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Designing Repeatable Self-Healing into Cementitious Materials

Mo Li and Shuai Fan
Department of Civil and Environmental Engineering, University of California, Irvine

ABSTRACT

Designing self-healing into cementitious materials can open a new world of opportunities for resilient concrete infrastructure under service loading conditions. The self-healing process should be robust as well as repeatable, allowing for self-repair after multiple damage events. The repeatability poses great challenges when self-healing strategies mainly rely on the formation of low-strength calcium carbonate healing product, complicated by the localized cracking behavior of cementitious materials. This study aims at formulating a new cementitious material system with designed physical and chemical characteristics that favour repeatable self-healing. Advanced experimental methods, coupled with micromechanics theory, are adopted to probe and design repeatable self-healing into cementitious materials.

1. INTRODUCTION

Concrete is the most widely used man-made material (Ashby, 2010) but is inherently brittle (Bazant & Planas, 1997). As a result, concrete infrastructures often suffer from cracking due to various factors such as drying shrinkage at early age or fatigue loading during its service life (Weiss & Shah, 2002). Cracking compromises concrete transport properties, allows "easy" paths for water or aggressive chemicals to reach reinforcing steel, and accelerates other deterioration processes such as steel corrosion (Mehta & Gerwick, 1982). Cracking will also impair concrete mechanical properties, causing local distress and stiffness reduction in structural members (Vaysburd, Brown, & Bissonnett, 2004). The reduction of service life of concrete infrastructure induced by concrete cracking has led to frequent maintenance and repairs and remains one of the most significant factors limiting the durability of concrete structures (Mehta, 1997; Mihashi & De Leite, 2004). These challenges can be potentially tackled by novel self-healing cementitious materials, which can autogenously regain material transport properties as well as mechanical characteristics after the crack self-healing process.

In the past decade, there have been remarkable progresses on self-healing concrete research. The self-healing approach is mainly based on the embedment of capsules containing self-healing compound, e.g., immobilized bacteria, within the composite (Jonkers, Thijssen, Muyzer, Copuroglu, & Schlangen, 2010; Wiktor & Jonkers, 2011). The immobilized bacteria will be activated by cracking and exposure to water to start to precipitate minerals. Other healing agents include cyanoacrylates or alkali-silica solutions (Tittelboom, De Belie, Loo, & Jacobs, 2011). These techniques allow instant actuation of the healing process once cracking breaks through the capsules. However, questions still remain as to whether repeatable self-healing can reliably occur to allow for self-repair after multiple damage events. The repeatability poses great challenges when self-healing strategies mainly rely on the formation of low-strength and low-toughness healing product (e.g., calcium carbonate), complicated by the localized cracking behavior of cementitious materials. Once reloaded, localized cracking will mostly reoccur along the sealed crack. Even for the recovery of transport properties only (aka "sealing"), the localized cracking at the healed region during reloading will soon deplete the healing agents, ending the healing process.

In this study, it is hypothesized that repeatable self-healing in cementitious materials can be possible if a combination of conditions are met: (a) the material exhibits a self-controlled, distributed damage process rather than localized cracking; (b) a multitude of healing compounds are present that can be randomly triggered by each damage event and react with natural actuators present in the environment; and (c) the healing process and reaction kinetics can lead to the formation of high-strength and high-toughness healing products (i.e., C-S-H) with sufficiently large volume, leading to the recovery of both mechanical and transport properties. In this paper, we focus on testing this hypothesis through formulating a new cementitious material system with designed physical and chemical variables. The results can shed light on whether repeatable self-healing can be achieved in cementitious materials and how we can measure repeatable self-healing.

2. MATERIAL DESIGN

The material design requires satisfying a set of physical and chemical criteria. Only two criteria selected among a few are highlighted in this paper: one is a physical criterion, i.e., distributed damage with intrinsic crack width control; the other is a chemical criterion, i.e., promoted formation of C-S-H-dominant healing product. It should be noted that these are necessary, but not sufficient conditions. Also, the two criteria very often are not independent. In addition to the material design criteria, environmental exposure conditions (e.g., temperature, relative humidity, environmental pH, CO_2, and Cl^-) are taken into account as constraints, depending on the geographical application of the material. Ideally, the chemical compounds within the material can be activated upon cracking by contact with natural actuators present in the environment, forming healing products with adequate strength and toughness comparable to the uncracked region. In this paper, only alternating water and dry cycles are considered. For each cycle, the specimens were first submersed into water at 20°C for 24 h and then naturally dried in ambient air at 20 ± 1°C and 45 ± 5% RH for 24 h.

