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MODELLING AUTOGENOUS SELF-HEALING WITH DISSOLUBLE ENCAPSULATED PARTICLES USING A PHASE FIELD APPROACH

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Abstract. In this paper, a modelling approach for autogenous self-healing is presented that is initially based on the healing potential of encapsulation of various cement particle fractions with time. The healing potential of a blended cementitious system will be provided that consists of original cementitious particles mixed with so-called Dissoluble Encapsulated Particles (DEPs). The self-healing principle of this system is based on a most basic healing concept, where the evolution of the healing material can be separated into the late hydration of DEPs and the carbonation of calcium hydroxide. In this regards, a phase-field model is presented that is based on thermodynamics and kinetics of the prevailing chemical reactions. The concept enables to predict the healing potential of DEPs inside a cement-based system and analyse the most dominant parameters affecting the microscopic and macroscopic properties of (re-)hydrated microstructure. For this, the liquid-solid interfaces of the dissolution and/or precipitation mechanism is considered as a continuous density field driven by a reaction equation. The results show the potential of the healing mechanism to bridge a certain crack width, and shows the ability of the proposed modelling approach for autogenous self-healing.

1 INTRODUCTION

Many different ways that encourage the self-healing potential of cementitious materials have been developed over the last decades (Ferrara et al., 2018). One of the methods that drives self-healing is by adding encapsulated containers filled with agents. These latter can be liberate whenever their containers (capsules) break, when hit by a crack. The disadvantage of this method is that often concrete incompatible materials are brought into the crack space. An alternative method close to this one is the so-called Dissoluble Encapsulated Particle (DEP) method (Koenders, 2012), where a number of predefined cement fractions are encapsulated by a membrane that dissolves whenever affected by a crack. Cementitious crack formation will trigger a DEP membrane to open due to i) dissolution mechanisms in lower pH-conditions (i.e., due increased CO2 ingresses), or ii) induced by mechanical fracture stresses. The potential of this technique can be evaluated at different scale levels and at different time of age. In this, the initial quality of a cementitious microstructure will be the reference and complies with its predefined specifications. From this, the long-term durability performance, along with its initial quality, are the main parameters that determine whether self-healing materials are necessary and likely become activated during its service-life.

The self-healing potential of a concrete compatible agent might be necessary to maintain the microstructural quality of the initial material or to repair (micro and macro) structural damages. There are already several modelling approaches available for simulating the self-healing behavior of concrete, but only a few models simulate the evolution of self-healing products from the perspective of the prevailing reaction mechanisms, thermodynamics and chemical kinetics. The phase field method has been applied to various phenomena in materials research, such as, solidification, solid-state phase transformation, recrystallization, grain growth, fracture, and electromigration (Karma, 1998; Nambu, 1994; Kim, 2006; Wang, 2001; Wen, 2012; Kobayashi, 1998). The classical phase-field method is formulated based on the theory of thermodynamics and can be employed to solve morphological evolution processes, which are rather difficult to achieve through traditional sharp interface models. The evolution of the field, over time and space, is controlled by the nonlinear diffusion Cahn-Hilliard equation and through the relaxation by the Allen-Cahn equation. It is worth noting that, solidification and precipitation processes are quite similar to many solute-solvent systems, like self-healing process in cement based composites actually are. There are various studies on self-healing mechanisms and microstructure evolution, which provide an overview of the use of phase-field methods (Garlan, et al., 2002; Voyiadjis, et al, 2011; He, et al., 2011; Jefferson, et al., 2018).

In this paper, a phase field model is proposed to describe the healing potential of DEP-cement systems (Figure 1). When cracks occur or the internal microstructures are damaged, which harm the encapsulation cover, the self-healing mechanism is activated.

