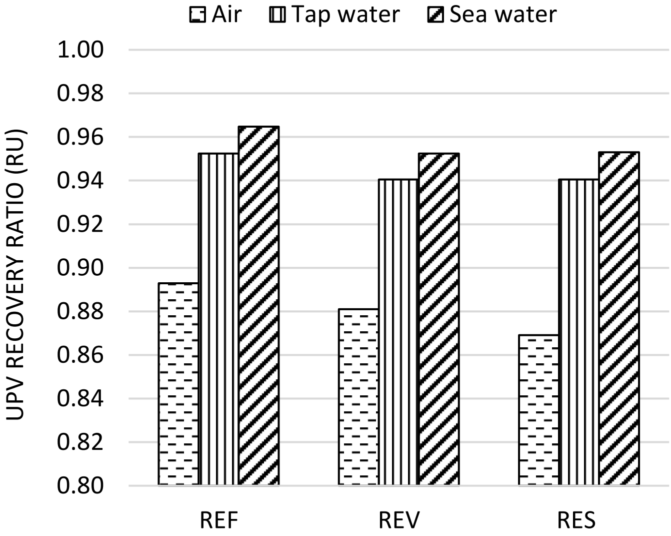


Fig. 3.9 UPV recovery ratio (R_U) of groups REF, REV, and RES exposed to different environmental conditions

As demonstrated in Fig. 3.9, the numbers obtained for R_U are in the range of 0.80 – 1.00, which are very close and relatively high. However, as described in section 3.2.3. the compression wave will travel through the shortest path in concrete, which in this study was observed to be the crack mouth where formation of autogenous healing products (e.g. calcite) is more likely to occur [43]. As a reason, a high UPV recovery ratio will not necessarily confirm a totally filled crack. Regardless, aligned with the results of last section, R_U values prove that sea water is the most effective environment in terms of filling the cracks with ~95% recovery in all groups, while air dry showed the least recovery in RES condition with ~87%.

Considering the fact that the only difference between REV and REF groups is the compression cycle that was applied to REV group in the process of self-healing, the R_U results indicate a slight decrease in the values for REV in all three exposure conditions. It could be claimed that while the compression cycle in REV group closes the crack width, it compresses and crushes the newly formed autogenous healing products. This issue is more obvious in specimens exposed to air dry condition, where the healing products inside the cracks are assumed to be more brittle due to lack of moisture.

3.4.3. XRD Analysis

To investigate the microstructure and material characteristics of autogenous healing products in this experimental program, X-Ray Diffraction (XRD) test was performed on the powder samples scratched from inside of cracks in ECC specimens after the final loading. Two groups of tap water and sea water exposures were selected for this test due to their higher efficiency in terms of crack healing and also to determine the different healing products formed in these conditions. Fig. 3.10 demonstrates XRD patterns of samples for ECC in sea water and tap water obtained using an X-Ray diffractometer with Cu Ka radiation and 2theta ranging between 0 to 80 degrees. As predicted, brucite $(Mg(OH)_2)$ was observed in ECC specimens submerged in sea water, which indicates the presence of Mg ions in sea water, also confirms the formation of additional healing products that enhance the autogenous healing efficiency in this exposure condition. Calcite $(CaCO_3)$ was observed in both groups as a premier product of autogenous self-healing in later ages, indicating the presence of dissolved carbonate ions in tap and sea water. Quartz (SiO_2) peaks are also determined in the samples, which could be related to the silica in the sand and FA used in ECC mixtures, and the CSH sources.

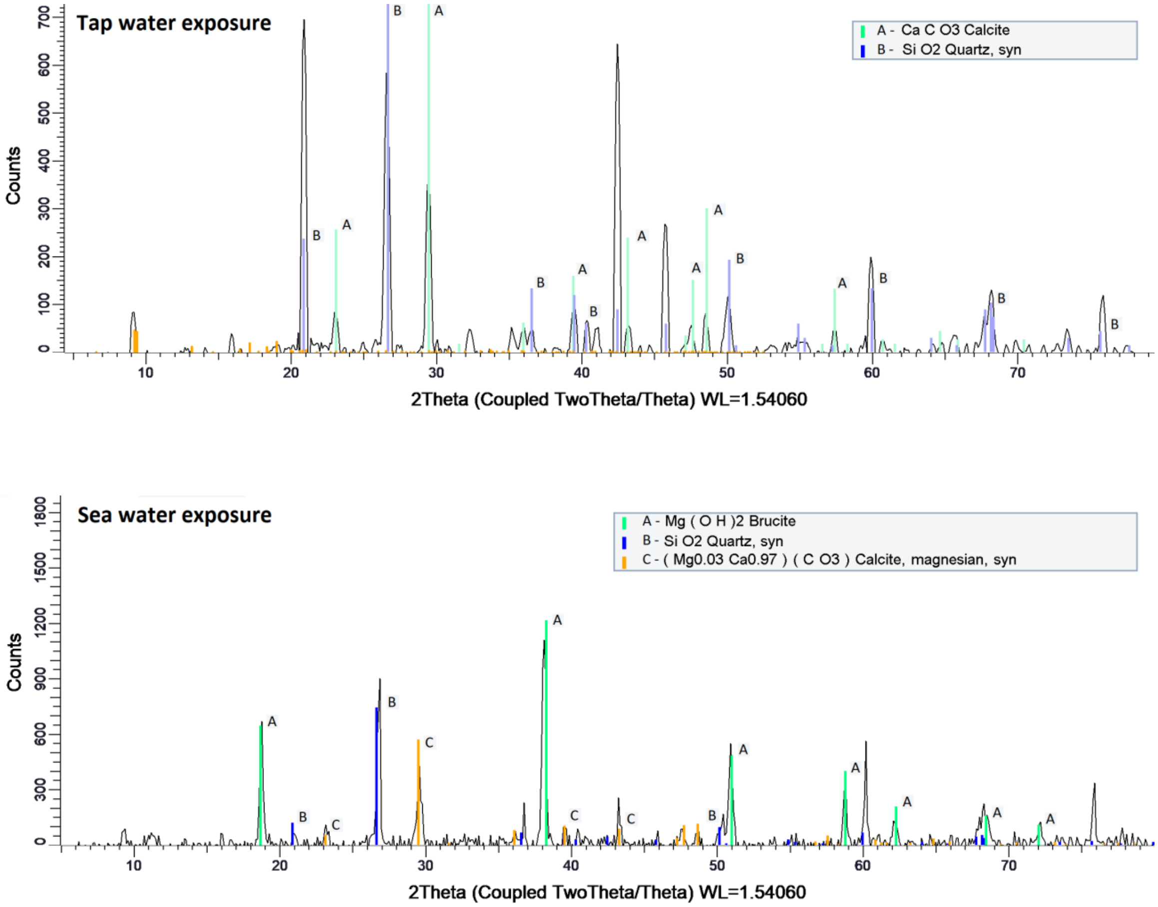


Fig. 3.10 XRD analysis of ECC specimens exposed to tap water and sea water condition

3.5. CONCLUSION

The presented experimental program was carried out to evaluate the improved autogenous self-healing efficiency of ECC prism specimens under instant and sustained reverse loading cycles. Three different exposure conditions of sea water, tap water, and air dry were selected as the surrounding environment of specimens for the duration of the tests. Recovery of mechanical properties, UPV test and XRD analysis were used to evaluate the self-healing efficiency in this investigation. The main objective of this research was to determine whether applying a compression cycle in between repetitive tension cycles needs to be considered while assessing the repeatability of autogenous self-healing mechanism. Stiffness recovery ratio R_S was defined based on mechanical properties obtained from four-point bending tests. The values indicate that applying a compression cycle on partially healed cracks can have adverse effects on the stiffness recovery, such that it destroys the brittle structure of newly formed healing products (e.g. $CaCO_3$), and reduces the amount of stiffness that could be recovered over time. RES group that represented a sustained reverse loading condition on ECC prisms proved lower recovery ratios in terms of stiffness. UPV results also confirm this behavior in ECC specimens. It can be stated that while the repeatability of self-healing in ECC is yet an issue under investigation, it should be considered that compression cycles and sustained loading condition will reduce the efficiency of improved autogenous self-healing in partially healed cracks.

