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Self-healing of microcracks in Engineered Cementitious Composites under sulfate and chloride environment

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HIGHLIGHTS

- ECC is durable under aggressive sulfate and chloride ions environment.
- Self-healing of microcracks within ECC material were observed.
- ECC heal faster and more completely in such environment than in water.

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ABSTRACT

Hydraulic structures are subject to high risk of deterioration associated with cracking and sulfate-chloride attack. Application of Engineered Cementitious Composites (ECC) with self-controlled tight microcracks and self-healing capacities could potentially lead to enhanced durability performance of hydraulic structures even after the formation of cracks under combined environmental and mechanical loadings. This research experimentally investigated the self-healing behavior of ECC under aggressive sulfate and chloride conditions. Resonant frequency (RF) and mechanical properties including stiffness, first cracking strength, ultimate tensile strength and tensile strain capacity were experimentally determined for ECC specimens that were preloaded to 1% strain and exposed to sulfate and sulfate-chloride solutions to simulate the service environment of hydraulic structures. The performance of ECC was found not to be adversely affected by the aggressive solutions. Instead, self-healing of the microcracks was observed leading to partial recovery of the mechanical properties. It was also found that ECC tends to heal faster and more completely in sulfate solutions than in water. These results demonstrate that ECC material remains durable under sulfate-chloride environment, which is beneficial for improving the long-term performance of hydraulic structures in such aggressive environments.

1. Introduction

Sulfate attack is a common deterioration mechanism for concrete hydraulic structures in western China and the "alkali flats" of the arid western United States. According to the report from Dam safety office [1], it is listed among the top three deterioration mechanisms for hydraulic structures, and hydraulic structures in such environment can be severely deteriorated within a few years after construction, which is far below the expected service life. The mechanism for sulfate attack of concrete is that sulfate ions penetrate into concrete, especially through cracks, and react with calcium hydroxide and calcium aluminate hydrates to form expansive products including gypsum and ettringite, resulting in internal pressure and associated cracking and deterioration of concrete [2]. Sulfate attack could happen alone, or in more common cases, e.g. in Northwestern China and marine environments, sulfate attack and chloride attack can occur simultaneously [3,4]. The effect of sulfate-chloride environment on concrete is different from that of sole sulfate environment, since the presence of chlorides limits the formation of ettringite, thereby the deterioration of concrete caused by sulfate attack is impeded. Therefore, resistance to

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sulfate and sulfate-chloride attack have both to be considered for hydraulic structures.

Sulfate and sulfate-chloride attack can be accelerated when cracks exist in hydraulic structures. Chemical attack, restrained shrinkage, thermal deformations, mechanical loads and many other factors in field conditions can all lead to concrete cracking [5]. Cracks connect the pores and form a path for aggressive ions (sulfate and chloride ions) to penetrate into the concrete, which drastically accelerates the deterioration of concrete structures. It is also found that the diffusivity of aggressive ions increases significantly with increasing crack width [6]. Therefore, it is critical to control the crack width of concrete hydraulic structures in order to achieve satisfactory long-term durability performance under sulfate and sulfate-chloride environments.

Engineered Cementitious Composites (ECC) is a class of high performance fiber reinforced cementitious composites featuring high tensile ductility and self-controlled tight cracks [7–10]. Unlike normal concrete or conventional tension-softening fiber reinforced concrete (FRC), ECC shows a strain-hardening behavior under uniaxial tension accompanied by multiple microcracks. The tensile strain capacity of ECC typically ranges from 2% to 5%, which is 200–500 times that of normal concrete. Moreover, the cracks formed in ECC are typically less than 60 μm wide. As demonstrated in previous studies [6,11,12], with such tight crack widths, the permeability and diffusivity of cracked ECC specimens remains comparable to that of uncracked concrete, which greatly delays further deterioration of the structure.

The durability study on ECC under sulfate and sulfate-chloride environment has been investigated by the authors earlier [13]. In that paper, compressive and tensile behavior of ECC under sulfate and sulfate-chloride conditions were experimentally characterized. Micromechanical study was also carried out to investigate the microscopic mechanisms underlying the composite level behavior of ECC under those aggressive environments. The experimental results obtained in [13] demonstrated that ECC remains more durable than normal cementitious materials under sulfate and sulfate-chloride environment, suggesting the potential to apply ECC as a protective surface layer for new hydraulic structures or as surface repairs for damaged hydraulic structures for enhanced long-term performance of these structures.

In addition to the superior cracking control ability and durability of ECC, potential self-healing of microcracks of ECC could further delay the deterioration of ECC and extend the service life of the structures. Self-healing refers to the phenomenon that cracks diminish autogenously in width over time. Self-healing of cracks in concrete material in the presence of water is a complex chemical and physical process. The healing of concrete cracks has been attributed to the hydration of unreacted cement, swelling of C—S—H, crystallization of calcium carbonate, closing of cracks by impurities in the water and closing of cracks by spalling concrete particles [14]. Based on previous studies [15–17], self-healing extent is inversely related to crack width. It is for this reason that ECC with tight microcracks could promote self-healing, and therefore recovers the transport properties, and in some cases even the mechanical properties of the concrete material, greatly improving the durability of the concrete structures [17–19].