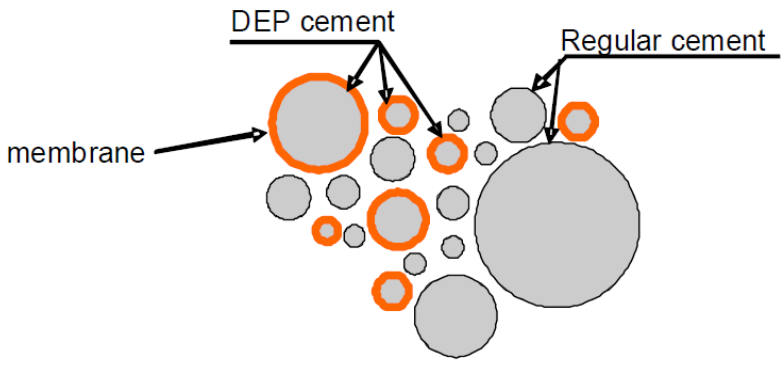


Figure 1: Schematic representation of regular cement blended with DEP cement (Koenders, 2012)

Whenever the membrane dissolves after coming into contact with a crack, DEP cement will commence to react with the remaining capillary pore water or absorb it from the humid environment via moisture diffusion or transport through cracks. From there, newly formed hydration products will develop and heal the damaged material.

2 MODELLING ENCAPSULATED PARTICLES

Modelling the encapsulated particles is achieved by creating a particle grading that has properties, which can be controlled explicitly during the hydration process. In this way a parameter study could be conducted showing the performance of the reacting DEPs particles at later ages. For the hydration model, regular cement particles are blended with a predefined amount of DEPs particles that follow a certain range of fractions and having defined hydrational properties. Therefore, focus of the model is on the different combinations of the encapsulated DEPs particles, blended in a regular cement, and stacked randomly inside a virtual microstructure. Most effective combination in terms of cement and DEP fractions, in combination with the ability to close a crack will be analyzed. In this respect it is also relevant to know the ultimate crack width at which the healing mechanism will still work properly.

Therefore, regarding the numerical simulations, the following DEP combinations have been considered:

- 2.5%, 5% and 10% replacement of cement by DEPs particles (see Figure 2);
- Replacement of the cement percentage is the same for all predefined fractions;
- The grading of DEP is equivalent to the grading of the cement;
- Particles are stacked randomly;
- The simulated volume is equal to 100 × 100 × 100 μm³.

In order to get an impression of the replacement rates of the DEP particles in a cementitious system, Figure 2 shows random stacked particles at three different percentages. For this, the particles of both the original cement and the DEP fractions were placed according to the size distribution function of Rosin-Ramler (1) as follows:

$$G(x) = 1 - \exp(b \cdot x^n) \tag{1}$$

being x the particle diameter, while n and b shape factors.

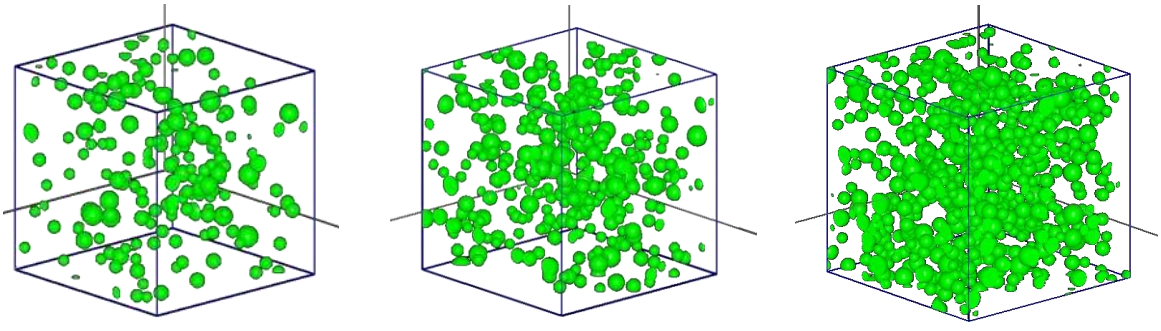


Figure 2: Impression of microstructures with displayed the 2.5%, 5% and 10% replacement of the regular cement by DEPs inside a 100 × 100 × 100 μm3 cube

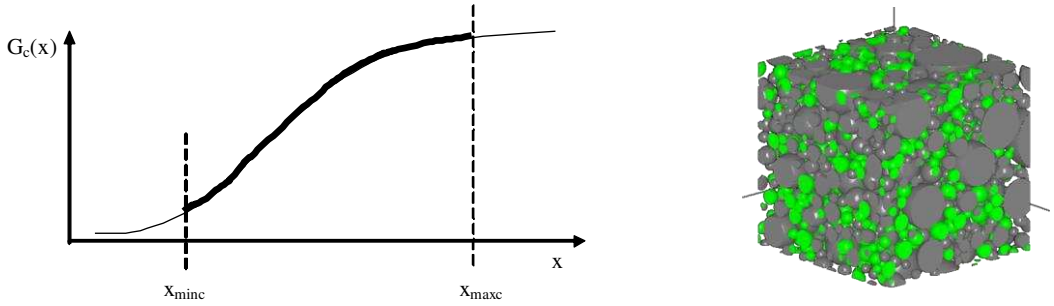


Figure 3: Left: Rosin-Ramler particle size distribution function for DEP and cement. Right: Blended initial microstructure with 10% DEP and 90% cement particles