Furthermore, X-Ray Diffraction (XRD) analysis was carried out on healing products collected from inside the healed cracks. Formation of additional healing products such as brucite was reported in specimens exposed to sea water, which enhanced the efficiency of self-healing in ECC. R_S results show about 80% recovery in flexural stiffness for specimens in the REF group that were submerged in sea water for six months. This recovery ratio was found to be around 73% and 64% for REV and RES groups, respectively. Apparently, sea water is a favorable condition for the improved autogenous self-healing in ECC material, even at high displacements. XRD patterns also confirmed the presence of calcite which is a well-established autogenous healing product.

Further investigation is suggested to be conducted on the structural aspects of improved autogenous self-healing in ECC with more emphasis on different loading amplitudes and durations, that represent real service conditions of concrete infrastructure.

ACKNOWLEDGMENT

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CHAPTER 4 EFFECT OF CRYSTALLINE ADMIXTURE ON THE SELF-HEALING OF ENGINEERED CEMENTITIOUS COMPOSITES (ECC) EXPOSED TO DIFFERENT ENVIRONMENTS[3]

ABSTRACT

Self-healing of cracks in cementitious material is an active method of filling the cracks with the material coming from the concrete and its surrounding environment that prevents the ingress of harmful substances into cracks and helps minimize durability issues. The process is inherently performed through two main mechanisms of hydration of unhydrated binders in the matrix and precipitation of calcite, and it is highly dependent on the presence of water in the surrounding environment. Engineered Cementitious Composites (ECC) is a particular category of High-Performance Fiber Reinforced Cementitious Composites (HPFRCC) that has been extensively investigated for self-healing purposes. The high portions of fly ash and PVA fibers in the mixture favor self-healing; however, small crack widths were reported to be healed in this material. The current experimental program aims at determining the extent of self-healing in large deflections by providing favorable conditions. Crystalline Admixture (CA) is also used to promote the capacity of self-healing in ECC. Three different exposure conditions of air dry, tap water, and sea water were tested using a water permeability (WP) test. The results indicate high sealing capacities in a short period for specimens made with CA and submerged in sea water.

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[3] This chapter will be submitted to a journal.

4.1. INTRODUCTION

Durability of concrete is generally regarded as its resistance towards a particular environment to which it will be exposed during its service life. Durability issues such as freezing and thawing, sulfate attacks, carbonation, and steel corrosion are able to be controlled due to the fact that they share a common ancestor, i.e. the cracks [1]. Open cracks can facilitate the ingress of harmful substances such as chlorides ($\mathrm{Cl^-}$) that destroy the protective layer on the steel reinforcements, leading to steel oxidation and subsequently, structural damage [2]. Currently, repairing cracks after the construction of a concrete structure considers to be a practical method, however, there are many demerits for that. The manual repair demands high budget and labor work, and sometimes requires pausing the serviceability which adds indirectly to the life cycle cost [3, 4]. Also, the process may be difficult or impractical due to the damage's location, e.g. cracks in underground concrete structures. Even though manual repair techniques have considerably improved through recent years, most of these repairs can only last ten to fifteen years [5, 6].

On the other hand, self-healing mechanisms in concrete have been under investigation over the last two decades, trying to replace the current repairing system with employing a more modern mechanism capable of filling the cracks with the products coming from the concrete itself [7-11]. Autogenous and Autonomous mechanisms are the two major methods of self-healing recognized in cementitious material. Autogenous healing is an inherent property of concrete that existed from the first time man used Portland cement in concrete, and it was first observed by the French Academy of Science in 1836 [12]. The mechanism mainly relies on the hydration of unhydrated cement particles existing in the cracks to produce further calcium silicate hydrate (C-S-H) or portlandite ($\mathrm{CA(OH)_2}$), and the crystallization of calcium carbonate ($CaCO_3$) which is a result of the reaction between calcium ions leaching from cracks and dissolved carbonate ions in the surrounding environment Although ,the formation of these healing products is highly dependent on the properties of the surrounding environment. The presence of water, changes in pH and temperature levels, and ion concentration are reported to be effective on the extent of autogenous self-healing [13-16]. In particular, sea-water exposure has reported promising results of autogenous self-healing in cementitious materials. While the extend of healed cracks in water exposure condition is about 100-200 μm [13, 17], the healed crack width for sea water exposure is ranging between 200-700 μm [18-20]. This is due to the presence of magnesium (Mg^{2+}) and sulphate (${SO_4}^{2-}$) ions in sea water that can react with hydroxyl (OH^-) and calcium ions (Ca^{2+}) inside cracks and in a favorable condition, precipitate brucite ($Mg(OH)_2$) and ettringite [21, 22].

As described, autogenous self-healing mechanisms are functions of the chemical reaction between material in the surrounding environment and material coming from the concrete itself. By replacing cement with Supplementary Cementitious Materials (SCM), a group of silicate and calcium-rich waste products, the chances of autogenous self-healing increases [23, 24]. SCMs such as fly ash and steel slag provide latent hydraulic reaction, in which silica and calcium react chemically in an aqueous alkaline environment to form portlandite or C-S-H [23, 25]. These chemical reactions of SCMs usually proceed slower than the reaction of the cement phase; therefore, they can provide late hydration, which favors autogenous self-healing [26]. Also, they provide additional hydroxyl (OH^-) and calcium ions (Ca^{2+}) to help with precipitation of calcite, brucite and ettringite in a favorable environment [24, 27]. A very famous group of cementitious composites in this regard is

Engineered Cementitious Composites (ECC) which include high portions of fly ash in its mix design [28, 29]. The micromechanics of ECC demand for dense fraction of micro-fibers which limit the crack widths and provide nucleation sites for healing products, both lead to promoting the autogenous self-healing [30-33]. In addition to SCMs, some other mineral and chemical admixtures are reported to be effective in terms of crack healing [11, 34, 35]. Crystalline Admixture (CA) is a group of hydrophilic admixtures containing active chemicals that form water-insoluble pore-blocking precipitates upon reaction with water. This characteristic of CA helps with the densification of CSH to resist water and gas penetration (reduce concrete's permeability), also the unreacted portion of this material will fill the cracks through late crystallization [36]. When mixed with concrete at 1-4% of cement weight, it has proven to improve the self-healing capability considerably [37, 38], and better results are reported when combined with other expansive and swelling minerals in the mixture [39].

In this study, ECC specimens incorporating CA are tested for self-healing results. Three different exposure conditions of sea water, tap water, and air dry are adopted for exposure condition of specimens during curing periods. Since the previous studies have reported relatively high values of crack healing for specimens in sea water, in this study large crack deformations are evaluated to investigate the extent of self-healing when using SCMs, CA, and fibers together. To measure the self-healing efficiency through recovery of transport properties which is directly related to durability, Water Permeability (WP) test was carried out on disk specimens.

4.2. EXPERIMENTAL PROGRAM

The effect of CA on the efficiency of self-healing in ECC specimens exposed to different exposure conditions was investigated through an experimental program. Disk shape specimens were fabricated for two series of ECC and ECC-CA, then cracked and exposed to three different exposure conditions of tap water, sea water, and air dry for two months. The disk specimens were fabricated for measuring the crack sealing through water permeability test. To monitor crack propagation and to measure the crack opening displacement, Digital Image Correlation (DIC) technique was adopted in this study. XRD (X-Ray Diffraction) analysis was also conducted on the healing products scratched from inside the cracks after the end of test duration.