The self-healing of ECC under various environments have been studied by many scholars. Precipitation of calcium carbonate and continuous hydration of unreacted cement are considered the two major contributors to self-healing of microcracks in ECC [19]. Both Yang et al. [18] and Kan et al. [19] found that wet/dry cycles are beneficial for promoting self-healing of ECC. Herbert and Li [20] reported that the self-healing of ECC is not limited to controlled laboratory environment, but is also observed in a natural environment with variable temperature and precipitation. Zhu et al. [21] studied the self-healing of ECC under freeze-thaw cycles. Sahmaran and Li [22] proved that ECC could heal sufficiently under freezing and thawing cycles in the presence of de-icing salt. Li and Li [23] and Sahmaran and Li [24] investigated self-healing of ECC in chloride and high alkaline environment, respectively. Their results show that ECC, both cracked and uncracked, remains durable under those environment exposures, and self-healing of microcracks were observed under all investigated environments, further contributing to the high durability. In addition, Qian et al. [25] and Sisomphon et al. [26] explored the influence of curing condition (air curing, water curing, cyclic wet/dry curing and 3% CO_2 concentration curing) on the self-healing of ECC incorporating different cementitious materials.

Despite the growing body of literature on self-healing of ECC, little research has been carried out on the self-healing behavior of ECC under sulfate and sulfate-chloride environment. In order to fully evaluate the potential of applying ECC in hydraulic structures, research is needed to characterize the mechanical and self-healing performance of ECC under such aggressive environments. Since typical sulfate and chloride attack involve cracking due to formation of expansive substance, the use of fly ash, the high tensile strength and ductility of ECC may help resist such failure and result in higher performance. In addition, the formation of ettringite/gypsum associated with sulfate attack may even facilitate healing of cracks through tighter sealing. These hypotheses need to be experimentally validated. This investigation together with the prior study by the authors [13] form a comprehensive experimental system for understanding the performance of ECC under sulfate and sulfate-chloride environment.

In this study, the mechanical property and self-healing of microcracks in ECC under sulfate, and sulfate-chloride environments were experimentally investigated. Specifically, ECC specimens were pre-tensioned to 1% strain level to simulate the formation of cracks in field conditions, and then exposed to sulfate and sulfate-chloride solutions for a time period of 30, 60 or 120 days. The resonant frequency and residual mechanical properties of ECC including ultimate tensile strength and strain capacity, stiffness and first cracking strength were measured after the environmental exposure to assess the performance of ECC. The research findings are expected to provide new knowledge for future application of ECC in hydraulic structures exposed to aggressive environments.

2. Experiment investigation

2.1. Materials

The same ECC mixture used in the previous study [13] was adopted in this investigation. The mix proportion of this ECC is shown in Table 1. The raw materials include Type I Portland cement, Class-F fly ash, fine silica sand, water, poly-vinyl alcohol (PVA) fibers, and a high range water-reducing admixture (HRWRA). The chemical composition of cement, fly ash and the properties of the PVA fiber used in this study are listed in Tables 2–4 respectively. Previous studies [12,13] have proved the feasibility of using this ECC mix to enhance the long-term performance of hydraulic structures.

The preparation of the mixture follows a typical ECC mixing procedure as detailed in [27]. After mixing, the fresh mixture was casted into 9 in. × 3 in. × 0.5 in. coupon specimen molds. All specimens were demolded after 24 h and air cured under laboratory conditions at a room temperature of 23 ± 3 °C and 20 ± 5% RH for 28 days.

2.2. Specimen preloading and environmental exposures

In order to investigate the durability performance and self-healing of cracked ECC under aggressive environments, ECC specimens were preloaded to 1% strain using uniaxial tensile test as shown in Fig. 1 to introduce cracks. Prior to tensile testing, four aluminum plates were glued to the ends of the specimen to facilitate gripping. The test was carried out using a 25 kN capacity testing frame under displacement control at 0.5 mm/min. Two linear variable displacement transducers (LVDTs) were mounted to the specimen to monitor the specimen extension. When

Table 1
Mix proportions of ECC (kg/m^3).

Material	Cement	Aggregates	Fly ash	Water	HRWRA	Fiber
ECC	393	457	865	311	5	26

Table 2
Chemical composition of cement.

SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	SO_3 (%)
19.6	4.8	2.9	63.5	2.1	2.7

the tensile strain reached the designated strain level of 1%, the loading was aborted and the specimens were removed from the testing frame and placed in aggressive sulfate and sulfate-chloride solutions.

Two aggressive solutions, which were the same with the previous study [13], were used in this study as exposure environment for ECC. The first solution is 5% (wt%) sodium sulfate solution, and the second solution contains 5% (wt%) sodium sulfate and 3% (wt%) sodium chloride. The two solutions were used as recommended by previous researchers [6,23,28]. Both preloaded specimens and non-preloaded sound specimens were exposed to aggressive solutions under laboratory conditions (23 ± 3 °C and 20 ± 5% RH). A set of 3 preloaded specimens was taken out of each solution and air-dried for 24 h before conducting the mechanical and resonance frequency tests at 30 day, 60 day, and 120 day, respectively. In addition, preloaded and sound specimens were also placed in water, the standard healing condition that has been extensively studied in previous researches, for 30, 60, and 120 days, and assessed for their self-healing conditions as a control group.

