Modeling of self-healing efficiency for cracks due to unhydrated cement nuclei in hardened cement paste

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Abstract

Nuclei of unhydrated cement particles left in hardened cement paste after maturation can provide self-healing capability to micro-cracked matrix under favorable conditions. In this present study, a model study is conducted to characterize the influence of hydration reaction of the unhydrated cement nuclei on self-healing efficiency of cracks in hardened cement paste. Based on two different cracking modes of unhydrated cement nuclei, i.e., the splitting crack mode and the dome-like crack mode, the mathematical expressions on the self-healing efficiency are presented from the viewpoint of geometrical probability. Recurring to a generalized hydration reaction model of cement particles, the self-healing efficiency model quantitatively consider the influence of the volume fraction, particle size distribution and cracking modes of unhydrated cement nuclei randomly distributed in hardened cement pastes.

1. Introduction

The phenomenon of self-healing in cementitious materials has been known for many years. It has been observed that some cracks in old concrete structures are lined with white crystalline material suggesting the ability of concrete to self-seal the cracks with chemical products by itself, perhaps with the aid of rainwater and carbon dioxide in air. One such example is on an 18th century bridge in Amsterdam, where microcracks were self-healed by the recrystallization of calcite\textsuperscript{[1]}. This suggests that under certain circumstances (e.g. when rainwater and carbon dioxide is available) concrete was able to heal its own damage (e.g. microcracks) with chemical products by itself. In most concrete and particularly in those

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with a low water/cement ratio, the amount of unhydrated cement is expected to be as much as 25% or higher. These unhydrated cement particles are known to be existing for a long time in matrix. Thus, under favorable conditions, the phenomenon of self-healing in concrete is well established[2, 3].

Self-healing of cracks has been investigated extensively by Hearn[4-6] and Edvardsen[7]. Otsuki[8] suggested that self-healing of microcracks could have been the reason for densification of the concrete cover, thus reducing the rate of migration of chloride ions into the concrete. Many experimental results have demonstrated that cracks in concrete have the ability to heal themselves and water flow through cracks was reduced with time. In the study of water flow through cracked concrete under a hydraulic gradient, Edvardsen[7] noted a gradual reduction of permeability over time, again suggesting the ability of the cracked concrete to self-seal itself and slow the rate of water flow. The observations under ESEM and XEDS confirmed[9] that the microcracks in the specimens submerged in water were healed with significant amount of calcium carbonate, very like due to the continuous hydration of cementitious materials. Reinhardt[10] established the dependency of permeability and self-healing behavior of cracked concrete on temperature. Zhong[11] has investigated the effect of the degree of damage on the self-healing ability of normal-strength and high-strength concrete. For a cause of reduced chloride ingress, self-healing of microcracks has also been suggested by Fidjestol[12] and Bakker[13].

Besides permeability enhancement, many researchers also looked into the mechanical property recovery as a result of self-healing in concrete materials. In recent years, there is increasing interest in the phenomenon of mechanical property recovery in self-healed concrete materials. For example, the recovery of flexural strength was observed in pre-cracked early age concrete beams while clamped and submerged in water[14]. Recent work by Heide[15], as overviewed by Ghosh[16], has therefore focused on examining both the mechanical strength gain and reduction in permeability of early-age concrete which has been cracked and allowed to heal autogenously. Furthermore, it was observed that recovery of many mechanical related properties was possible after water immersion, e.g. the resonance frequency of damaged by freeze-thaw actions[17], the stiffness of pre-cracked specimens[18] and the compressive strength of pre-damaged cylindrical specimens[19]. The self-healing observed from these investigations was associated with continued hydration of the unhydrated cement nuclei in matrix. On the other hand, Granger[20] carried out an experimental program of mechanical test on ultra high performance concrete and concluded that the self-healing of the pre-existing crack was mainly due to hydration of anhydrous clinker on the crack surface. Joseph[21] concluded that the compressive stress applied to the crack faces was found to be very beneficial to close the initial crack, which was typically 50 mm wide. As indicated above, the phenomenon of self-healing has been demonstrated to be effective on transport and mechanical properties recovery in concrete materials.