In order to achieve distributed damage instead of localized cracking in a fiber-reinforced brittle matrix composite [Hypothesis (a)], the crack needs to propagate within the composite as a steady-state crack rather than a Griffith-type crack (Griffith, 1921; Marshall & Cox, 1988; Wu & Li, 1995). The crack propagation mode is governed by the fiber bridging "spring law," which describes the fiber bridging stress across a single crack versus the opening of the crack. For a certain cementitious composite material, once this "spring law" is established, either experimentally or analytically, it should yield a complementary energy higher than the cementitious matrix crack tip energy to ensure steady-state cracking. This fiber bridging "spring law" is governed by the debonding and pullout behaviour of fibers with statistical orientations and embedment lengths across the crack, as a combined outcome of cementitious matrix, fiber, and fiber/matrix interfacial properties. This "spring law" can thus be tailored based on micromechanics through material mixture design that results in desired micromechanical parameters.

In addition, Fan and Li (2015) discovered that if the healing process within cementitious materials solely relies on continued hydration and carbonation through the material itself, without any embedded capsules containing healing agents, the material crack width must be controlled to be very low (i.e., lower than 15 μm; Figure 1) in order to efficiently heal a crack volumetrically. The results were based on three-dimensional computed microtomography, which directly measured and quantified the healing extent (i.e., healed crack volumetric ratio; Figure 1) within a crack. This method provided more complete and accurate information on the three-dimensional healing process, in comparison with the observation of healing solely from crack surface through scanning electron microscopy.

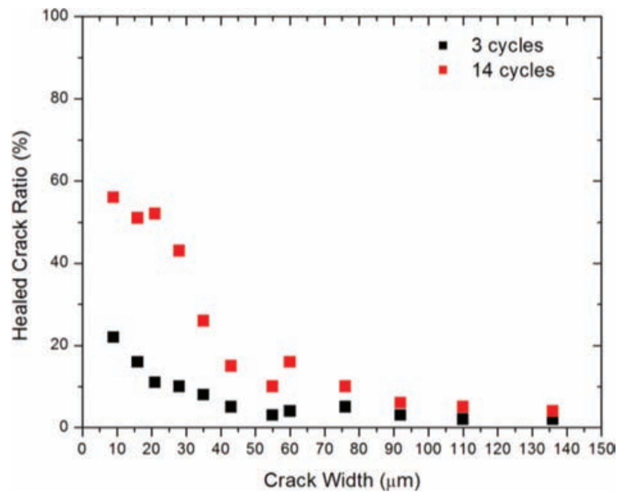

Figure 1. Effect of crack width on healed crack volumetric ratio based on three-dimensional microcomputed tomography. Environmental exposure condition: wet–dry cycles.

Designing steady-state crack propagation with an intrinsically controlled crack width below 15 μm required us to manipulate the fiber bridging "spring law." As shown in Figure 2, the fiber bridging stress versus crack opening (σ~δ) relation was measured through uniaxial tension test on a coupon specimen notched from both sides; the stress concentration at the notches forced a single crack to propagate through the cross section along with the notches. The test was performed under displacement control. The crack opening was measured by a high-resolution digital image correlation system. Two fiber-reinforced cementitious materials (Mix #1 and Mix #2) were formulated and tested. For both mixtures, the complementary energy calculated from the σ~δ curve (Figure 2) was higher than the crack tip energy of the cementitious matrix, thus favouring steady-state crack propagation. Compared with Mix #2, Mix #1 was strategically designed to feature a higher maximum fiber bridging stress and critical crack opening (i.e., the crack opening corresponding to the maximum fiber bridging stress). This led to a smaller width of the steady-state crack of Mix #1 than Mix #2, while maintaining the steady-state crack propagation and multiple cracking behaviors. Under uniaxial tension test, both Mix #1 and Mix #2 exhibited tensile strain-hardening behaviour accompanied by multiple microcracking behaviours (Figure 3). Such distributed damage pattern allows for random actuation of healing process at different cracking locations within the material; each damage event can generate new cracks at different locations than the original crack. This maximizes the capacity of the healing compounds distributed within the material to participate into the healing process, making it possible for repeatable self-healing. The crack pattern and width of the specimens from each material design were then evaluated. The statistical distribution of crack width along the specimen during strain-hardening stage is shown in Figure 4. It can be seen that through tailoring the fiber bridging stress and crack opening relation, Mix #2 achieved significantly smaller average crack width than Mix #1 (12 versus 67 μm), offering one of the most critical prerequisites for robust and fast self-healing.