2.3. Testing procedure

2.3.1. Resonant frequency measurement

Resonant frequency (RF) measurements of ECC specimens based on ASTM C215 were used to qualify the damage and healing condition of ECC specimens. This technique has been proved to be an effective method and therefore extensively used to evaluate both the rate and the extent of the self-healing of microcracks within ECC [18]. The RF of ECC specimens was measured before and after each preloading and reloading test.

The RF ratios ($RF_{s-ratio}$) of sound ECC specimens can be determined by the following equation

$$RF_{s-ratio} = \frac{RF_{s-envt}}{RF_{s-28d}} \tag{1}$$

where RF_{s-envt} is the RF value of sound ECC specimen measured after various environmental exposure time (immersed in aggressive solutions or water), and RF_{s-28d} is the RF value of sound ECC specimen measured at 28 days before any environmental exposures.

For preloaded ECC specimens, self-healing of microcracks is expected to lead to increasing RF values. In order to eliminate the effects of continuous hydration and sulfate attack within uncracked matrix, and to obtain the change of RF values that is only attributed to the self-healing of microcracks, the RF measurements of preloaded ECC specimens are normalized using the following equation

$$RF_{p-ratio} = \frac{RF_{p-envt}}{RF_{s-envt}} \tag{2}$$

where RF_{p-envt} denotes the RF values of preloaded ECC specimens measured before exposure and RF values of preloaded ECC specimens after exposure to solutions or water for various amounts of time, while RF_{s-envt} denotes the RF values of sound ECC specimens subjected to the same environmental exposure.

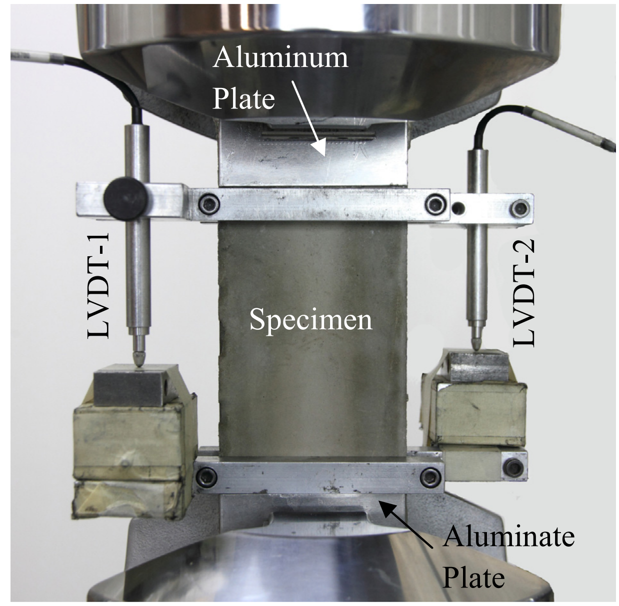


Fig. 1. Uniaxial tension test setup.

2.3.2. Uniaxial tensile test (Reloading)

In order to assess the mechanical properties of ECC under aggressive environments and their recovery due to self-healing, uniaxial tensile test was conducted to reload the preloaded specimens until failure after their exposure to the solutions (or water for the control group). The test was carried out following the same procedure described previously in Section 2.2. The tensile stress-strain relationships were measured and recorded, from which the stiffness, first cracking strength, ultimate tensile strength, and tensile strain capacity of ECC specimens were determined. Then the recovery of stiffness and first cracking strength were calculated by normalizing the values of the above obtained data by the corresponding values acquired during preloading procedure to evaluate the durability of ECC and the level of self-healing.

3. Experimental results and discussion

3.1. Resonant frequency recovery

The RF ratio ($RF_{s-ratio}$) of sound ECC specimens is plotted in Fig. 2. As the figure shows, $RF_{s-ratio}$ increases over time for specimens subjected to all environmental conditions. The increase of resonant frequency is typically considered to be associated with continuous hydration of cement and pozzolanic reaction of fly ash [20] in the presence of water that densifies the microstructure.

From Fig. 2, it can also be seen that all the specimens follow the same trend: the $RF_{s-ratio}$ increases by about ten to fifteen percent during the first 30 days of exposure to solutions (or water), after which the rate of increase becomes much slower. Comparing the three curves, The RF ratio of specimens that were immersed in sul-

Table 3
Chemical composition of fly ash.

SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	SO_3 (%)	Na_2O (%)	K_2O (%)
42.20	22.51	9.20	15.66	3.2	1.85	0.98	1.53

Table 4
Properties of PVA fiber.

Length (mm)	Diameter (μm)	Elongation (%)	Density (kg/m^3)	Young's Modulus (GPa)	Nominal strength (MPa)
12	39	6	1300	42.8	1600

fate and sulfate-chloride solutions is higher than those in water. It is likely that apart from continuous hydration and pozzolanic reaction, sulfate ions also contribute to the increase of RF values by penetrating into the specimen and reacting with calcium hydroxide and calcium aluminate hydrates in ECC to form ettringite and gypsum [29–32], which is the underlying mechanism for sulfate attack of concrete material. This hypothesis is further confirmed with experimental observations as will be discussed in the following section.

The normalized RF ratio ($RF_{p-ratio}$) versus exposure time relationships are plotted in Fig. 3 for all specimens. As can be seen, the changes of $RF_{p-ratio}$ of specimens exposed to different environmental conditions all follow similar trends. After preloading, the $RF_{p-ratio}$ decreased dramatically from 100% to 51% because of the formation of multiple microcracks under tension. However, the $RF_{p-ratio}$ experienced a rapid increase to around 85% over the next 30 days, which was followed by a relatively stable period. This trend is consistent with the characteristics of self-healing, which happens fast initially and then stabilizes. As Fig. 4 shows, the microcracks were almost fully healed by crystals only after 10 days.

