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Characterization and quantification of self-healing behaviors of microcracks due to further hydration in cement paste

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ABSTRACT

It has been reported by previous studies that cracks in cementitious materials can be healed by further hydration of unhydrated cement particles. However, by now, neither the physicochemical process nor the potential of self-healing due to further hydration is completely understood. In this paper, in order to gain insight into self-healing by further hydration, healing behaviors due to further hydration were characterized and quantified. The mineralogy of healing products was qualitatively determined and the percentage of each mineral was specified. The formation of healing products as a function of time was quantified as well. Moreover, self-healing of microcracks was simulated by a reactive transport model. The calculated filling fraction by the healing products in microcracks was consistent with the experimental results. The healing process slowed down markedly after 300 h. In addition, in younger cement pastes, larger amounts of unhydrated cement lead to greater filling fraction of microcracks.

1. Introduction

Cracks, caused by external loading and time dependent effects, are unavoidable in reinforced concrete structures. These cracks facilitate the ingresses of aggressive and harmful substances into concrete and thus reduce the durability of reinforced concrete structures.

Fortunately, previous experimental investigations and practical experience have demonstrated that the smaller cracks in cementitious materials are able to heal under certain circumstances [1,2]. When water and dissolved CO_2 access into cracks, the cracks can be healed by the precipitation of calcium carbonate [3]. Self-healing of cracks can be also contributed by further hydration of unhydrated cement particles when water presents in cracks. For example, Jacobsen and Sellevold investigated self-healing in high strength concrete after deteriorated by freeze/thaw and found some newly formed hydration products in cracks [4]. Schlangen and Heide also detected newly formed C–S–H in cracks after the cracked samples were cured in water [5]. The conditions for the further hydration in cracks are different from these inside the bulk cement paste. For example, there is more water in cracks than that in the bulk cement paste. Moreover, the space for the formation of hydration products in cracks is larger than that in the bulk pastes, which may influence the nucleation and growth processes of the hydration products.

By now, detailed information regarding self-healing due to further hydration in cracks is limited. The minerals formed and their corresponding percentages in healing products are still not clear. In addition, the amount of healing products newly formed in cracks as a function of time is obscure. In order to better understand self-healing by further hydration, self-healing behaviors were characterized and quantified in this paper.

To characterize the healing products in cracks, there are several techniques, such as environmental scanning electron microscope (ESEM) equipped with an energy dispersive spectroscopy (EDS), Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) [6–9]. For using FTIR or XRD to characterize self-healing products, it is difficult to separate the healing products from the matrix. Li et al. obtained some powder which includes healing products and surrounding cement paste both by drilling into the cracks and scratching the crack surfaces. The healing products were determined by comparing the FTIR and XRD results of the obtained powder with those of the cement paste [7]. In this research, healing products were separated from the matrix. With these obtained healing products, not only the mineralogy of healing products is known, but also the percentage of each constituent was quantified by combining the techniques of EDS, FTIR and TGA.

In order to study the self-healing efficiency, water permeability, acoustic emission and resonant frequency tests are usually used. For instance, Reinhardt and Joss investigated the influence of temperature and crack width on self-healing by water permeability test [10]. Granger et al. characterized self-healing in ultra high performance

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cementitious materials by means of mechanical tests and acoustic emission analysis [11]. Resonant frequency test was also performed to investigate the self-healing [4,12]. All these methods can be used to quantify self-healing indirectly. However, the amount of healing products formed in cracks cannot be quantified by these methods. In this research, the amount of healing products formed by further hydration in microcracks was quantified by back-scattered electron (BSE) image analysis. In addition, based on reactive transport model, the self-healing processes in microcracks due to further hydration were simulated and the simulation results were validated by the experimental results.

2. Materials and experiments

2.1. Materials and specimens

The materials used in this study were Portland cement paste which was prepared with CEM 42.5N. The chemical and mineral composites of Portland cement are shown in Tables 1 and 2. The mineral composition was calculated based on Bogue equation [13]. The water to cement ratio (w/c) of the cement paste was 0.3.

As shown in Fig. 1, there are two series of specimens used in this research. Series specimens were prepared for the characterization of self-healing products while Series II for the quantification of self-healing by BSE image analysis. The detailed information of these specimens is described below.