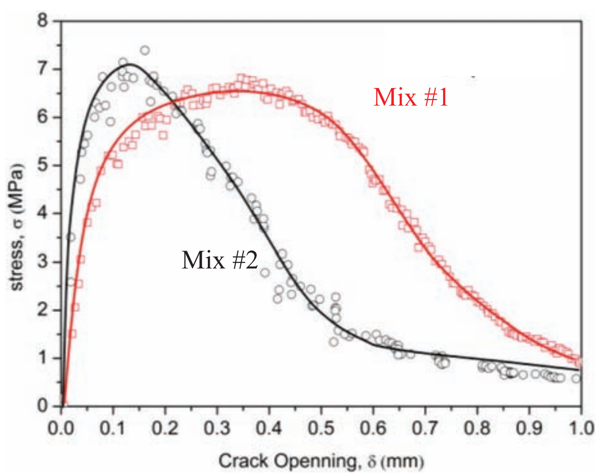

Figure 2. Fiber bridging "spring law" of two fiber-reinforced cementitious composites designed in this study with multiple steady-state cracking behaviors.

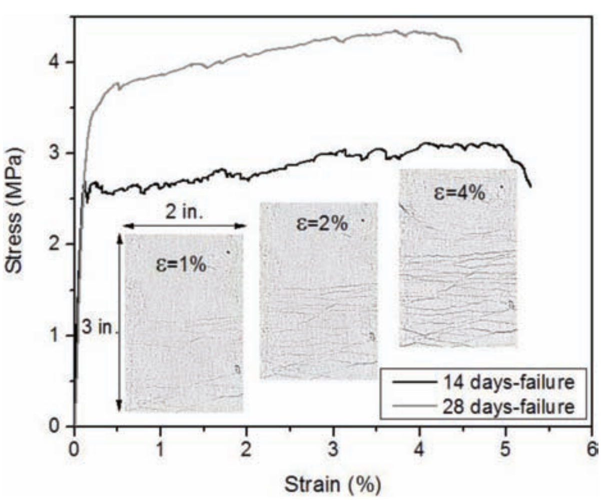

Figure 3. Tensile stress–strain relation and distributed damage behavior of Mix #2.

The chemical composition of Mix #2 was designed to promote the formation of C-S-H-dominant product. This was achieved through evenly dispersed unhydrated cement and pozzolanic ingredients (e.g., slag or fly ash) within the material. While the tight crack width below 15 mm offers a prerequisite for fast healing, the continued hydration of cement as well as the pozzolanic reaction (aka "secondary reaction") leads to further formation of C-S-H after cracking occurs. Pozzolanic reaction takes place between calcium hydroxide, one of the hydration products, and silicic acid to form calcium silicate hydrate. C-S-H is mainly responsible for the mechanical properties and durability of cementitious materials, as well as the healed region within the cracks.

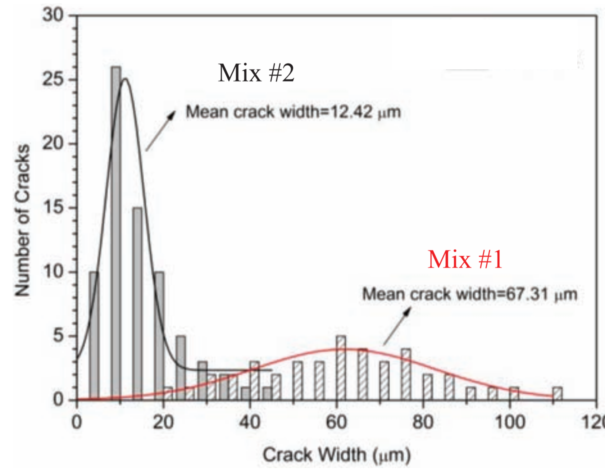

Figure 4. Crack width distribution within the two fiber-reinforced cementitious composites designed in this study with multiple steady-state cracking behaviors.