This equation allows calculating the mass of each fraction that exceed a certain diameter. A schematic impression of the particle size distribution curve is shown in Figure 3 (left) and the initial result of the blended cement/DEP structure is shown in Figure 3 (right). The particle structure represents the starting point for the simulations conducted to determine most dominant parameters for the DEP self-healing mechanism. The encapsulated system will have their own reaction potential and are treated fully independently from the cement hydration. The hydration simulations are conducted with the Hymostruc (van Breugel, 1991) simulation model, which was developed at Delft University of Technology and is used to simulate the hardening process of the cement/DEP matrix. The Hymostruc model (Figure 4) is a 3D code that can be used to simulate the hydration evolution of a virtual microstructure of cementitious materials. The hydration process of the various particle reactions can be distinguished in different categories, including morphological, physical, chemical and thermo-dynamical issues. In view of the development of the cementitious microstructure, all these categories have their own particular characteristic and affect the hydration reaction in a certain way. This also holds for DEPs, which will be in the main focus of the parameters that were changed during simulations.

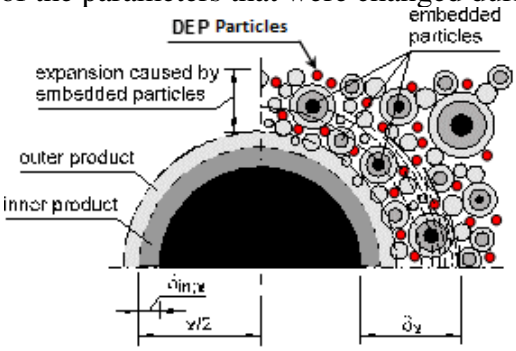


Figure 4: Schematic representation of expansion mechanism used in Hymostruc. The cement matrix is composed of hardening cement particles and unhydrated DEP grains. These will be activated after cracking and moistening

3 SIMULATIONS: MULTIPLE FRACTIONS APPROACH

Analyzing the potential of the microstructural model that was consisting of cement and DEPs, various grain configurations of cement/DEP blends were modelled and their hardening calculated. The basis of the model was based on adopting a microstructure with dimensions of 100 × 100 × 100 µm³ (CEM I, w/c 0.45, Blaine 400 m²/kg as shown in Figure 5). In the middle of this virtual microstructure, a crack (of 30 µm) has been initiated by means of shifting the initial randomly positioned particle to the left and right, while creating a void growth (crack) in the middle with a predefined thickness. This crack is the actual focus of this research and is influenced by the various parameter variations done in this numerical study.

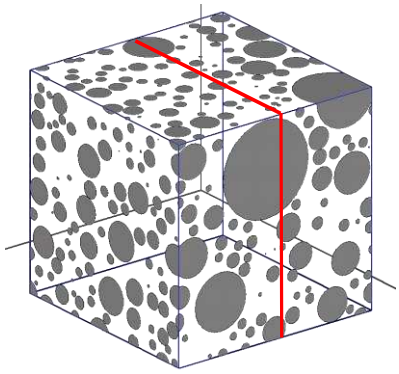


Figure 5: Schematic representation of the microstructure with the position of the crack in the middle indicated

The first parameter variation is on the replacement of a range of single fractions. In this so-called "multiple fractions approach", 10% of the following cement fractions were replaced by DEP granulates, 5 - 10 µm, 10 - 20 µm, 20 - 30 µm and 30 - 40 µm. The grain structures of this cement and DEP matrices are shown in Figure 6. The microstructures give an impression of the partitions and DEP granules in the cement matrix and thus also give an indication of the geometric potential of the DEPs in the matrix. The fine grains are the most abundant in number, but their expansion potential is relatively little. Larger grains are less abundant in number, but their expansion potential is much larger. What contributes most to the healing potential is analyzed hereafter and the optimum particle replacements are presented (Figure 7).