4.2.1. Material Properties and Specimen Fabrication

Two groups of ECC mix designs labeled as ECC (the reference ECC) and ECC-CA (ECC with Crystalline Admixture (CA)), were tested in this study. The mixtures consisted of Class-F fly ash (FA), type GU Portland cement (C), micro-silica sand (S) with an average aggregate size of 225 μm, water (W), high-range water-reducing admixture (HRWRA) and polyvinyl alcohol (PVA) fibers. The nominal tensile strength of PVA fibers were 1100-1400 MPa, with a diameter of 38 μm, length of 8 mm and specific gravity of 1.3. Table 4.1 provides details on the portions of the mix designs. The CA used in this study is Masterlife 300D which is a crystalline capillary waterproofing admixture product of BASF (Pinnacle Agencies Ltd., Dartmouth, NS, Canada). Based on the literature's recommendation [38, 40, 41], 2% of cement wight was selected as the CA portion in the ECC-CA mixture. Water to cementitious material ratio (W/FA+C) was 0.27. The relatively high FA/C ratio of 2.2 was selected to promote the healing efficiency of ECC by late hydration [32, 42]; also, it reduces the cement portion in the mixtures.

Table 4.1 Mixture designs (for 1 m3) and compressive strengths

Mixture	Amount (kg/m^3)						
	FA	C	S	W	PVA	HRWRA	CA
ECC	823	375	435	318	26	3	-
ECC-CA	823	375	435	318	26	3	7.5

Since moderate dispersion of PVA micro-fibers has a significant effect on the mechanical properties of ECC, a blade mixer was used to mix ECC ingredients properly. First, fly ash, cement, and micro-silica sand (and also CA for ECC-CA mixture) were mixed for 15 minutes. Then, water was added and gradually after that, PVA fibers were added. Finally, the HRWRA was added, and the mixing process continued for another 15 minutes. The mixed ECC and ECC-CA batches were poured separately into disk shape molds of 100 mm (diameter) × 50 mm (thickness). After keeping the fabricated specimens under plastic sheets in a curing room with 95% relative humidity for 24 hours, the molds were removed, and the specimens were placed back again in the humidity room up to the age of 28 days. After the moisture curing was completed, the specimens were taken out of the curing room (see Fig. 4.1). It should be mentioned that due to COVID-19 pandemic, there was a gap between specimen fabrication and cracking. The specimens were pre-cracked at the age of 6 months and they were kept in room temperature during that time. Table 4.2 presents the ion concentration of the sea water used in this investigation based on the composition of standard sea water [43] and the salinity of the local area of Halifax, NS,.

Table 4.2 Concentration of major constituents in surface sea water based on the salinity of the collected area

	At salinity 30%					
	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	HCO_3^-
Weight (g/kg)	9.24	0.34	1.10	0.35	16.58	0.11

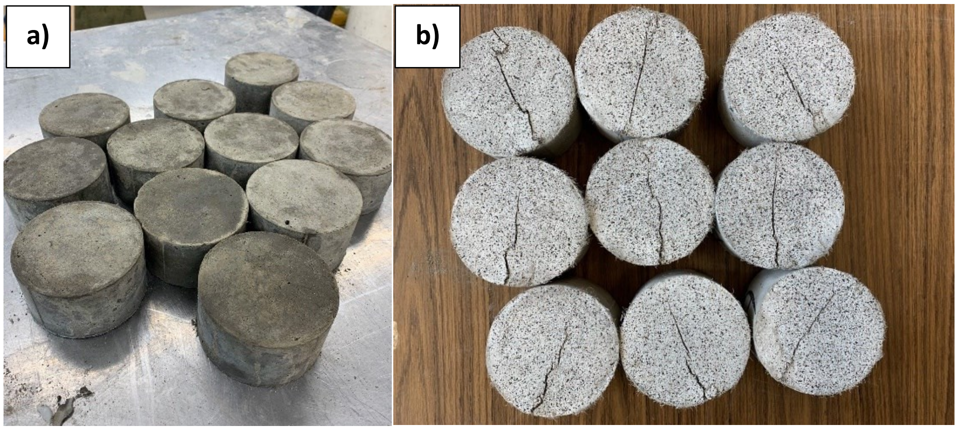


Fig. 4.1 ECC and ECC-CA disk shape specimen, a) after finished 28-day curing and, b) after cracking

4.2.2. Test Plan and Exposure Condition

The current research investigates the effects of CA and different exposure conditions of sea water, tap water and air dry on the self-healing capability of ECC specimens. Disk specimens were cracked using the split tensile test and then Water Permeability (WP) test was carried out at different time intervals to record the crack healing efficiency through recovery of transport properties. Three identical disk specimens were tested in each case of material and exposure condition and average of results is presented. A summary of the test plan and exposure conditions is presented in Table. 4.3.

After the initial 28-day curing was finished, the specimens were kept at room temperature and humidity for five months. Disk specimens were cracked then using a split tensile test.

The cracking process was conducted using a universal testing machine, and the loading process was monitored using DIC technique. Before starting the first exposure condition and to set a reference point for crack healing, specimens were tested for water permeability (WP1) right after the cracking. After spending the first curing period of 1 month in different exposure conditions, the specimens were tested again for water permeability (WP2). This process is repeated for another cycle after, and water permeability test is conducted at the end of the second curing period (WP3).

Table 4.3 ECC and ECC-CA test plan

Group name	Test timeline					
	Cracking disk specimens with split tensile test	Water Permeability test (WP1)	Exposure condition (1 month)	Water Permeability test (WP2)	Exposure condition (1 month)	Water Permeability test (WP3)
ECC			Tap water		Tap water	
			Sea water		Sea water	
			Air dry		Air dry	
ECC-CA			Tap water		Tap water	
			Sea water		Sea water	
			Air dry		Air dry	
Note: Three specimens were tested for each case of study, making a total number of 18 specimens.						

4.2.2.1. Cracking Specimens

In this study, the scope is to investigate the extent of self-healing in a favorable condition. ECC that possesses fly ash and fibers, added up with crystalline admixture and exposed to marine environment is the favorable condition provided in this experiment. Therefore, large deformations are generated as single-cracks to provide space for healing products to form. A split tensile test was conducted on both ECC and ECC-CA disks, and cracks with maximum widths of 1-2mm were generated. The cracks generated were observed to have triangular geometry that represent a more common cracking shape in practice [43]. The specimen's dimensions and apparatus configuration were in accordance with ASTM C496. As shown in Figure 4.2.a, rectangular wood strips were placed at the top and the bottom of the specimens as recommended in the standard. To avoid concrete crushing at the interface under pressure and to generate neat cracks, loadings was applied with a loading rate of 100kN/min, and one data was recorded per 0.5 seconds.

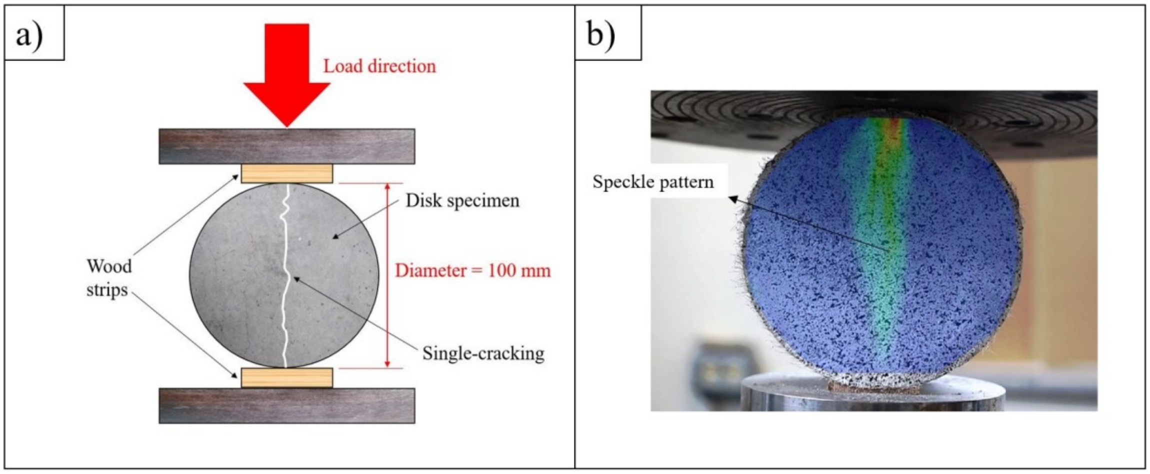


Fig. 4.2 Cracking disk specimen, a) test setup and specimen dimensions and, b) DIC processed image