Li and co-workers[2, 22, 23] have investigated the self-healing behavior of engineered cementitious composite (ECC) under a number of exposure conditions based on the well controlled crack width. Besides the small crack width, the low water/binder ratio added the large amount of fly ash in their mixture also helps promote self-healing via continued hydration and pozzolanic activities. Others references on mineral admixtures for self-healing can be found in Refs.[9, 24]. For self-healing capability of ECC, Li[25] also concluded that self-healing of the induced micro cracks in ECC was observed not only by formation of a distinct deposition inside the cracks but also by almost complete recovery of the pre-cracking stiffness. Homma[26-28] reported the summary of a series of experimental study on the self-healing capability of fibre reinforced cementitious composites (FRCC). They concluded that volume fraction of polyethylene fibre was indicated to have a great influence on self-healing and to decrease the water permeability coefficient, that tensile strength was improved significantly.

Using an advanced history dependent contact model, Herbst[29] proposed a model for local self-healing that allows damage to heal during loading such that the material strength of the sample increases and failure/softening is delayed to larger strains. By a concurrent algorithm-based computer simulation system
with the acronym SPACE, He\cite{30} investigated the influences of w/c ratio and cement fineness on the microstructure of unhydrated cement nuclei that is underlying concrete’s self-healing capacity in hardened cement paste. It is an interesting way to investigate the self-healing phenomenon in concrete materials by modeling approach as well as computer simulation technology. Of course, the hydration model of cement particles and particles expansion are important factors in self-healing process. Further information on the hydration model of cement particles and microstructures formation can be found in Refs.\cite{31-33}.

Clearly, the self-healing process in cementitious materials is relatively slowly. Hence, if it is expected that the phenomenon of self-healing can play an important role in healing the cracks of matrix, then it is necessary to consider the self-healing efficiency or amount of the hydration product due to unhydrated cement nuclei. Up to now, most researchers conducted experiment studies on the self-healing mechanisms and mechanical properties of self-healing materials, while the work of quantitatively characterizing the self-healing efficiency in cementitious materials is seldom. It believes that the volume fraction, particles size distribution, spacing and cracking mode of unhydrated cement nuclei are all expected to be important factors for self-healing efficiency of cementitious materials under given hydration conditions. In this contribution, a model study is conducted to characterize the self-healing efficiency of hydration reaction of the unhydrated cement nuclei on crack in hardened cement pastes. Based on two different cracking modes of unhydrated cement nuclei, i.e., splitting crack mode and dome-like crack mode, theoretical models on the self-healing efficiency are presented during the self-healing process. Recurring to a generalized hydration reaction model of cement particles, the self-healing efficiency model will quantitatively consider the influence of the volume fraction, particle size distribution and cracking modes of unhydrated cement nuclei randomly distributed in hardened cement paste.

2. Two cracking modes and particles size distribution

Concrete is a complex particulate material at different scales of the material structure and unhydrated cement nuclei govern the self-healing capacity of the micro-cracked matured material. Meanwhile, at very low volume fractions, the particle dispersion will predominantly reflect the state of chaos, or three-dimensional “randomness”\cite{34}. Here, it believes that the volume of unhydrated cement nuclei is relatively low compared to the volume of matrix of cementitious materials after a stage of hydration period. Hence it is well-defined that unhydrated cement nuclei are randomly dispersed in the hardened cement paste as shown in Fig. 1.

![Fig. 1. Three different hydration stages of the model cement paste with water/cement=0.3 based on HYMOSTRUC3D model \cite{31},
(a) α= 0\%  (b) α= 25\% (c) α= 65\%](image)

A tendency of cracks to follow the external surface of the unhydrated cement nuclei was found experimentally due to the unhydrated cement nuclei as strong inclusions in the hardened cement paste.
For convenience, this type crack pattern is named as “dome-like crack mode” in our model as illustrated in Fig. 2(b). Meanwhile, since a lot of unhydrated cement nuclei have left in ultra high performance concrete, it is probable that unhydrated cement nuclei will crash or split once cracking occurs in the matrix [37]. For convenience, this type crack pattern is named as “splitting crack mode” in our model as demonstrated in Fig. 2(a). Generally speaking, for unhydrated cement particles on a specific crack path, both splitting crack mode and dome-like crack mode happens.

![Fig. 2. Two practical crack patterns for unhydrated cement nuclei in hardened cement paste due to different mechanisms, (a) Splitting crack mode, (b) Dome-like crack mode](image)

Prior to investigating the self-healing efficiency of unhydrated cement nuclei in hardened cement paste, some assumptions and conventions are set as following.