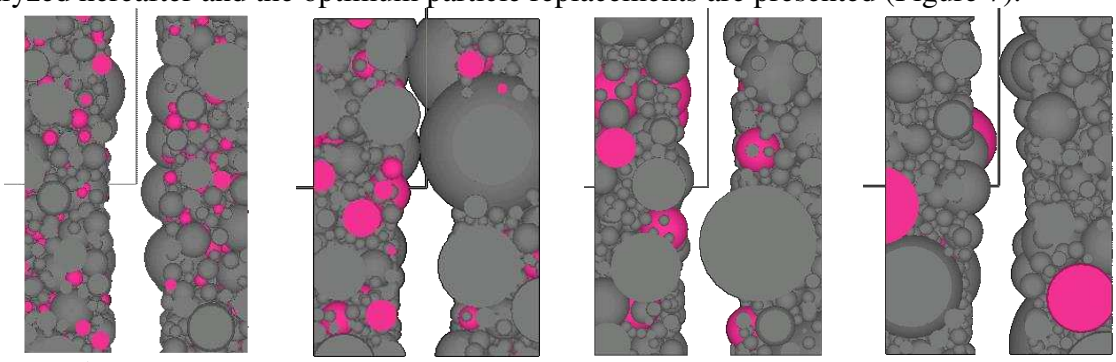


Figure 6: Multiple fractions approach: Initial state of microstructure by 10% cement replacement by DEP

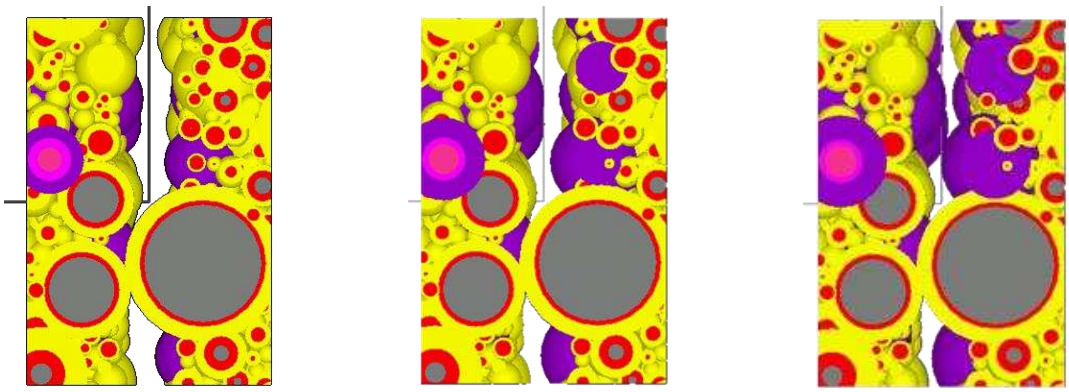
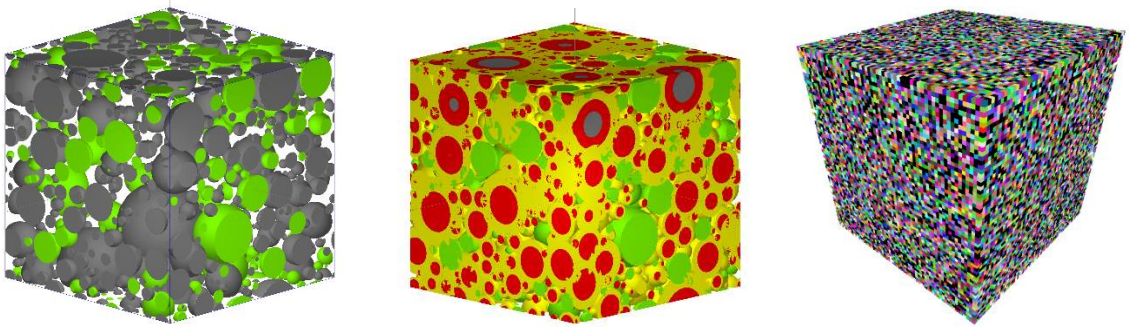


Figure 7: Single fractions approach (40 days.): left, 10% cement replacement by DEPs for the fractions 20 – 30 µm. Middle: same fractions replaced with double expansion of DEP particles. Right: same fractions replaced with three times the expansion potential. Hardening of cement and DEPs started at the same time