Fig. 5(a) shows a micrograph of a specimen that was exposed to sulfate solution after 10 days. A large amount of needle-shaped ettringite crystals (also confirmed with EDX energy spectra in Fig. 5(b)) can be observed within the ECC matrix as well as inside the microcracks. The EDX analysis results of self-healed products subjected to water is presented in Fig. 6. This is in line with the previous studies that show the majority healing products are C—S—H and $CaCO_3$ with a mixture of $Ca(OH)_2/CaCO_3$, and no ettringite was observed here. Thus it can be seen that the presence of sulfate ions contributes to the formation of ettringite, which in turn enhances the extent of self-healing.

Besides, it can be observed that almost all microcracks (crack width up to around 150 μm) were fully closed at the surface after 120 days (Fig. 7). Since the extent of self-healing also depends on the crack depth [33,34], more investigations with X-ray technique should be applied in the future to clarify the self-healing degree at greater depths. However, the recovery of RF values is associated with the self-healing of cracks. The specimens in sodium sulfate solution reached almost 100% recovery in RF values after 120 days (Fig. 3), the higher level of RF recovery for specimens exposed to sulfate solution indicates a higher level of self-healing, which might be attributed to the formation of ettringite/gypsum within the microcracks that enhances the self-healing phenomenon.

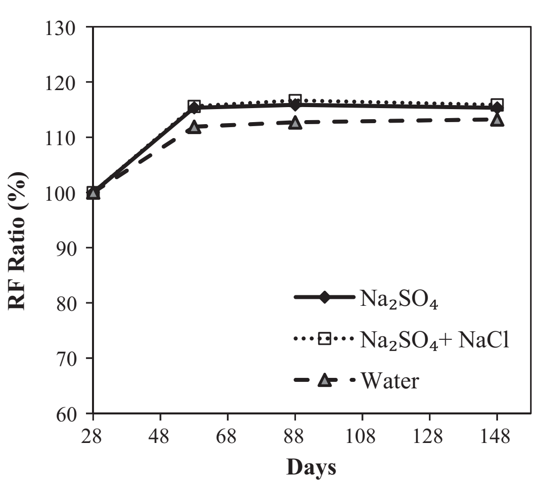


Fig. 2. RF ratio of sound ECC specimens subjected to different environmental exposures.

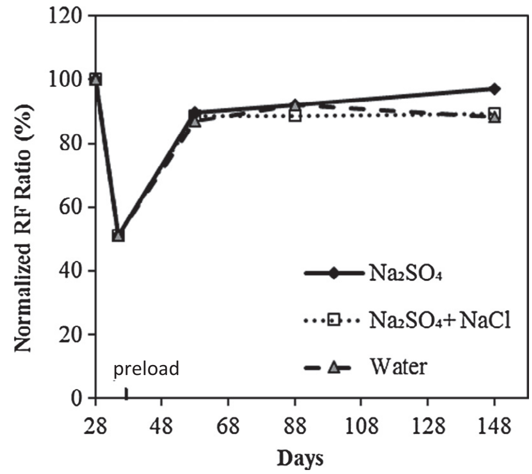


Fig. 3. Normalized RF recovery of preloaded ECC specimens under aggressive solution and water for different exposure time.

3.2. Mechanical property recovery

3.2.1. Tensile properties of preloaded ECC after exposure

Table 5 summarizes the first cracking strength, ultimate tensile strength, and tensile strain capacity of ECC before and after environmental exposure. The data listed as "28 days in air" is measured on sound ECC specimens after curing in air for 28 days, which is similar to that of the sound specimens that was immersed in water for 120 days but with a slightly higher tensile strain capacity. The rest of the data are measured using preload specimens that are reloaded after exposure to various conditions. The ultimate tensile strength and tensile strain capacity in this study was respectively defined as the peak stress and corresponding strain values on the tensile stress-strain curve. According to JSCE design recommendation [35], the first cracking strength presented in the table was defined as the stress value when the first crack was initiated under tensile loading, where the assumption of linear elasticity could not hold any more. Representative stress-strain relationships of the ECC specimens are shown in Fig. 8.

It is clear that specimens exposed to sulfate solution, sulfate-chloride solution, and water all show an increasing trend of both the first cracking strength and the ultimate tensile strength with increasing exposure time, see Table 5. The specimens that are exposed to sodium sulfate solution experienced the most significant strength increase. The first cracking strength recovers to 1.77 MPa and the ultimate tensile strength rises to 4.67 MPa after 120 days of exposure. As a comparison, the specimens that are exposed to water exhibit average first cracking strength of 0.95 MPa and average ultimate strength of 4.05 MPa after 120 days of healing, which are lower than that of the specimens exposed to aggressive solutions. Previous studies [19,36] have suggested that the enhancement of ultimate strength of specimens healed in water is associated with the increase of fiber/matrix interfacial bond, resulting from the continuous hydration of cement. When exposed to sulfate solution, the formation of ettringite/gypsum within the specimens may further enhance the above mentioned trends, leading to further strength increase.