1. Unhydrated cement particles are randomly and separately dispersed in the representative volume element of cement paste and initiates hydration from the moment that it contacts with water.
2. With hydration process going on, the anhydrous cement keeps spherical shape as well. Moreover, the new hydration products are formed at the surface with no restriction of interparticle contacts.
3. The particles with the same surface exposed to water have the same rate of hydration. And the particle size distribution of cement can be approximated by Rosin-Rammler function. The Rosin-Rammler function is commonly employed to characterize Portland cement mixtures. The cumulative size distribution function is provided as a continuous mathematical function given by [31, 38],

\[
F_r(D) = 1 - \exp(-bD^n)
\]

with constants \(b>0\) and \(n\) so that \(F(D \rightarrow \infty) = 1\) and \(D\) represents the diameter of cement particles.

As the unhydrated cement nuclei keeps spherical shape, the Rosin-Rammler function is also employed to express the particles size distribution of the remaining unhydrated cement nuclei in hardened cement paste. In the meantime, \(b, D, n\) will be altered.

3. Self-healing efficiency based on splitting crack mode

The model is based on a cubic representative volume element (RVE) \(V_T\) that contains a certain number of unhydrated cement nuclei distributed at random, such that nuclei do not overlap. We assume that the particles size distribution follows the Rosin-Rammler function in the RVE. Since the variable parameter in Rosin-Rammler function in Eq. (1) is diameter of particle, we now employ the radius \(R\)
(D=2R) to express the particles size distribution. After a transformation, the volume-based probability distribution function of the unhydrated cement nuclei is

$$f_v(R) = 2^n b n R^{n-1} \exp(-2^n b R^n) , \quad R_{min} \leq R \leq R_{max}$$

To calculate the self-healing efficiency of unhydrated cement nuclei at a particular crack plane at a test plane Q at a random position but parallel to one of the faces of the RVE axes was defined as shown in Fig. 3(a). Obviously, the probability for a single particle with radius $R$ to be intersected is

$$P(R) = \frac{2RA}{V_{RVE}}$$

where $A$ is the cross-sectional area of the RVE with volume $V_{RVE}$.

We denote $V_T$ by the volume fraction of unhydrated cement nuclei in the hardened cement paste and consider it as a constant. Clearly, $V_T$ is determined by several of impact factors, such as the water cement ratio, curing temperature and so on. The total number of particles whose radius lies in the range $[R, R+dR]$ in the RVE is

$$N_{RVE}(R)dR = \frac{3V_{RVE}V_T f_v(R)dR}{4\pi R^3}$$

Then, the mean value of the number of particles that are intersected by a random plane Q that cuts $V_T$ is $P(R)N_{RVE}(R)dR$. At the same time, let $\phi(\sigma , R)$ be the probability density function of the intersecting area $\sigma$ of $Q \cap V_T$, then $\phi(\sigma , R)d\sigma$ is the interval probability of a plane chosen at random having an intersection of area in the range $[\sigma , \sigma +d\sigma]$. Multiplying $P(R)N_{RVE}(R)dR$ by the probability distribution $\phi(\sigma , R)$, the number of particle intersected by plane sections $Q \cap V_T$ with radius in the range $[R, R+dR]$ and $\sigma$ in the range $[\sigma , \sigma +d\sigma]$ is obtained

$$h_N(\sigma , R)dRd\sigma = P(R)N_{RVE}(R)\phi(\sigma , R)dRd\sigma$$

By integration over $R$, from $R=(\sigma/\pi)^{1/2}$ to $R=R_{max}$, we get the total number of unhydrated cement nuclei...
intersected by intersections $Q \cap V_T$ whose area lies between $\sigma$ and $\sigma + d\sigma$, namely
\[
\int_{(\sigma/\pi)^{1/2}}^{R_{\max}} h_N(\sigma, R)dRd\sigma = \int_{(\sigma/\pi)^{1/2}}^{R_{\max}} P(R)N_{RVE}(R)\phi(\sigma, R)dRd\sigma
\]
(6)

It is worthwhile noting that the lower limit of the integral in Eq. (5) is $(\sigma/\pi)^{1/2}$. Since the maximal intersecting area of particles with radius $R$ is $\pi R^2$, it should satisfy $\sigma \leq \pi R^2$ such that the particle could be intersected. If a particle of radius $R$ does intersect the plane, the probability that its centre lies at a distance $x$ from the plane is $dx/R$ and the area of the intersecting circle is $\sigma = \pi (R^2 - x^2)$ as shown in Fig. 3(b). Hence, the probability density function of the intersecting area $\sigma$ is
\[
\phi(\sigma, R) = \frac{1}{2R\sqrt{\pi^2 R^2 - \pi\sigma}}
\]
(7)