Digital Image Correlation (DIC) technique was used in this experiment to monitor the crack width through the loading process and after unloading. The technique provides an optical measuring system that tracks the movement of a speckle pattern on the surface of the specimen at any point of time with regards to a desired reference pattern (See Fig. 4.2.b). DIC is capable of considering the relaxation after unloading therefore actual size of the crack is being considered. After testing and analyzing a few dummy specimens, it was found that DIC results are more reliable at higher displacements, hence large cracks provided in this investigation help with identifying the crack size healed through DIC monitoring more accurately. The procedure requires a camera to record the test process and software to further analyze the results. In this study, DIC analysis was conducted using the software GOM Correlate 2018. A Canon 750D equipped with a 35 mm lens was adopted to record the test for all stages of loading. The surfaces that were supposed to be recorded were first sprayed with a white paint and after drying, painted with a black speckle spray, providing the speckle pattern. The camera was placed at a distance of approximately 500 mm from the specimens and at a perpendicular angle to the front side.

4.2.2.2. Water Permeability Test

The water permeability test investigates the amount of water that passes through a crack, and is able to represent the crack filling (sealing) efficiency over time. Different techniques were adopted in the literature to evaluate the self-healing of concrete through measuring the reduction in the permeability of cracked specimens [19, 44-46]. The test setup fabricated for this study is schematically shown in Fig. 4.3 (dimensions are not to scale). The setup used in this investigation consists of three major sections, i.e. bottom half and top half of the plastic chamber and the pipe. After finishing the cracking process, each disk specimen was placed inside the bottom half of the fabricated plastic chamber, and the gap between the specimen and the inner surface of the chamber was sealed with plastic wires and plumbers' putty. Next, the upper half of the chamber was placed on the bottom half, and the two parts were fixed using six bolts provided around the middle of the chamber. The water was then poured from the top of an 8 mm tube attached to the chamber, and the time that water traveled inside a 1000 mm length of the tube was measured with a stopwatch. The test was repeated three times for each specimen, and the average of the recorded time was used for comparison. A plastic valve was also attached to the chamber to release the air trapped inside, so the pure water pressure determines the travel time. The water permeability test was conducted after each 1-month exposure condition, and the time values obtained were further used to measure the crack healing efficiency.

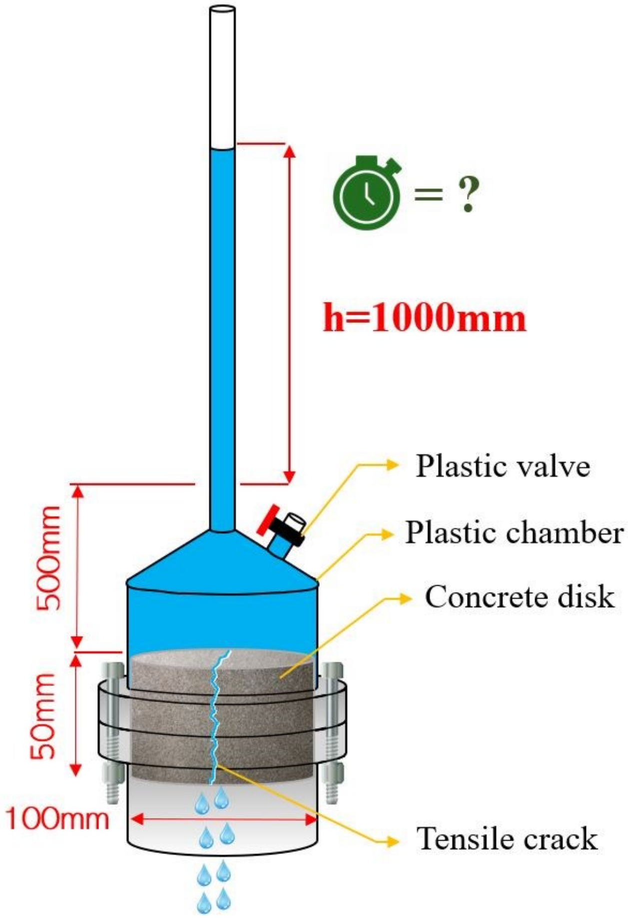


Fig. 4.3 Water permeability test setup

4.3. RESULTS AND DISCUSSION

4.3.1. Water Permeability Results

The Water Permeability (WP) test setup was designed to measure the time that water traveled through the 1000mm length of the tube. After cracking, the travel time obtained through WP was reported to be between 2-55 seconds. The cracks generated in this study are not the same size, and the travel time depends on the free space within cracks. Also, ECC possesses high fractions of PVA fibers that could help with clogging the water pathway in some specimens. To normalize the results, the travel time recorded (T) through WP test was converted into flow rate (Q), using the following equation:

$$Q = \frac{V}{T} \qquad \text{Eq.4.1}$$

Where V is the constant volume of the tube in 1000mm length. To consider the effect of crack width on the recorded time, the calculated Q was then used for finding velocity (U) through the following equation:

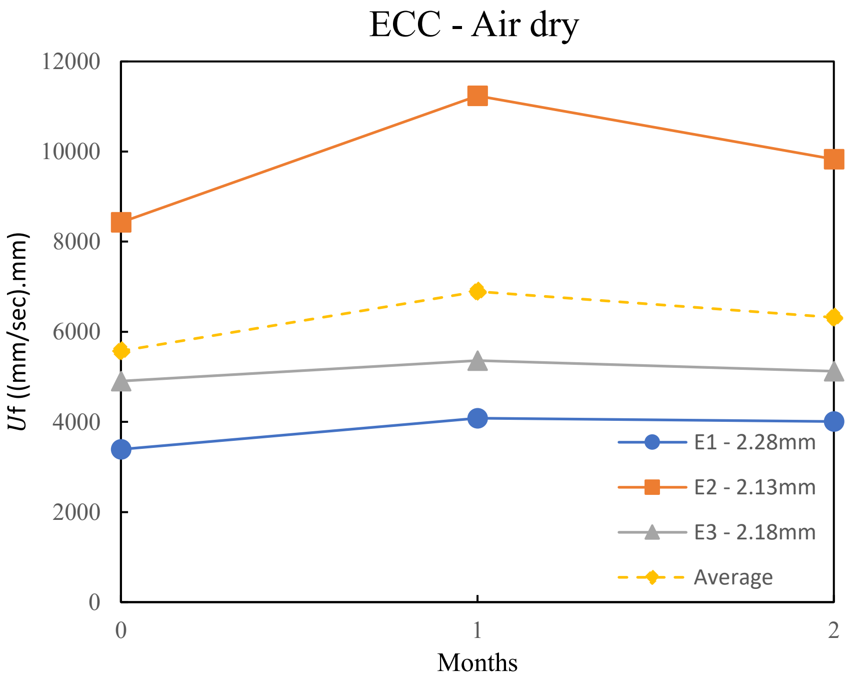
$$U = \frac{Q}{A} \qquad \text{Eq.4.2}$$