In addition, previous studies [3,4] pointed out that the presence of chloride ions could inhibit the formation of ettringite and gypsum, and slow down the deterioration caused by sulfate ions. In this study, strength increase of specimens exposed to sulfate-chloride solutions was slightly smaller as compared to that of sulfate solution. Such slight difference may reflect the same underlying mechanisms as described in the literature, however, longer

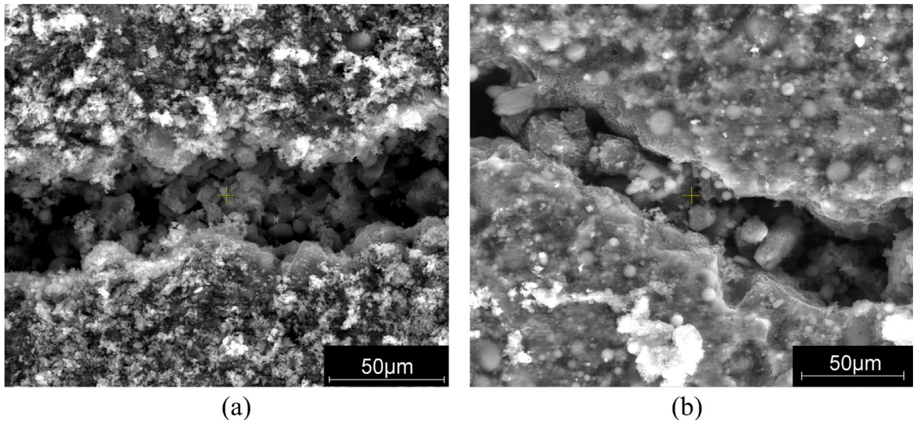


Fig. 4. Microscopic observation of self-healing for ECC subjected to (a) sulfate solution and (b) sulfate-chloride solution after 10 days.

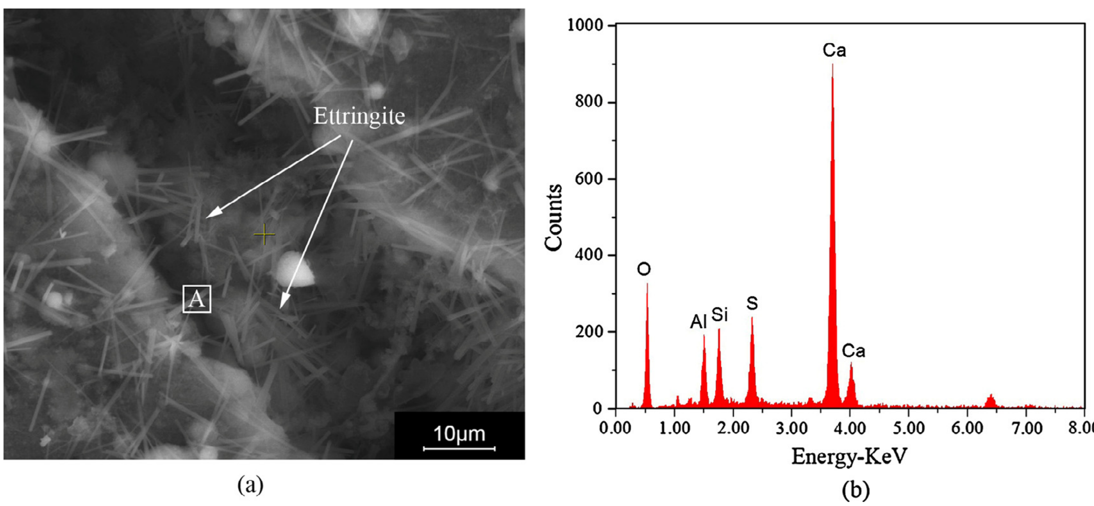


Fig. 5. (a) SEM micrograph and (b) EDX spectra (point A) of specimens exposed to sulfate solution.

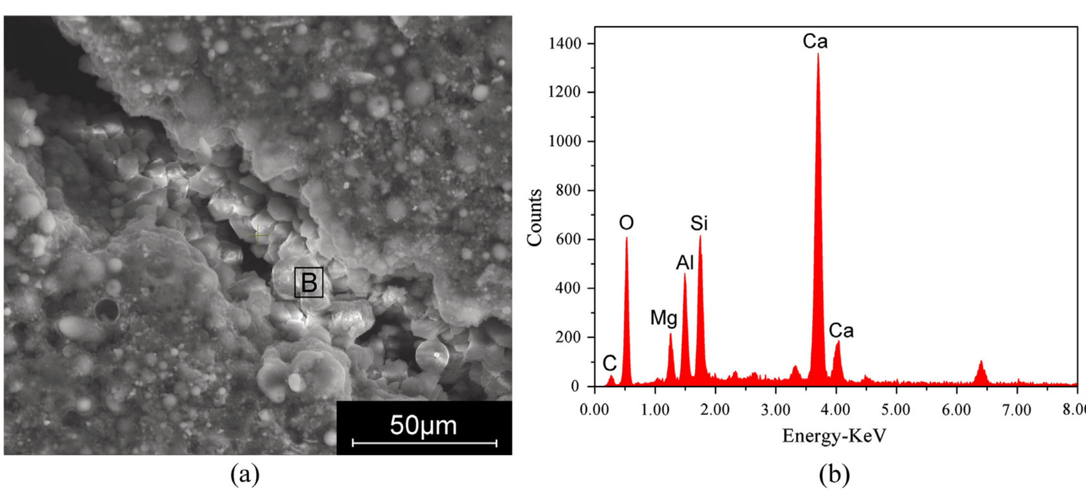


Fig. 6. (a) SEM micrograph and (b) EDX spectra (point B) of specimens exposed to water.

exposure time might be needed in the future to better understand the coupled influence of chloride ions and sulfate ions on self-healing of ECC.