In this research, FTIR and TGA were employed to characterize the healing products. However, the difficulty for using FTIR or TGA to characterize self-healing products is the separation of the healing products from the matrix. In this study, in order to separate the healing products from the matrix, artificial planar gaps in Series I specimens were made, instead of real cracks, as shown in Fig. 1. To prepare these gaps, pre-casted cement paste was first sliced. The slices of cement paste were carefully ground with P320, P500 and P1200 sand papers to guarantee the surface of the slices flat enough. After that the slices were pressed together. Because of the flat surfaces of the slices, the gap width between the slices was less than 30 μm measured by a microscopy. The pressed slices at the age of 7 days and 28 days were cured in water for 200 h (The detailed environmental conditions for self-healing will be introduced in Section 2.2.). Similar to the case in real cracks, healing products can be formed by further hydration in the planar gaps between slices after being cured in water. Because the bonding between the healing products and the slice surfaces was weak and the slice surfaces were flat, the healing products can be easily scratched off from the slice surfaces with a plastic sheet. With this method, the healing products obtained only contained very little materials from matrix. It should be mentioned that the planar gaps have no influence on the chemical natures of the healing products formed by further hydration, compared with the real cracks. FTIR and TGA measurements were performed on these obtained healing products.

To quantify the healing products as a function of time, Series II specimens were prepared for ESEM observation. As shown in Fig. 1, prisms with the size of 40 mm × 40 mm × 160 mm were casted and pre-cracked by three-point bending. The crack width was controlled to be about 10 μm by linear variable differential transducers (LVDT). The pre-cracked specimens were cured in water for self-healing (The detailed environmental conditions for self-healing will be introduced in Section 2.2.). In order to investigate the influence of the amount of unhydrated cement on self-healing, the pre-cracked specimens started to heal at the ages of 7 days, 14 days and 28 days. After healing for a certain time, the specimen was impregnated with epoxy and cut along the dashed lines shown in Fig. 1 and thereby 3 cross sections of each crack were exposed. The samples with the cross sections of cracks were prepared for ESEM observation.

Table 1
Chemical composites of Portland cement (CEM 42.5 N).

Compound	CaO	SiO_2	Al_2O_3	Fe_2O_3	K_2O	Na_2O	SO_3	MgO	Total
Weight (%)	64.40	20.36	4.96	3.17	0.64	0.14	2.57	2.09	98.33

Table 2
Mineral composition of Portland cement (CEM 42.5N) based on Bogue equation [13].

Compound	C_3S	C_2S	C_3A	C_4AF	Total
Weight (%)	64	13	8	9	94

2.2. Conditions for self-healing by further hydration

To promote further hydration of unhydrated cement for self-healing, the specimens with gaps or cracks were cured in water. In this study, the volume ratio of the additional water to cement paste is 0.12. As shown in Fig. 1, with such limited amount of water, only the bottoms of the specimens were submerged. Due to capillary force, the water was absorbed into cracks/gaps. For avoiding carbonation, the container was sealed in order to prevent the dissolution of CO_2 into the curing water. The environment temperature was fixed at 20 ± 1 °C.

2.3. Characterization of self-healing products

After self-healing for 200 h, the cement paste slices of Series I specimens were separated and dried by vacuum for 2 h. ESEM equipped with EDS was used to observe the morphology of healing products on slice surfaces and to investigate their chemical natures.

The healing products were ground into powder after being scratched off from the slice surfaces. FTIR and TGA were employed to determine the mineralogy of the healing products and the corresponding percentage of each constituent in the healing products. FTIR measurements were conducted in transmission model in which the scan resolution is 4 cm^{-1} and there are 20 scans averaged for each measurement. TGA tests were performed in argon atmosphere at 1.5 bars. The heating rate was 10 °C/min and the final temperature is 1100 °C.

2.4. Quantification of self-healing due to further hydration

The amount of healing products formed by further hydration as a function of time was quantified by BSE image analysis. As introduced in Section 2.1, after self-healing the cracks were impregnated with epoxy and 3 cross sections of a crack were exposed by cutting. After being ground and polished, the 3 cross sections of the crack were observed by ESEM to quantify the amount of healing products in cracks. The magnification of the BSE images was 400 times and for each cross section of a crack, 35 images were obtained. Thereby, 105 images in total for one crack were used for the analysis. The width of the crack in each image was measured as well.

3. Experimental results and discussion

3.1. Morphology of healing products formed in planar gaps

The surfaces of planar gaps after self-healing were observed by ESEM. Fig. 2 shows the morphology of healing products in planar gaps after self-healing for 7 days. From the image, it is easy to distinguish the healing products, because the surfaces of the slices before self-healing are very flat. As shown in Fig. 2, there are two kinds of products with different morphologies on the slice surfaces. One of them is gel-like and the other is crystal-like. The size of the crystal-like product is larger than that of the gel-like product.