We assume that the expansion thickness $\delta = \delta(\sigma, t)$ of each of the splitting unhydrated cement nuclei which continues hydrating at time $t$ is constant and the thickness of hydration product which may be a function of degree of hydration is determined by the nature of unhydrated cement nuclei such as the component of nuclei, surface density, and the external environment such as curing temperature, water content. Therefore, it obtain the volume of the hydration product in per unit area of crack surface, i.e., the self-healing efficiency,
\[
V_A(\delta) = \frac{1}{A} \int_{\sigma_{\min}}^{\sigma_{\max}} \int_{(\sigma/\pi)^{1/2}}^{R_{\max}} (\delta(\sigma; t) \cdot \sigma)P(R)N_{RVE}(R)\phi(\sigma, R)dRd\sigma
\]
(8)

where $\sigma_{\min}$, $\sigma_{\max}$ represent the minimal and the maximal area of the intersecting circle of unhydrated cement nuclei, respectively.

Specifically, substituting Eq. (2), Eq. (3), Eq. (4) and Eq. (7) into Eq. (8) gives
\[
V_A(\delta) = \frac{3V_T 2^{n-2} n}{\pi^{3/2}} \int_{\sigma_{\min}}^{\sigma_{\max}} \int_{(\sigma/\pi)^{1/2}}^{R_{\max}} \delta(\sigma; t)\sigma R^{n-4} \exp(-2^nbR^n) \frac{dRd\sigma}{\sqrt{\pi R^2 - \sigma}}
\]
(9)

In a matter of fact, the self-healing efficiency is double of $V_A(\delta)$ because both of splitting faces will continue hydrating in the splitting crack mode during the self-healing process. In this splitting crack mode, Eq. (9) shows that the self-healing efficiency of cracks is quantitatively depended on the volume fraction, particles size distribution and the expansion thickness of unhydrated cement nuclei and the volume fraction is a key factor for self-healing capacity of hardened cement pastes.

4. Self-healing efficiency based on dome-like crack mode

This section will deal with the dome-like crack mode for self-healing efficiency as illustrated in Fig. 2(b).

The model is also based on a cubic representative volume element (RVE) $V_T$ that contains a certain number of unhydrated cement nuclei distributed at random, such that nuclei do not overlap as shown in Fig. 3(a). The particle size distribution follows the Rosin-Rammler function, and then $f(R)dR$ will be the cumulative volume probability of unhydrated cement nuclei whose radius lies in the range $[R, R+dR]$. To calculate the self-healing efficiency of unhydrated cement nuclei at this special crack face a “test plane W” at a random position but parallel to one of the faces of the RVE axes was defined as shown in Fig.
Furthermore, for this “test plane”, i.e., the crack, when the crack meets an unhydrated cement particle the crack will contour the minor portion of the unhydrated cement particle and form a dome, while the major will be embedded in matrix.

As the above section described, the probability for a single particle with radius \( R \) to be intersected by the test plane is showed in Eq. (3) and the total number of unhydrated cement nuclei whose radius lies in the range \([R, R+dR]\) in the RVE is expressed in Eq. (4). Consequently, the total number of particles that are intersected by the test plane \( W \) that cuts \( V_T \) is \( P(R)N_{RVE}(R)dR \).

On the one hand, let \( \phi(s, R) \) be the probability density function of the intersecting dome-like surface area \( s \) of \( W \cap V_T \), so that \( \phi(s, R)ds \) is the interval probability of the “test plane” chosen at random having a curved surface intersection of area \( s \) in the range \([s, s+ds]\) for an unhydrated cement particle with radius \( R \), where \( W \cap V_T \) represents the crack surface. Multiplying \( P(R)N_{RVE}(R)dR \) by the probability function \( \phi(s, R)ds \) yields the number of unhydrated cement nuclei in crack surfaces \( W \cap V_T \) with radius in the range \([R, R+dR]\) and \( s \) in the range \([s, s+ds]\). Namely,

\[
g_N(s, R)dRds = P(R)N_{RVE}(R)\phi(s, R)dRds
\]