In terms of tensile strain capacity of the specimens, there is a slight decline when compared to that of sound ECC specimens tested at the age of 28 day. The average tensile strain capacity measured at 28 day is around 2.81%, however, after 120 days of exposure, the specimens exposed to sulfate solution, sulfate-chloride solution and water all exhibit relatively lower tensile strain capacity with an average of 2.56%, 2.03% and 2.38%, respectively. It

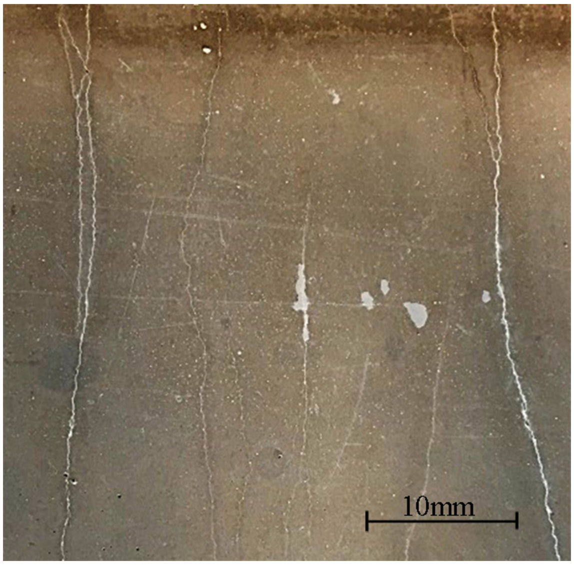
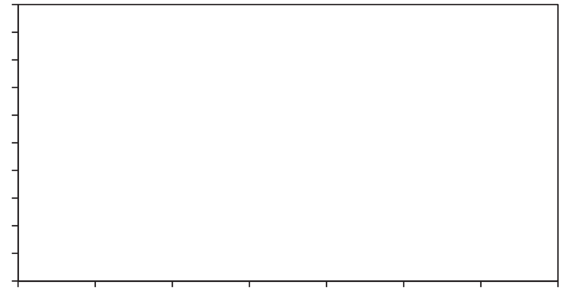


Fig. 7. Self-healed microcracks after 120-day exposure to sulfate solution.



should be noted that the tensile strain capacity reported for the reloading specimens does not include the residual strain following the precracking load. By neglecting this residual strain, the measured tensile strain capacity is on the conservative side.

The decreasing strain capacity is directly related to the change of the micromechanical parameters under sulfate and chloride environment. Based on the previous study [13], the continuous hydration of cement, the pozzolanic reaction of fly ash and the formation of ettringite and gypsum in aggressive solutions lead to a notable increase in matrix toughness and fiber/matrix interfacial frictional bond. On the other hand, due to the reduction of the concentration of aluminum and calcium ions at the fiber/matrix interface, chemical bond showed a decreasing trend. Although the average tensile strain capacity experiences a slight decrease over time, ECC specimens still show significant strain-hardening. The tensile strain capacity at the age of 148 days (after 120 days of environmental exposure) was still two orders of magnitude higher than that of normal concrete. In addition, as can be seen from Fig. 8, the tensile strain capacity of ECC after self-healing is relatively higher than that of specimen without undergoing self-healing process. This may be attributed to the fact that the newly formed reaction products enhanced the fiber/matrix interfacial bond, resulting in the recovery of the fiber bridging mechanism, and therefore recovered the ECC tensile strain capacity.

The experimental results shown in Table 5 and Fig. 8 suggest that the mechanical properties including tensile strength and ductility of ECC specimens do not appear to be adversely affected by the presence of aggressive chemicals. ECC exposed to aggressive solutions shows higher increase of tensile strength than that of specimens exposed to water. In contrast, deterioration due to sulfate exposure typically occurs after 80–100 days in normal concrete material [3,4,37,38], and it could happen even earlier when cracks are present. Remarkably, in ECC, after up to 120 days of exposure, the cracks formed during the preloading almost fully healed instead of further opening as shown in Fig. 5. This indicates that the self-controlled microcracks and self-healing capacity of

Table 5
Tensile properties of ECC healed under different exposure environments and durations.