3. REPEATABILITY OF SELF-HEALING: EXPERIMENTAL STUDY AND RESULTS

To validate the repeatability and efficiency of self-healing within the designed material, an experimental program was carried out. Each specimen was predamaged at different strain levels under uniaxial tension, exposed to certain environmental conditions (e.g., wet–dry cycles) for self-healing to occur, and then reloaded under uniaxial tension to evaluate the recovery of mechanical properties. This process was repeated for a number of times. The specimen geometry and uniaxial tension test set up are shown in Figure 5.

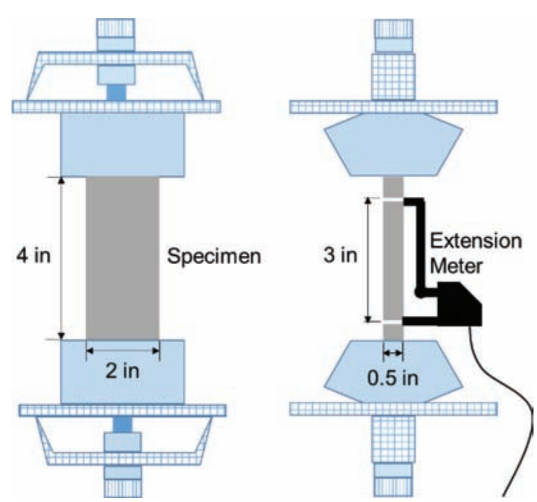

Figure 5. Uniaxial tension test.

The tensile stress–strain response was evaluated before and after each cycle of damage and subsequent self-healing. Figure 6 shows the results of a specimen loaded to 2% tensile strain for each damage event. A number of microcracks formed within the specimen during the strain-hardening stage, with an average crack width around 12 μm. After seven healing cycles, the specimen was reloaded to the same level of strain (i.e., 2%). This process was repeated up to four times. Comparing with the directly reloaded specimen without healing, the healed specimens repeatedly exhibited significant recovery of initial stiffness, first cracking strength, tensile strain capacity, and ultimate tensile strength. Even after four times of damage (2% applied tensile strain) and rehealing, the specimen regained most of its mechanical capacity. It should be noted that 2% applied tensile strain is considered as a high damage level that rarely can be reached under service loading for concrete infrastructure; the tensile strain capacity of concrete is only 0.01%.

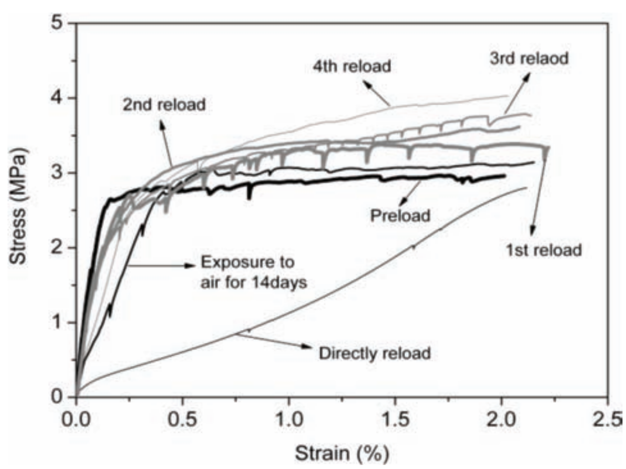

Figure 6. Uniaxial tensile stress–strain relation of Mix #2 before and after damage and self-healing, up to fourth reload.