The simulations (duration 40 days) showed that, according to the multiple fractions approach, the optimum replacement range is 20 - 30 µm. The balance between the number of grains present in the system and the potential expansion appears to be the most optimal for this replacement range. Figure 7 (left) shows the healing potential of this particular blend, with the potential expansion of the DEP granules be equal to the expansion potential of cement. Figure 7 (middle), shows the simulation result of the same configuration with the DEP granules having an expansion potential of 2x the expansion potential of cement. From the results, it can be observed that the expansion potential has a relatively large influence on the healing potential. In Figure 7 (right), a simulation result is shown where the DEP granules expand 3x more than cement. These results show an even larger impact on the self-healing potential.

4 TOWARDS MICROSCALE VOXEL-BASED FEM FOR SELF-HEALING

The micro-mechanical behavior of the self-healing process has been evaluated numerically by analyzing a representative volume element (RVE) of the DEP-cement paste system. Since the main interest of this study was to investigate the effect of the fracture and cracking evolution affecting the DEPs, several 3D-microscale geometries are currently under investigation. The aim is to analyze different sizes and distributions of DEPs on both the mechanical and porosity modification due to self-healing. 3D virtual DEP-cement microstructures were generated by the Hymostruc hydration model, where the microgeometries and hydration process are based on several input parameters: e.g., particle size distribution of the (anhydrous) cement, type of binder, water-to-cement ratio, age, mix temperature and DEPs distribution (Figure **8**a-b). Then, a structured voxel-mesh can be straightforwardly obtained as result of the microscale analysis (Figure **8**c).



(a) (b) (c)

Figure 8: 3D microstructure: (a) initial anhydrous cement and DEPs, (b) hydrated structure and (c) schematic voxel-based FE mesh

The test specimens take into account mainly four (micro-) phases: (i) hydrated cement phase, (ii) unhydrated cement phase, (iii) DEPs and (iv) voids. For the fracture analysis, the phases (i) and (iii) mainly represent the “crackable” ones (being DEPs the weakest zone between them), while the (ii-) phase is mainly considered as a rigid body embedded in the system.

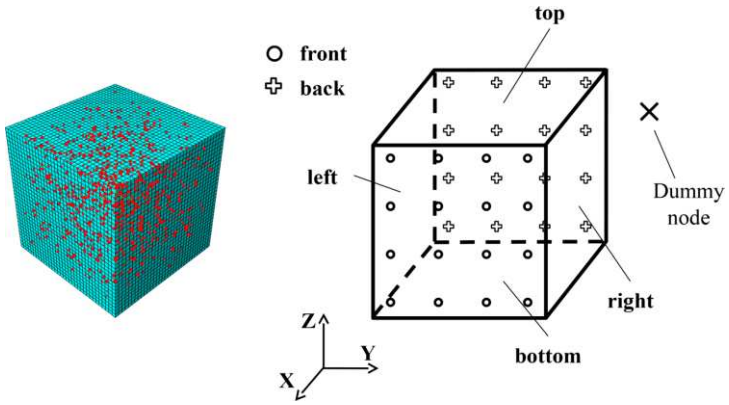


Figure 9: 3D RVE geometry (left) and general scheme of the boundary condition assumptions on the front/back and top/bottom surfaces

The numerical strategy thus tries to quantify the self-healing character of the DEPs by mechanically introducing cracks under general stress states. More specifically, in order to evaluate the self-healing capacity of the microscale specimens, three numerical steps will be sequentially considered into the micro-FEM analyses:

(i) in the **first stage**, the specimen was *"pre-cracked"* up to a certain level (namely residual crack opening level). At this stage, due to the imposed cracking, several DEPs will be broken and are able to develop self-healing mechanisms;

(ii) **Conditioning stage**: in this second step the self-healing processes develops. Hydration activities of DEPs aim at closing the fracture in the crack surface and also allow to consider possible mechanical recoveries and/or developments at the crack front.

(iii) **Final crack stage** which allows to evaluate the total failure of the specimen and with which it can evaluate the self-healing potential at a mechanical standpoint.