Environmental exposure condition		First cracking strength (MPa)	Ultimate tensile strength (MPa)	Tensile strain capacity (%)
28 days in air (sound specimens)		3.46 ± 0.15	3.87 ± 0.17	2.81 ± 0.14
Reload after 30 days' exposure	5% Na_2SO_4	0.92 ± 0.29	4.17 ± 0.26	2.01 ± 0.03
	5% Na_2SO_4 + 3%NaCl	0.93 ± 0.66	3.95 ± 0.09	2.37 ± 0.54
	Water	0.65 ± 0.18	3.47 ± 0.23	2.13 ± 0.16
Reload after 60 days' exposure	5% Na_2SO_4	1.18 ± 0.40	4.41 ± 0.23	2.63 ± 0.63
	5% Na_2SO_4 + 3%NaCl	1.37 ± 0.27	4.36 ± 0.18	1.94 ± 0.13
	Water	0.71 ± 0.08	4.05 ± 0.19	2.24 ± 0.16
Reload after 120 days' exposure	5% Na_2SO_4	1.77 ± 0.46	4.67 ± 0.33	2.56 ± 0.04
	5% Na_2SO_4 + 3%NaCl	1.26 ± 0.08	4.25 ± 0.20	2.03 ± 0.03
	Water	0.95 ± 0.26	4.05 ± 0.05	2.38 ± 0.23

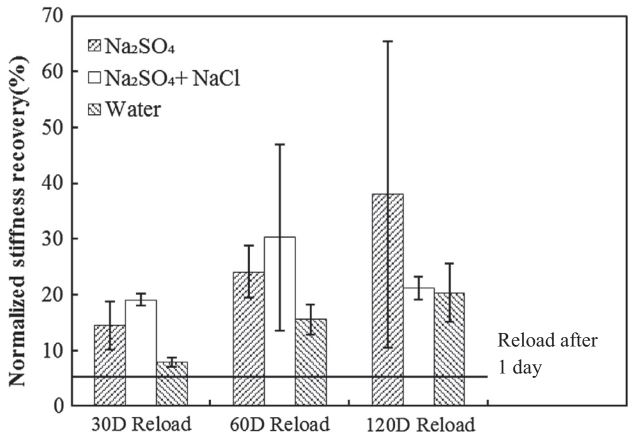


Fig. 9. Effect of exposure environment and time on recovery of stiffness.

ECC contribute to high sulfate attack resistance and better durability performance.

3.2.2. Stiffness and first cracking strength recovery

The self-healing of ECC under various environmental conditions can be assessed by investigating the recovery of stiffness and first cracking strength. Fig. 9 shows the stiffness recovery (stiffness after self-healing normalized by the stiffness of sound specimens measured during preloading) of ECC specimens exposed to sulfate solution, sulfate-chloride solution and water, respectively. The stiffness of ECC specimens reloaded after 1 day without undergoing self-healing process is also shown in Fig. 9 (the solid line) for reference. The secant stiffness was measured using a linearized stress-strain curve between tensile stress of 0.5 and 2.0 MPa, as suggested by previous research [20]. As Fig. 9 shows, the normalized stiffness recovery increases with the exposure time, and the values reach 40% for specimens exposed to sodium sulfate solution and 20% for those exposed to sulfate-chloride solution and water after 120 days. Compared to the stiffness of specimens that did not undergo self-healing (around 5%), such recovery is considered significant. Similar experimental results were obtained previously for ECC specimens healed in natural environment, where the stiffness of ECC specimens that were preloaded to 1% strain recovered to around 35% of its original stiffness after 3 months [20]. It should also be noted that in that research, above 100% recovery of stiffness was observed after 12 months under natural environment. Thus, even though the stiffness did not fully recover after 120 days in the present study, higher stiffness recovery could be expected with longer healing time.

The stiffness recovery shown in Fig. 9 is attributed to be largely the healing of the microcracks. If there was no self-healing of microcracks, the initial portion of the stress-strain curve of Fig. 8 would have resembled that of specimens reloaded 1 day after preloading, since the existing cracks would have reopened first before the rest of the specimens could engage. In such case, the stiffness recovery should have been very limited. This hypothesis can be further verified by the experimental observations. By comparing the same specimen after 120 days of healing in sulfate solution before and after reloading, new microcracks were found to form before the reopening of self-healed cracks. The healed cracks reveal themselves as white lines (Fig. 10 (a)), but the new cracks generated as a result of reloading reveal themselves as black lines (Fig. 10(b)). This implies that the self-healed cracks were strong enough to transmit tensile load without reopening, therefore contributing to the stiffness recovery. The continuous hydration and formation of ettringite/gypsum within uncracked matrix could also contribute to the stiffness recovery, although their contribution is considered secondary.

Additionally, as shown in Fig. 11, the stiffness recovery of ECC specimens healed in the aggressive environments is faster than those healed in water. This may indicate that the formation of reaction products within the cracks also enhances the self-healing of microcracks.

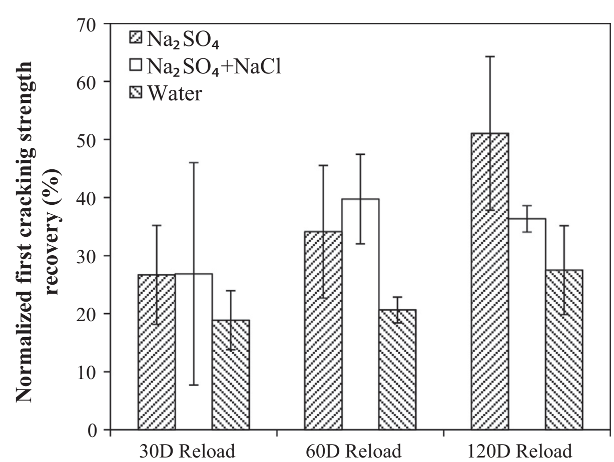


Fig. 11. Effect of exposure environment and time on recovery of first cracking strength.