The self-healing repeatability was also evaluated by resonant frequency test according to ASTM C215 (2014), which measures how elastic wave propagates through cementitious materials. The measured resonance frequency of a damaged specimen compared to its original state indirectly reflected the internal damage level of the specimen. Longitudinal resonance frequency was measured before and after each time of uniaxial tensile loading to quantify the damage and then after each wet–dry cycle to monitor the rate of self-healing. In order to compensate the further bulk hydration that caused changes in RF values but was not directly related to the healing process, control specimens without cracks were placed in identical conditions, for which the resonance frequency measurements were taken at the same time. The standardized resonance frequency ratio was thus defined as follows:

$$\text{Standardized RF ratio} = RF_{cracking} / RF_{control} \times 100\%$$

In this way, the influence of other possible parameters besides self-healing can be removed. A standardized RF ratio of 100% represents a full recovery of RF from damage due to self-healing.

It was found that the standardized resonant frequency ratio dramatically dropped by approximately 40% after the specimen was preloaded to 2% tensile strain due to a number of cracks that formed (Figure 7). The standardized resonant frequency ratio then was gradually recovered after each wet–dry cycle, indicating that self-healing took place. The recovery was fastest during the first three cycles. After seven cycles, the ratio increased back to 96% as a result of self-healing. Reloading the specimen further decreased the standardized resonant frequency ratio due to the redamage of the specimen. Again, when material self-healing occurred, bring the standardized resonant frequency ratio back to 93% after seven wet–dry cycles. Even after the fourth damage event caused by reloading, self-healing took place, increasing the standardized resonance frequency ratio from 51 to 90%.

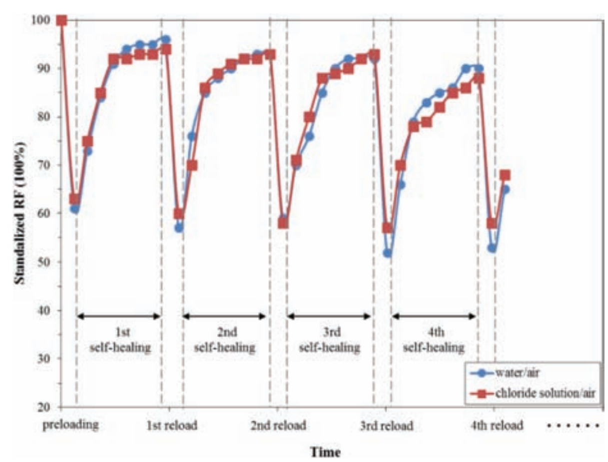

Figure 7. Standardized resonance frequency ratio before and after preloading, self-healing, and reloading.

Three-dimensional microcomputed tomography was conducted on a sample cut from the original specimen to quantify the self-healing extent at a single crack level. Each raw image contained a 2D array of contiguous squares (i.e., pixels), consisting of 256 possible levels (0–255) of gray intensity. The gray level of each pixel in the images represented a density value that corresponded to the linear attenuation coefficient of the element contained in that pixel. Image segmentation was then carried out to separate the digital image into solid phase and gas phase by applying a global threshold. For the gas phase, to further separate the crack from the air pore network, a mathematically morphological method was employed.

The details of microcomputed tomography method for studying self-healing in cementitious materials can be found in Fan and Li (2015). The three-dimensional crack that was separated from other phases in the sample is represented in color before (in green) and after repeated times of self-healing (in blue) in Figure 8.

As shown in Figure 8, the crack volume decreased after each self-healing event, which means seven wet–dry cycles of environmental exposure. Based on the image analysis results, geometrical characteristics of the crack can be quantified, including crack volume, crack surface, crack width versus depth, crack perimeter, etc. The evolution of the crack due to each damage and subsequent healing event can thus be presented. It was calculated that 73% of crack volume was healed after the first healing (Figure 8B). The crack was then reloaded to represent the second damage event. After the second healing, 68% of crack volume was healed (Figure 8C). The crack was again reloaded to represent the third damage event. After the third subsequent healing, 70% of crack volume was healed (Figure 8D).