On the other hand, as illustrated in Fig. 4(b) we assume that the expansion thickness \( \delta=\delta(s; t) \) of each of the dome-like unhydrated cement nuclei which continues hydrating at time \( t \) is constant and the thickness which may be a function of degree of hydration is determined by the nature of unhydrated cement nuclei such as the component of nuclei, surface density, and the external environment such as curing temperature, water content. In fact, the thickness can be developed from the individual cement particles on reaction kinetics \([31, 39]\), but will not be discussed in this paper. Then, since an unhydrated cement particle with radius \( R \) whose contact area with water is \( s \), the volume of hydrated product for one particle is

\[
V(\delta; s; R) = \pi \delta \left\{ \frac{s}{\pi} + R\delta + \frac{s\delta}{2\pi R} + \frac{2\delta^2}{3} \right\}
\]
Therefore, by integration Eq. (10) over \( R \) and \( s \), it obtains the volume of the hydration product in per unit area of crack surface, i.e., the self-healing efficiency,

\[
V_A(\delta) = \frac{1}{A} \int_{s_{\text{min}}}^{s_{\text{max}}} \int_{\frac{s}{2\pi}}^{R_{\text{max}}} V(\delta(s; t); s; R) P(R) N_{\text{RVE}}(R) \phi(s, R) dR ds \tag{12}
\]

where \( s_{\text{min}}, s_{\text{max}} \) represent the minimal and the maximal area of the dome-like surface of unhydrated cement nuclei, respectively. Generally speaking, \( s_{\text{max}} \) is lower than the half of the surface area for the largest unhydrated cement particle. It is worthwhile noting that the lower limit of the integral for variable \( R \) in Eq. (12) is \((s/2\pi)^{1/2}\). Since the maximal dome-like surface area of a particle with radius \( R \) is \( 2\pi R^2 \), it should satisfy \( s \leq 2\pi R^2 \) such that the particle is contributing to play a role in hydration for a given \( s \).

Because the minor portion of the particle is exposed to the water and can be continuous hydrating, the maximal dome-like surface area is \( 2\pi R^2 \). If the unhydrated cement particle of radius \( r \) is intersected by the test plane \( W \), the probability density function that its centre \( O \) lies at a distance \( x \) from the plan is \( 1/R \).

Hence, the probability density function of the dome-like surface area \( s \) is

\[
\phi(s, R) = \frac{1}{2\pi R^2} \tag{13}
\]

Substituting Eq. (2), Eq. (3), Eq. (4), Eq. (11) and Eq. (13) into Eq. (12), we have

\[
V_A(\delta) = \frac{3V}{\pi} \frac{2^{n-2} b n}{\pi} \int_{s_{\text{min}}}^{s_{\text{max}}} \int_{\frac{s}{2\pi}}^{R_{\text{max}}} \delta \left( \frac{s}{\pi} + R\delta + \frac{sR}{2\pi R} + \frac{2\delta^2}{3} \right) R^{a-5} \exp(-2^n b R^n) dR ds \tag{14}
\]

For hardened cement paste with crack following dome-like crack mode as shown above and particles size distribution following the Rosin-Rammler function, the total volume of the hydration product at time \( t \) in per unit area can be expressed by Eq. (14). It demonstrates that the self-healing efficiency of crack via rehydration of unhydrated cement nuclei is quantitatively depended on the volume fraction, particles size distribution of remaining unhydrated cement nuclei and the expansion thickness of hydration products. Meanwhile, the volume fraction is a key factor for self-healing capacity of cracks in hardened cement pastes.

The reliability of the proposed models for self-healing efficiency could be evaluated by computer simulation technology, but will not be discussed here because of space limitations.

5. Conclusions

The natural self-healing of cementitious materials offers a more immediately promising solution to crack repair and improves the long-term durability and service life. In this present study, according to the practical cracking styles of unhydrated cement nuclei in the engineering projects, two cracking modes, i.e., splitting crack mode and dome-like crack mode, are presented to deal with the self-healing efficiency of cracks in hardened cement paste. It showed that based on the different cracking mode of unhydrated cement nuclei randomly distributed in the matrix, the self-healing efficiency has a distinction even for the same particles size distribution and fixed volume fraction of unhydrated cement nuclei. Combined the volume fraction, the particles size distribution and the expansion model of unhydrated cement nuclei, the self-healing efficiency obtained in proposed models can be used to quantitatively characterize and model the self-healing behavior of cracks in hardened cement paste.
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