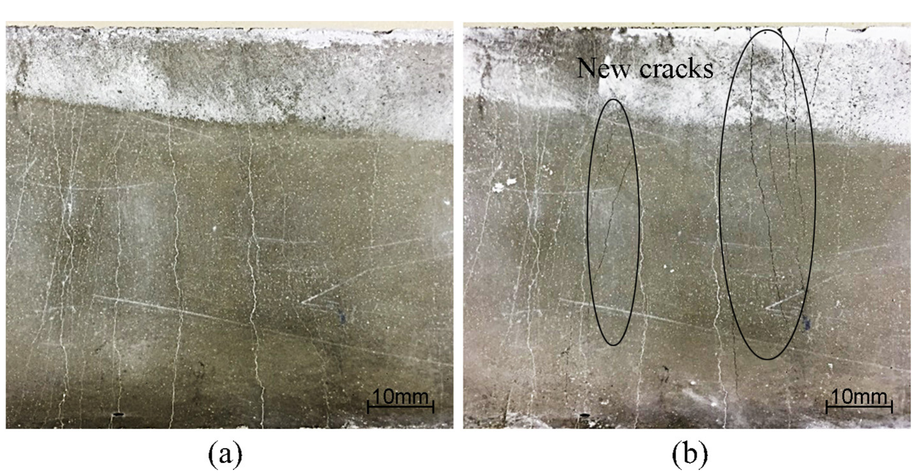


Fig. 10. (a) Self-healed microcracks before reloading; and (b) formation of new microcracks during reloading.

Large standard deviation of stiffness recovery was observed. It is mainly attributed to the fact that the extent and rate of self-healing are highly sensitive to the pattern of microcracks (crack widths and crack numbers) [20]. As demonstrated in previous studies, narrower cracks tend to heal faster and are more likely to be fully healed. The crack pattern varies from specimen to specimen, hence, larger standard deviation was observed for stiffness recovery. More research is needed to further improve the reliability of self-healing of ECC.

Likewise, the recovery of first cracking strength was also observed as a result of self-healing. As presented in Fig. 11, a rising trend was observed for specimens exposed to all three environmental conditions. The first cracking strength of ECC specimens that were exposed to sulfate solution reached over 50% recovery after 120 days. However, the recovery of first cracking strength of specimens healed in water was moderately lower, with an average of 28% recovery after 120 days. For the same reason as mentioned above, the first cracking strength recovery in aggressive solutions might be controlled by the coupled effect of continuous hydration of cement and formation of reaction products both within the microcracks and uncracked matrix. Further, the expansive effect of ettringite/gypsum may contribute to a more complete filling of microcracks that enhances resistance to reopening under reloading. In contrast, for specimens healed in water, only continuous hydration contributes to the recovery. Therefore, the first cracking strength recovery remains at a comparatively lower level.

As shown in Figs. 9 and 11, a decrease of stiffness and first cracking strength recovery from 60 to 120 days was observed for specimens subjected to sulfate and chloride solution. This phenomenon could be caused by the combined effect of self-healing and the presence of chloride ions. According to previous studies [39,40], the existence of chloride ions could increase the leaching of Ca^{2+}, causing the material's porosity to increase and the stiffness and first cracking strength to decrease. However, it is difficult to make a definitive conclusion due to the large variability of the data.

4. Conclusions

The mechanical properties and self-healing of ECC under sulfate and chloride environments were experimentally investigated in this study. Based on the research findings, the following conclusions can be drawn:

(1) ECC remains durable under aggressive environmental loadings (sulfate and chloride ions). Even with pre-existing microcracks, degradation of mechanical properties of ECC was not observed after 120 days of exposure to aggressive solutions, while normal concrete typically experiences noticeable deterioration under such conditions.
(2) Self-healing of microcracks within ECC material that were subjected to a high damage level (preloading to 1% strain) were observed under sulfate and chloride environments.
(3) Both resonant frequency (RF) and mechanical properties data show that ECC specimens exposed to sulfate and sulfate-chloride solutions heal faster and more completely than those healed in water. In particular, specimens exposed to sulfate solution show the highest level of self-healing. This is possibly due to the formation of ettringite and gypsum in the presence of sulfate ions that enhances the self-healing process.

The experiment results obtained here demonstrate the feasibility of applying ECC in hydraulic structures that are often subjected to combined mechanical (cracks) and environmental (aggressive ions) loadings. This study provides a basis for future deeper investigations into the microstructural change over time, particularly on the visualization of the progressive closure of the microcracks [34,41,42] exposed to sulfate and chloride solutions. In addition, further studies are needed for longer exposure time and field conditions to verify the stiffness recovery after longer healing time and to better understand the long-term durability performance and self-healing of ECC material in practical working environment of hydraulic structures.

In this study, experiments were performed with pre-loaded ECC specimens continuously immersed in sulfate and sulfate-chloride solutions. In field conditions, the portion of hydraulic structures in the splash zone is also of interest since wetting and drying cycles are expected to affect the self-healing of structures. According to previous studies, wet/dry cycles not only could enhance carbonation, but also could effectively promote the interaction of water, CO_2 and remaining unhydrated cementitious material inside ECC material, thereby enhancing the self-healing process [25,43]. However, for structures in splash zones, wet/dry cycles may also wash out the calcium hydroxide and the healed products. Therefore, more studies should be carried out in the future to investigate the self-healing performance of ECC under the combined effect of sulfate-chloride attack and wet/dry cycles.

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