4. CONCLUSION

It was concluded from this study that repeatable self-healing can be achieved in fiber-reinforced cementitious composite materials by satisfying a set of physical, chemical, and environmental conditions in material design. The self-healing process can recover both mechanical capacity and transport properties. The cementitious composite material designed in this study can intrinsically control its own crack width to approximately 12 μm on an average, exhibit a distributed damage process through multiple

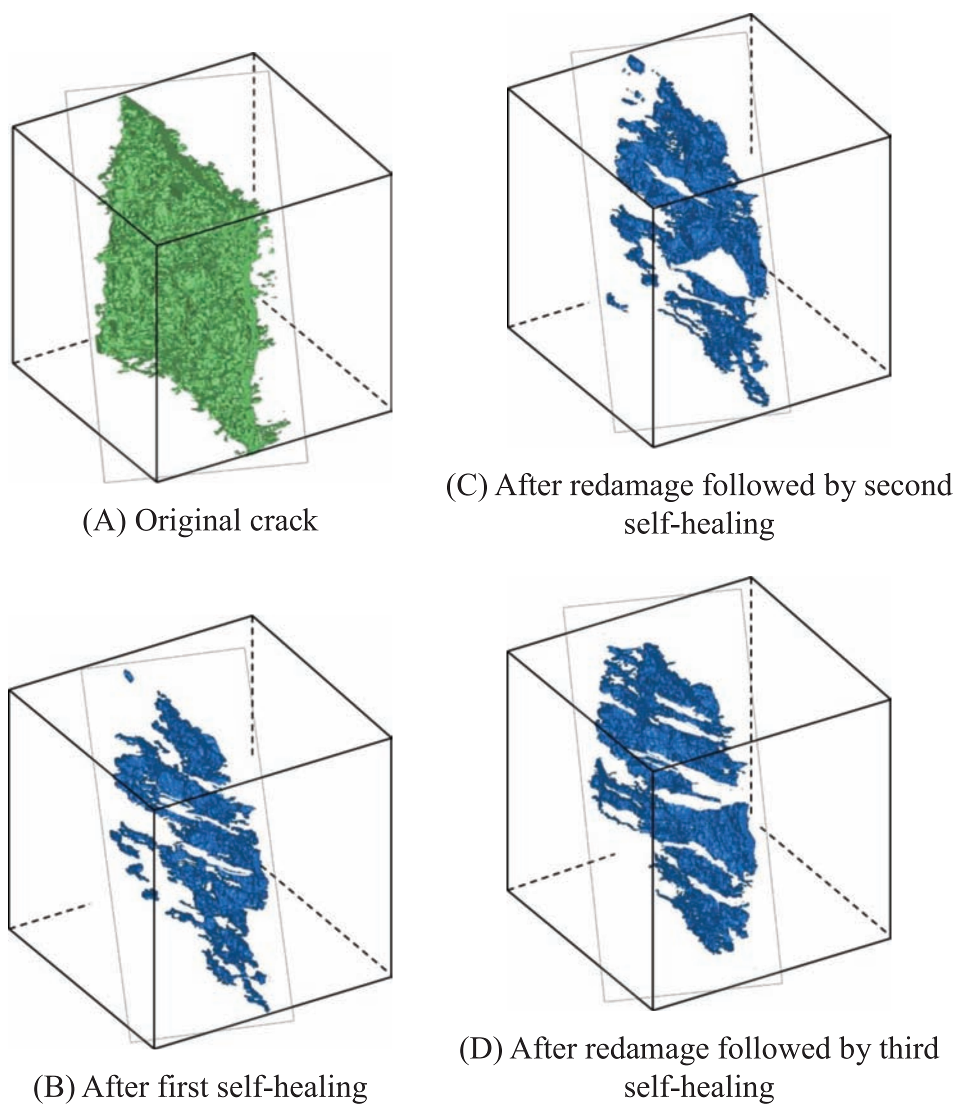

Figure 8. Three-dimensional microcomputed tomography of a crack before and after each self-healing event. Each self-healing event followed a predamage or redamage event.

microcracking behaviours, and contain abundant pozzolanic ingredients and unhydrated cement to promote the formation of C-S-H-dominant chemical products as self-healing progresses. Compared with self-healing method based on the formation of calcium carbonate, the C-S-H as healing product provides higher strength and durability, leading to the recovery of mechanical properties. The repeatability of self-healing was demonstrated at bulk material scale through mechanical testing and resonance frequency measurement and also at single crack scale through three-dimensional microcomputed tomography. The designed cementitious material with repeatable self-healing capacity has great potential for improving the durability of concrete infrastructure by minimizing maintenance and repairs during its service life.

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