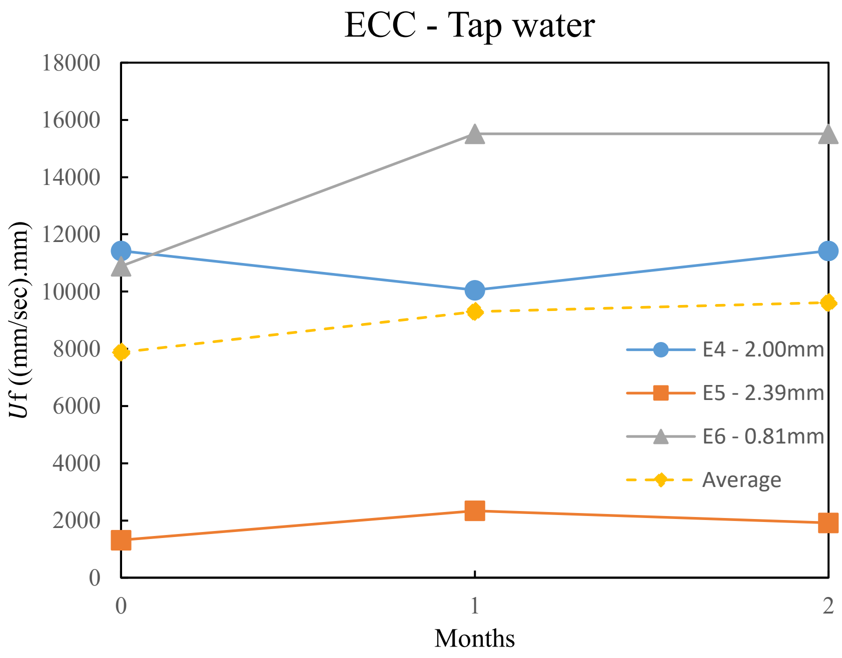
Eq. 4.2 considers the effect of crack width through the area (A) perpendicular to water travel direction. To do so, it is assumed that the area in this case is a rectangle with a width equal to the maximum crack width of each specimen (W_{max}) and a unit length. Maximum crack width was obtained for specimens by means of DIC measurements, and then used to normalize the velocity. Velocity factor (U_f) is finally defined as follows to compare the results.

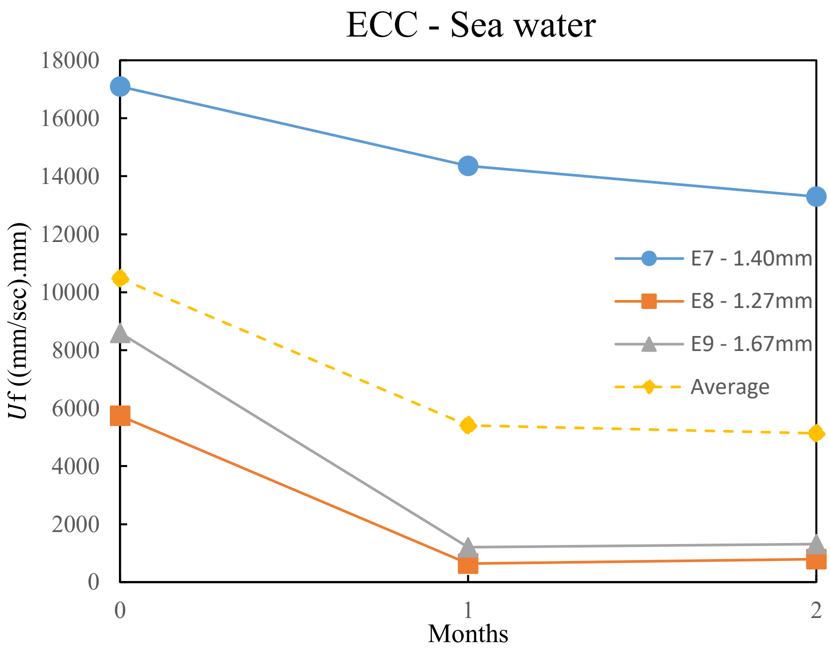
$$U_f = \frac{Q}{W_{max}} \qquad \text{Eq.4.3}$$

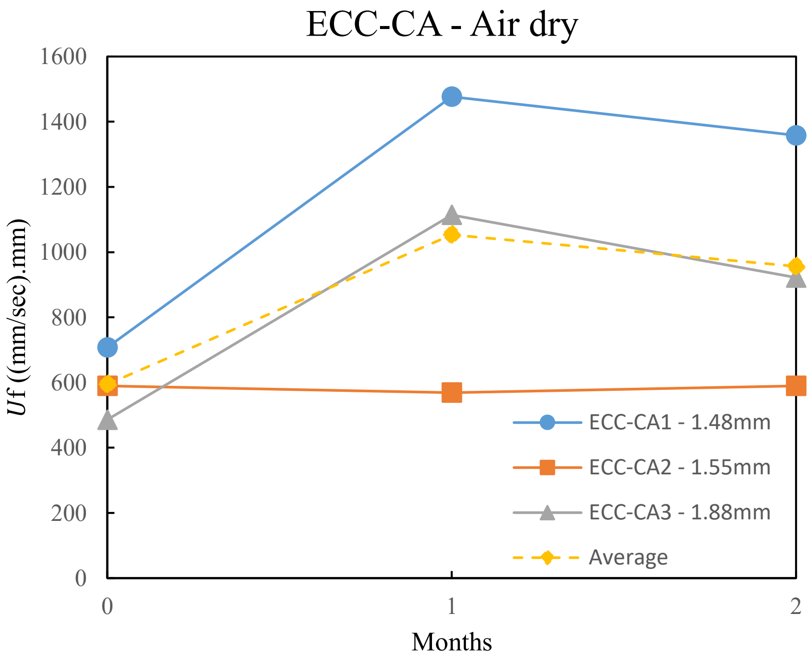
Fig. 4.4 demonstrates the U_f values obtained for each disk specimen at three time intervals (month=0,1,2). The two groups of ECC and ECC-CA are categorized based on the exposure conditions, and the maximum crack width (W_{max}) for each specimen is also labeled along the specimen's name on the charts. The curves for ECC and ECC-CA in air dry condition indicate almost no reduction in the velocity factor over time. This result suggests that healing of large cracks through hydration, carbonation or crystallization mechanisms is not feasible in the absence of moisture. Even some trends in air dry condition showed an increase in the velocity factor during the first month of exposure that could possibly be due to the shrinkage of the cementitious composite, which subsequently increases the gap between the two faces of cracks. This behavior was more vivid during the first curing period of specimens in group ECC-CA, with an average of 75% increase in the U_f value. For the same period, results show 23% increase in the average U_f for ECC specimens.

As demonstrated in Fig. 4.4, tap water curing condition is almost neutral in terms of improvement in transport properties of ECC and ECC-CA groups. Apparently, large deflections (>300μm) prevent the formation of healing products made through binder late hydration or calcite precipitation. Even if there is any small healing product formed inside the cracks, it is not impactful enough to resist the water flow. However, the results from specimens exposed to sea water prove significant reduction of velocity, specially over the first month of curing. The average reduction for ECC and ECC-CA groups were found to be 48% and 77% in the first month. During the second exposure period, the trend changed to 7-8% reduction for both ECC and ECC-CA groups. It could be concluded that due to the limited concentration of ions in the sea water, and the fact that sea water used in this experiment was kept unchanged throughout the experiment, most of the chemical reactions possibly took place during the first month and consumed the ions from the surrounding environment. Also, results confirm the high potential of sea water as a favorable surrounding environment for improved autogenous self-healing. Addition of CA to ECC makes the impact even greater. The active chemicals and minerals manufactured as CA are capable of reacting with ions transferred through sea water and precipitate new material. Even at large deflections and in a short time period, the self-healing capability of ECC-CA exposed to sea water can be confirmed. For instance, in specimen ECC-CA7 the maximum crack width measured via DIC was 1.80mm and it had an 82% reduction in the velocity factor over the first month.