Periodic Boundary Conditions (PBCs) are used in the above cracking stages (i and iii). For this, the boundary domain Γ_μ of the (micro-) cubic geometry in Figure 9 is divided in two sub-domains outlining the opposite unit normals (surfaces). Due to the structured mesh, and in light of the PBC, each node with coordinates $\vec{x}^+$ in Γ_μ^+ has a unique correspondent node $\vec{x}^-$ in Γ_μ^-.

The cracking behavior is accounted for by means of the XFEM discontinuous-based technique (Moës et al., 1999). One of the main advantages of this method is the (almost) mesh independency of the fracture propagation (when sufficiently refined meshes are employed) and there is no need to insert special interface (cracking) elements inside the voxel FE. In presence of a crack, additional DOFs enrich the nodes of the XFEM model, as shown in Figure 10.

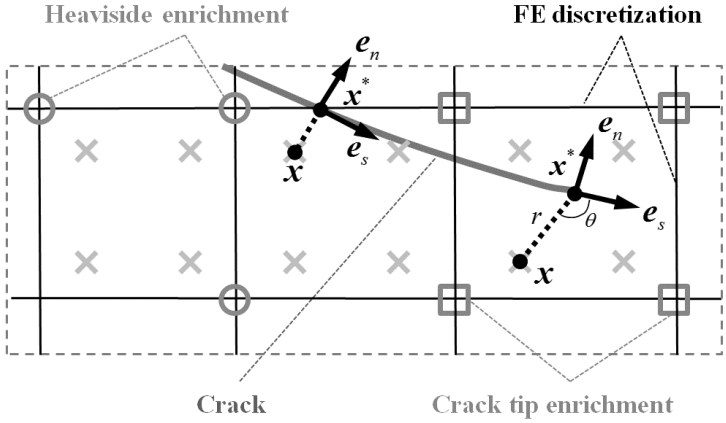


Figure 10: Enrichment of the nodes on the XFEM method employed in the voxel-based FE meshes

The so-called Level Set Method (LSM) (Chessa et al., 2004) is used to locate the crack within the domain. In the XFEM-LSM formulation two functions are classically needed to define the crack position. In this work, however, a traction-separation cohesive rule, which also accounts for self-healing mechanisms, is utilized to model the crack initiation and growth along and arbitrary cracking path. This implies that cracks will propagate across an entire element at a time. This permits to avoid the need of modeling the stress singularity of the near-tip, and therefore, only the displacement jump across a cracked element is modelled (Schicchi et al., 2017).

To account for the degradation and potential failure of the involved elements, the traction-separation cohesive behavior is based on the interface constitutive theory for cementitious materials under possible self-healing effects as proposed in (Caggiano, et al., 2017).

5 PHASE-FIELD MODEL FOR AUTOGENOUS SELF-HEALING

5.1 Introduction of phase-field model

In conventional modelling techniques for phase transformations and microstructure evolution, moving interfaces can be considered as infinitely sharp. The phase field model provides a powerful tool to explicitly tack the interface movements by using continuous order parameters, which are introduced to track the changing phases (Wheeler, 1992). Figure 11 illustrates a diffuse interface and a sharp interface within these processes.

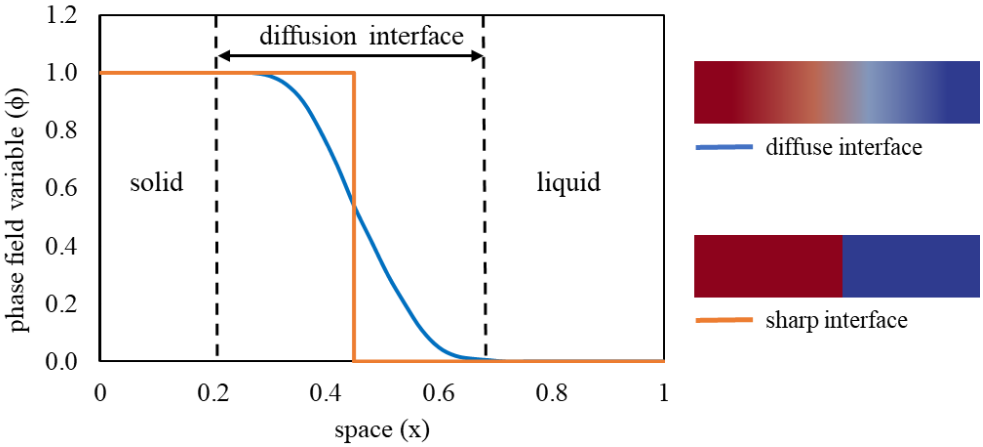


Figure 11: Schematic representation of sharp interface model and phase-field model