ECC - Sea water
Uf ((mm/sec).mm)
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
0
1
2
Months
E7 - 1.40mm
E8 - 1.27mm
E9 - 1.67mm
Average


ECC-CA - Air dry
Uf ((mm/sec).mm)
1600
1400
1200
1000
800
600
400
200
0
0
1
2
Months
ECC-CA1 - 1.48mm
ECC-CA2 - 1.55mm
ECC-CA3 - 1.88mm
Average

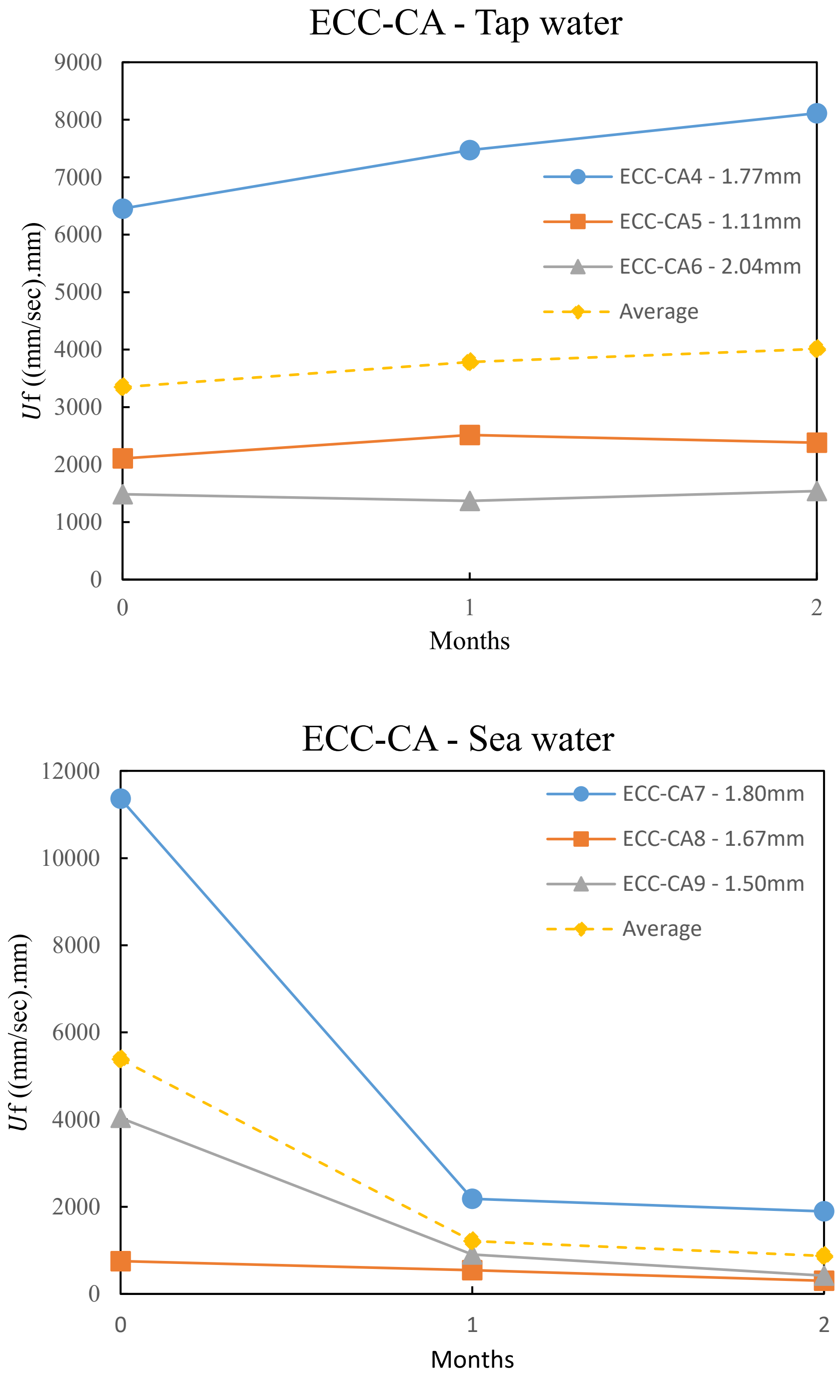


Fig. 4.4 Velocity factor (U_f) vs. curing time for ECC and ECC-CA specimens exposed to different exposure conditions

Fig. 4.5 presents a comparison of average U_f values for all three exposures in ECC and ECC-CA groups. It is shown that sea water was the only exposure condition that could improve the transport properties of largely cracked specimens. The other two exposures of tap water and air dry were determined to have either no or negative impact on cracks' permeability. Generally, the ECC-CA group demonstrated lower values for U_f, indicating lower water permeability.

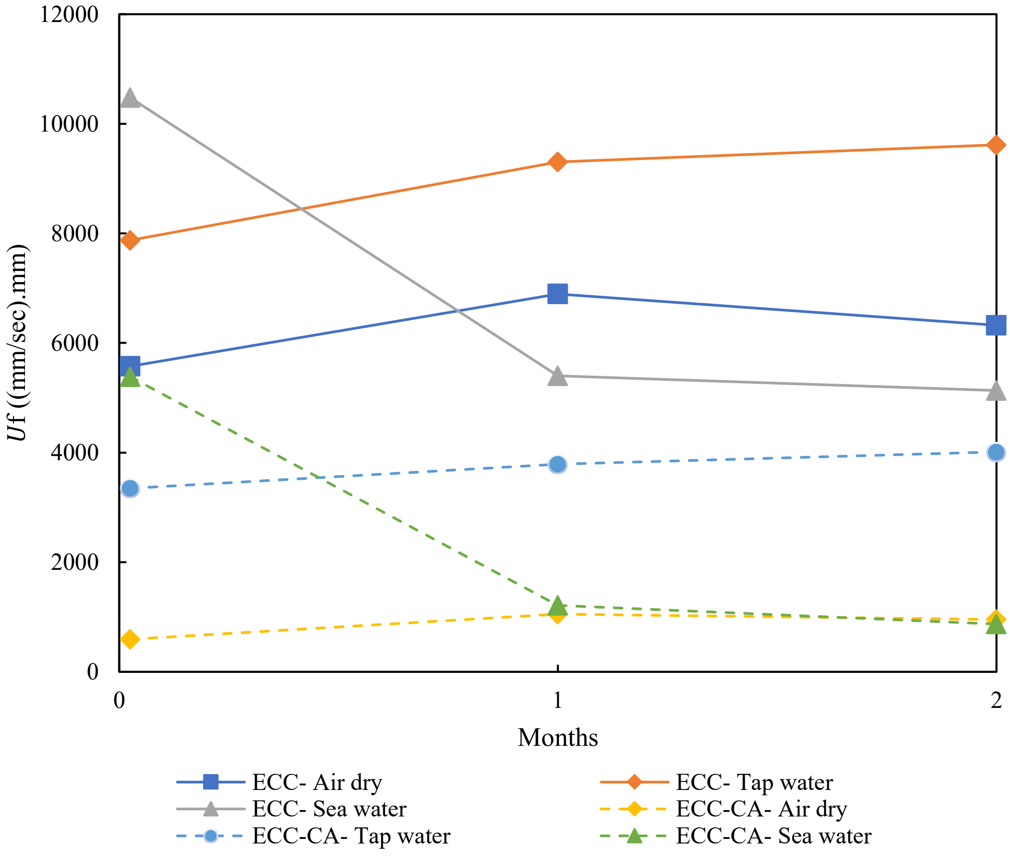


Fig. 4.5 Average Water Permeability (WP) results for ECC and ECC-CA specimens

4.3.2. XRD Analysis and Visual Observations

X-Ray Diffraction (XRD) test identifies the microstructure of powder samples by illuminating X-rays at them and recording its reflection. Via this test, the material characteristics of the healing products formed inside cracks in this experimental program were recognized. The test was performed on the powder samples scratched from inside of cracks in ECC and ECC-CA specimens after the final loading. Two groups of tap water and sea water exposures were selected for this test due to their efficiency in terms of crack healing and also to determine the different healing products formed in these conditions. As shown in Fig. 4.6.a, the formation of new healing products took place throughout the whole crack in ECC-CA exposed to sea water, which indicates the pervasiveness of self-healing in this case. However, the visual observations proved that this formation of new products is more significant in the vicinity of the crack mouth, as it was observed to be an excess of products leaching out from the cracks in specimen ECC-CA7 (see Fig. 4.6.b). It should be mentioned that the maximum crack width generated in this specimen was 1.80mm, and healing products were able to fill up that gap to a great extent (see Fig. 4.6.c).

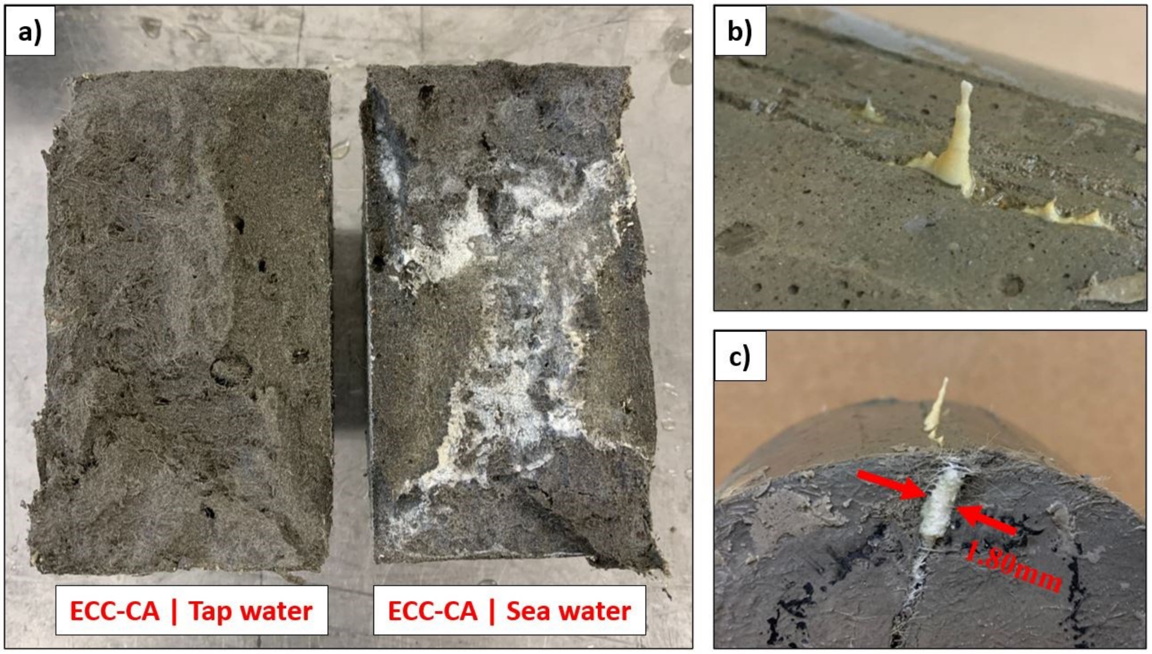
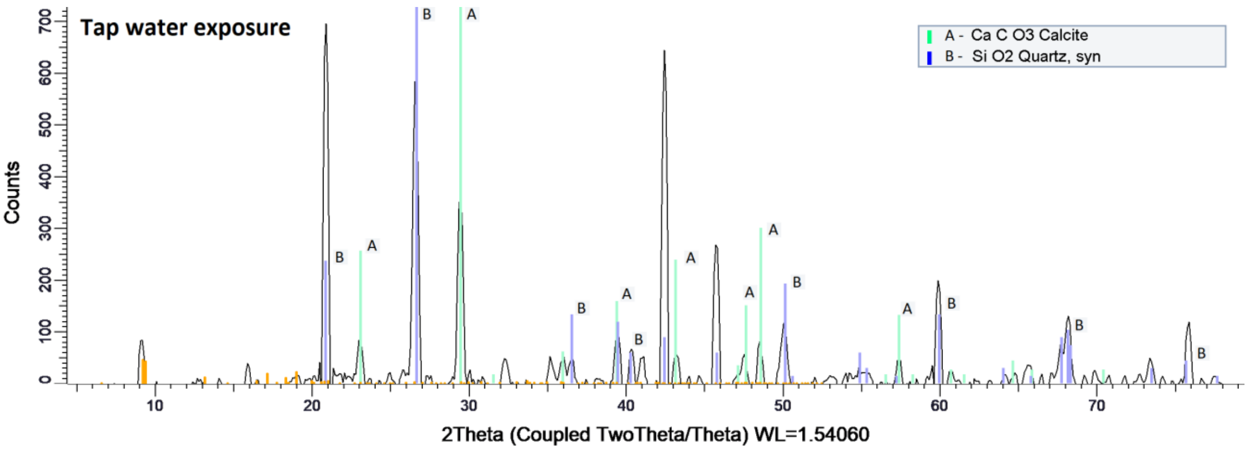


Fig. 4.6 ECC-CA disk specimens: a) opened up after the final water permeability test (WP3) to observe product formation inside cracks, b) healing products leaching out from the cracks and, c) 1.80mm crack filled with white precipitates

To identify the observed products, XRD patterns of samples for ECC and ECC-CA in sea water and tap water were obtained using an X-Ray diffractometer with Cu Ka radiation and 2theta ranging between 0 to 80 degrees. As results in Fig. 4.7 and Fig. 4.8 indicate, brucite ($Mg(OH)_2$) was observed in both ECC and ECC-CA specimens submerged in sea water, which indicates the presence of Mg ions in sea water, also confirms the formation of additional healing products that enhance the autogenous healing efficiency in this exposure condition. Calcite ($CaCO_3$) was observed in both groups as a premier product of autogenous self-healing in later ages, indicating the presence of dissolved carbonate ions in tap and sea water. Quartz (SiO_2) peaks are also determined in the samples, which could be related to the silica in the sand and FA used in ECC mixtures, and the CSH sources.



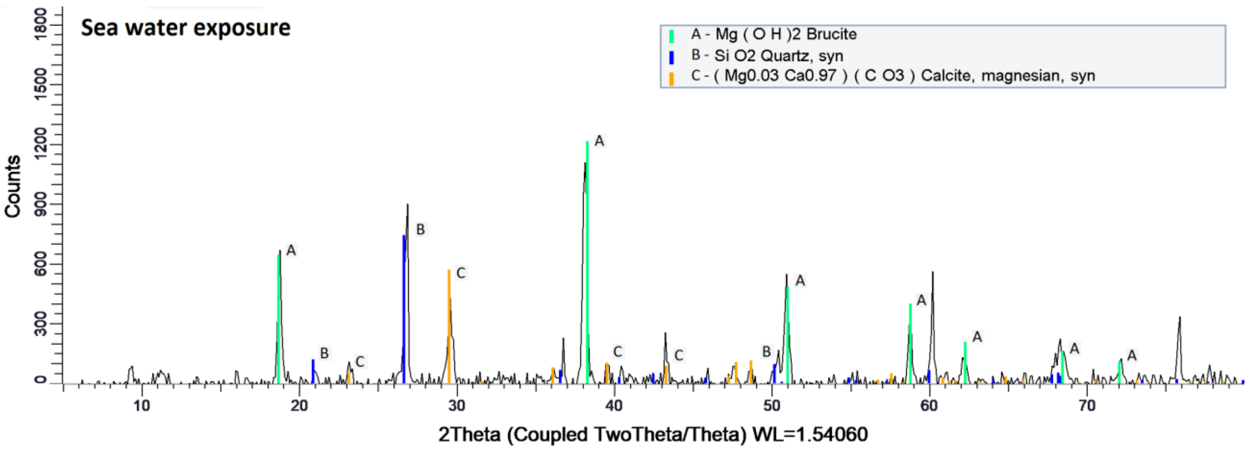


Fig. 4.7 XRD analysis results of ECC specimens exposed to tap water and sea water