5.2 Computational algorithm

The simulation of the self-healing mechanism in DEP-cement paste is performed for a two-dimension (2D) sample. A virtual microstructure with a crack is obtained from the Hymostruc and XFEM model, as mentioned in section 2. The healing process is thus simulated through the phase-field approach. Two simplified assumptions are made: (i) the Ca^{2+} is already dissolved from the hydrated cement into the solution and (ii) the concentration of HCO_3^- is assumed to be sufficient. Therefore, the reaction rate of carbonation depends mainly on the concentration of Ca^{2+} in the solution. In the phase-field method, the microstructure is represented by a phase-field variable ϕ. The effect of the ion diffusion is modelled with a concentration field variable, c', which introduces a normalized concentration, i.e., $c' = c/c_s$, where c is the molarity of the concentration of Ca^{2+} and c_s is defined as the density of the solid divided by its average molar mass. Figure 12 shows the local free energy density as a function of c. The two solid-liquid

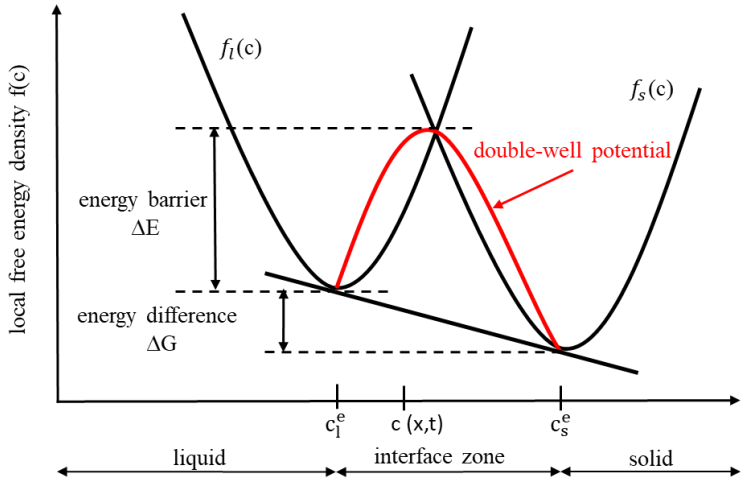


Figure 12: Free energy density curves of solid and liquid against composition

phases are in contact and therein a chemical reaction occurs, leading to an increase in the local free energy at the interface. The local free energy density has two minima, c_l^e and c_s^e, corresponding to the so-called equilibrium states.

The total free energy of the system is presented as:

$$\mathrm{F}(\mathrm{c}',\phi) = \mathrm{F_{loc}} + \mathrm{F_{int}} = \int_{\mathrm{v}} \left[\mathrm{f_{loc}}(\mathrm{c}',\phi) + \frac{\mathrm{k}}{2}|\nabla\phi|^2 \right] \mathrm{dV} \tag{2}$$

where F_{loc} is the local free energy of the system, F_{int} is the interfacial energy, and k is the gradient energy coefficient.

In the model, each point throughout the domain is a mixture of two phases with different chemical compositions. The local free energy is determined to be a fraction-weighted average value of both solid and liquid free energy, and an imposed double well potential $wg(\phi)$ as follows (Kim, 1999):

$$\mathrm{f}(\mathrm{c}',\phi) = \mathrm{h}(\phi)\mathrm{f_s}(\mathrm{c_s'}) + [1-\mathrm{h}(\phi)]\mathrm{f_l}(\mathrm{c_l'}) + \mathrm{wg}(\phi) \tag{3}$$

where the interpolation function $h(\phi)$ is built as $h(\phi) = -2\phi^3 + 3\phi^2$, and w is the height of the double well potential energy function given by $g(\phi) = \phi^2(1-\phi)^2$. The free energy density of each phase is approximated by a parabolic function with the same curvature A as follows:

$$\mathrm{f_s}(\mathrm{c_s}) = \mathrm{A}(\mathrm{c_s'} - \mathrm{c_{se}})^2 \tag{4}$$

$$\mathrm{f_l}(\mathrm{c_l}) = \mathrm{A}(\mathrm{c_l'} - \mathrm{c_{le}})^2 \tag{5}$$

where $c_{se} = c_s/c_s = 1$ and $c_{le} = c_{sat}/c_s$ are the Ca^{2+} concentrations at the normalized equilibrium in solids and liquids, respectively.

The evolution of the conserved field variables c' is defined using the Cahn-Hilliard equation, while the Allen-Cahn equation is used to describe the temporal evolution of the non-conserved variableϕ, i.e.:

$$\frac{\partial \mathrm{c}(\mathrm{x},\mathrm{t})}{\partial \mathrm{t}} = \nabla\cdot\mathrm{M}\cdot\nabla\frac{\delta\mathrm{F}}{\delta\mathrm{c}} \tag{6}$$

where M is the kinetic coefficient of diffusion;

$$\frac{\partial \phi(\mathrm{x},\mathrm{t})}{\partial \mathrm{t}} = -\mathrm{L}\frac{\delta\mathrm{F}}{\delta\phi} \tag{7}$$

where L is the kinetic coefficient related to the interface mobility.

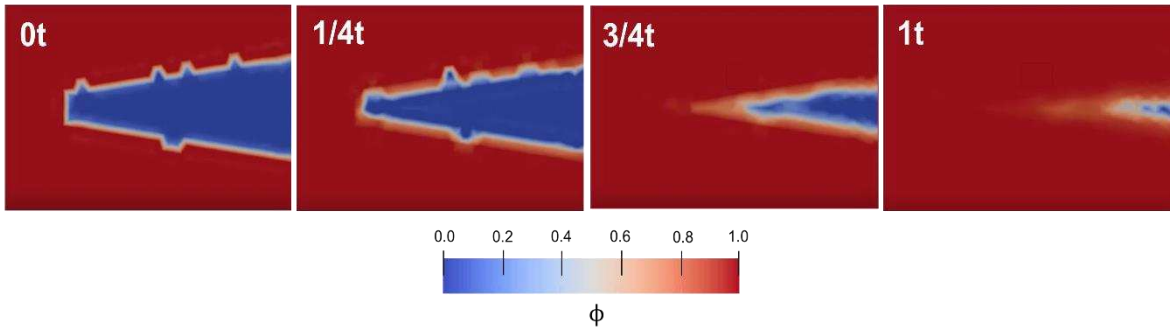


Figure 13: self-healing in DEP-cement paste

From Figure 13, it can be observed that the order parameter ϕ describes the evolution of self-healing in DEP-cement paste. The continuous diffusion of Ca^{2+} and carbonation reaction with HCO_3^- results in the evolution of precipitation of $CaCO_3$ on the crack surface. This makes the solid boundary gradually grow into the solution, while the crack will be heal. The coupling of the Cahn-Hilliard and Allen-Cahn equations by the use of a free energy function has enabled the complete description of the self-healing process using chemical free energies that are obtained from the thermodynamic database.

6 CONCLUSIONS

A modelling approach is proposed to evaluate the potential of a self-healing mechanism that partly contains encapsulated cement particles with a delayed hydration ability, which is achieved by an (artificial) encapsulation material. The microstructure simulations are conducted with the Hymostruc model where the original cement particles as well as the DEPs are explicitly modelled. Then a phase-field model, based on thermodynamics and kinetics of the chemical reaction principles, is proposed to evaluate the healing potential and crack closing.

Based on the presented theoretical models, the following conclusions can be drawn:

- Blended DEP systems can be well simulated with hydration models, such as Hymostruc;
- The particle grading and proportions of DEPs has a major influence on the healing potential;
- All-fractions approach for the involved cement and DEPs indicated the larges healing;
- The degree of hydration of the blended cement - DEP system has the potential to develop to the similar level as the original cement hydration, after activation of the DEPs;
- The porosity of the blended cement - DEP system approached to the same level after activation of the DEPs compared to the original cement system;
- Voxel-based micro-structurers analyzed with XFEM could be a successful approach to model the cracking mechanism that triggers the self-healing behavior of DEPs.
- The phase-field model is a powerful method for predicting the self-healing/closing of DEP-cement paste.
- Finally, by selecting the correct parameters, the phase-field model can be fully utilized to study any phase transitions resulting from chemical reaction and diffusion mechanism.

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