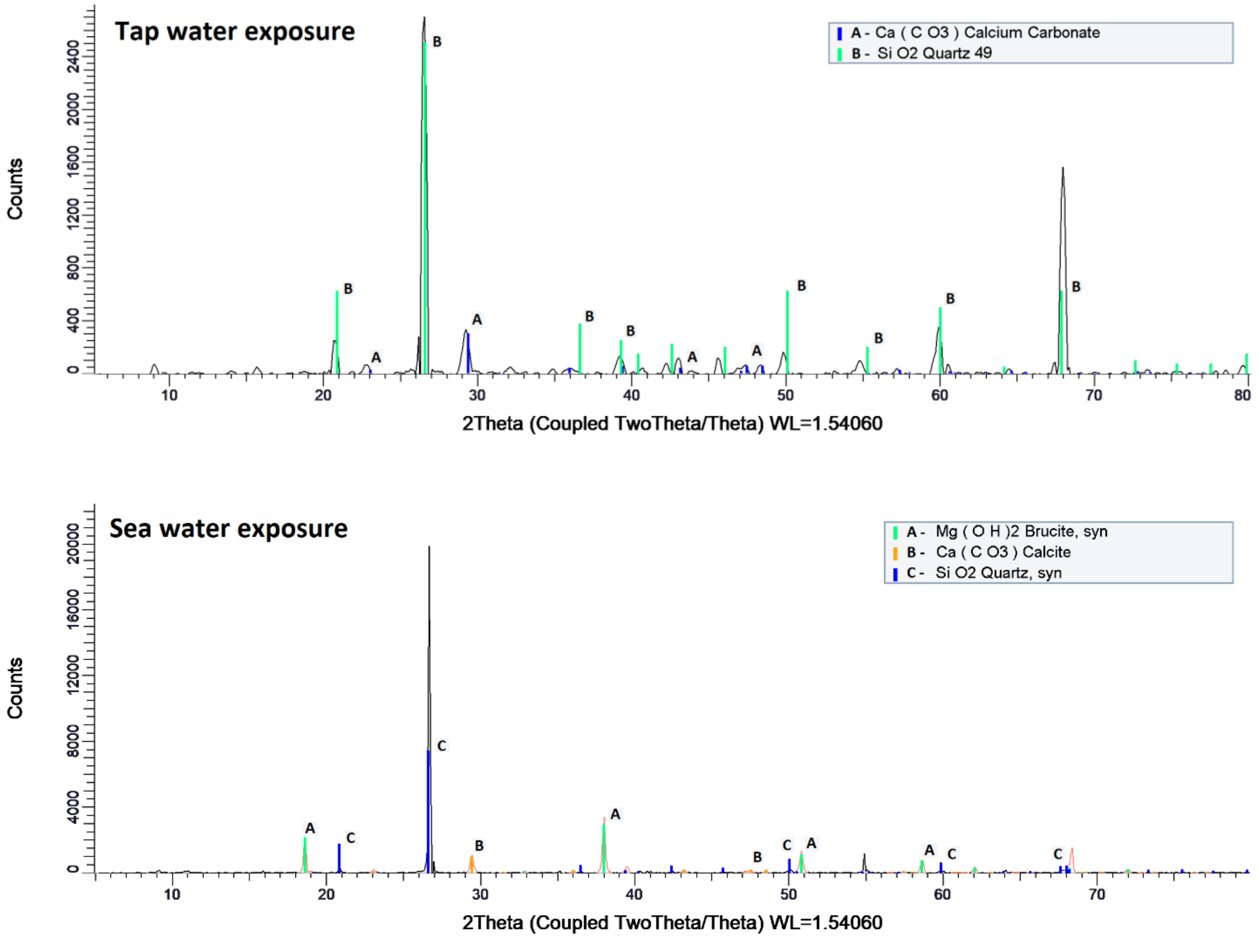


Fig. 4.8 XRD analysis results of ECC-CA specimens exposed to tap water and seawater

4.4. CONCLUSION

The presented experimental program measures the extent of self-healing in ECC specimens with and without crystalline admixture. Three different exposure conditions of air dry, tap water, and sea water were adopted for this purpose. Large crack openings of ~1-2 mm were generated in disk specimens using a split tensile test to provide enough space for healing products to form. The self-healing efficiency was measured via a water permeability test conducted at different time intervals, and XRD analysis was further performed to identify the healing products inside cracks.

Water permeability results indicate that when large cracks are generated in ECC specimens exposed to air dry and tap water conditions, the material is unable to fill the cracks with further hydration or calcite precipitation. This behavior remained unchanged for the ECC-CA group as well. On the other hand, the sea water exposure condition proved significant improvement in crack healing, such that cracks up to 2mm were filled in the ECC-CA group. The majority of the process took place in the first month of exposure, indicating the relatively high rate of reactions for self-healing process in the marine environment.

XRD analysis and visual observations proved the formation of extra healing products in the specimens exposed to sea water. Brucite and a mix of calcite and brucite were found to be the additional healing products formed during the curing period in sea water. Since the sea water used in this experiment was kept the same throughout the test, there is a chance that by replacing sea water at the start of each curing period, even higher self-healing levels would be observed in specimens.

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CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

The experimental program designed for this thesis evaluates the self-healing properties of ECC specimens exposed to three different exposure conditions of air dry, tap water, and sea water. In chapter 2 of the research, the effect of applying a compression cycle on the repeatability of self-healing was determined, and in chapter 3, the effect of the addition of Crystalline Admixture (CA) to the ECC mixture was measured through a water permeability test. The following conclusions were drawn from both chapters of the study:

- The results indicate that applying a compression cycle on partially healed cracks can have adverse effects on the stiffness recovery, such that it destroys the brittle structure of newly formed healing products (e.g. $CaCO_3$), and reduces the amount of stiffness that could be recovered over time. This contradicts the idea that applying a compression cycle to a crack will help the autogenous healing process by closing the crack and reducing the space required for healing production. That could be the case if the compression cycle were applied before the healing process initiated.
- Compression cycles and sustained loading condition will reduce the efficiency of improved autogenous self-healing in partially healed cracks.
- Water permeability results indicate that when large cracks are present in ECC specimens exposed to air dry and tap water conditions, the material is unable to fill the cracks with further hydration or calcite precipitation. On the other hand, the sea water exposure condition proved significant improvement in crack healing, such that cracks up to 2mm were filled in the ECC-CA group.
- XRD analysis and visual observations proved the formation of extra healing products in the specimens exposed to sea water. Brucite and a mix of calcite and

brucite were found to be the additional healing products formed during the curing period in sea water. Apparently, sea water is a favorable condition for the improved autogenous self-healing in ECC material, even at high displacements

- Self-healing of large cracks through hydration, carbonation or crystallization mechanisms is not feasible in the absence of moisture.
- The process of self-healing with crystalline admixture happens at a faster rate in the early ages. As time passes and the limited amount of substances get consumed, the process slows down.

In addition to the conclusions drawn based on the experimental study, the following recommendations are suggested to further expand on the research:

- In this study ECC specimens were tested for self-healing purposes. Addition of a group of normal concrete or normal FRC (which is more common in practice) for comparison of self-healing results could get a better reference point for the outcomes of the research.
- Studying wet/dry cycles of tap water and sea water (to mimic the splash zone) is recommended to understand the actual effect of surrounding environment on the self-healing of cracked concrete.
- The sea water used in this experiment was kept the same throughout the test, there is a chance that by replacing sea water at the start of each curing period, even higher self-healing levels would be observed in specimens.
- CO_2 sequestration into mineral forms of carbonates (e.g., calcite) has been introduced as an emerging branch of research on concrete materials. The study aims at developing techniques to insert CO_2 (gaseous or liquid form) into concrete during

mixing or curing process, establishing a sustainable mineral form of the greenhouse gas. Since autogenous self-healing is partially achieved via calcite precipitation in the cracks (which occurs through the sequestration of CO_2 from the surrounding environment), it seems that there is a link between these two fields of research. A mutual research interest could lead to exploring technologies to improve CO_2 sequestration in the self-healing process.

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