A COUPLED TRANSPORT-REACTION MODEL FOR SIMULATING AUTOGENOUS SELF-HEALING IN CEMENTITIOUS MATERIALS – PART II: VALIDATION THROUGH COMPARISON WITH EXPERIMENTS

Haoliang Huang (1), Guang Ye (1,2) and Denis Damidot (3)

(1) Microlab, Department of Civil Engineering and Geoscience, Delft University of Technology, the Netherlands

(2) Magnel Laboratory for Concrete Research, Department of Structural Engineering, Ghent University, Belgium

(3) Civil & Environmental Engineering Departement, Ecole Nationale Supérieure des Mines de Douai, Douai, France

Abstract

In this paper, the proposed coupled transport-reaction model adapted to simulate autogenous self-healing in Portland cement paste is validated with the experimental results. The parameters are studied for modelling the dissolution of cement, the diffusion of ions between the solution in the crack and in the bulk paste and the precipitation of reaction products in the crack. Simulation results for different parameters are compared with the experimental results. Discussion on the validity of the coupled transport-reaction model is presented.

Keywords: Autogenous self-healing, coupled transport-reaction model, validation, crack, Portland cement paste

1.   INTRODUCTION

The physico-chemical processes of autogenous self-healing is complex and involve the following mechanisms: ingress of water into the cracks, dissolution of unhydrated cement in contact with the solution in the cracks, diffusion of ions in the solution in the crack and in the bulk paste, equilibration with the already formed hydrates generally leading to their dissolution and precipitation of some solid reaction products in the crack.

In the Part I [1], the theoretical basis of a coupled transport-reaction model specially developed for simulating the physico-chemical processes of autogenous self-healing was described. Because the diffusion coefficient of CO_2 in water is 4 orders of magnitude smaller than that in air [2], carbonation is ignored when cracks are filled with water or a healing solution. The model only simulates the physic-chemical processes of autogenous self-healing before carbonation. In this second part, the parameters needed for modelling the dissolution of

cement, the diffusion of ions between the solution in the crack and in the bulk paste and the precipitation of reaction products in the crack are studied and discussed. The model is validated with the experimental results.

2. VALIDATION OF THE COUPLED TRANSPORT-REACTION MODEL

2.1 Microstructure of Portland cement paste

Portland cement paste is prepared with CEM I 42.5N. The mineral composition of CEM I 42.5N is listed in Table 1.

Samples are cracked at the age of 7 days, 14 days and 28 days, respectively, and then cured in water again for self-healing. From the microstructure of cement paste (see Figure 1 (a)) it is found that some unhydrated cement particles (UHC) are present at the crack surfaces, while others are embedded inside the bulk paste. The unhydrated cement particles at the crack surfaces can directly react with water in the cracks and the reaction products can be formed in the crack. Oppositely the unhydrated cement particles embedded in the bulk paste are surrounded by hydration products and thus can not directly react with the water in the crack. But after the time required for water molecules to diffuse through the hydration products, these unhydrated cement particles are hydrated and also facilitate self-healing of the crack.

In the simulation, the volume fraction of unhydrated cement particles present at the crack surfaces (see Figure 1 (b)) is comparable to experimental results from BSE image analysis on flat polished section of cement paste. Both the volume fraction of unhydrated cement particles and capillary porosity of the sample are quantified (Table 2). In order to achieve higher efficiency of autogenous self-healing, cement paste with low w/c ratio (0.3) is investigated.

Table 1: Mineral composition of Portland cement (CEM I 42.5N) calculated by Bogue equation [3]

Compound	C_3S	C_2S	C_3A	C_4AF	Total
Weight (%)	64.1	13.0	7.9	8.1	93.1

(a) BSE image of cement paste with a crack   (b) 2D sample of microstructure for simulation
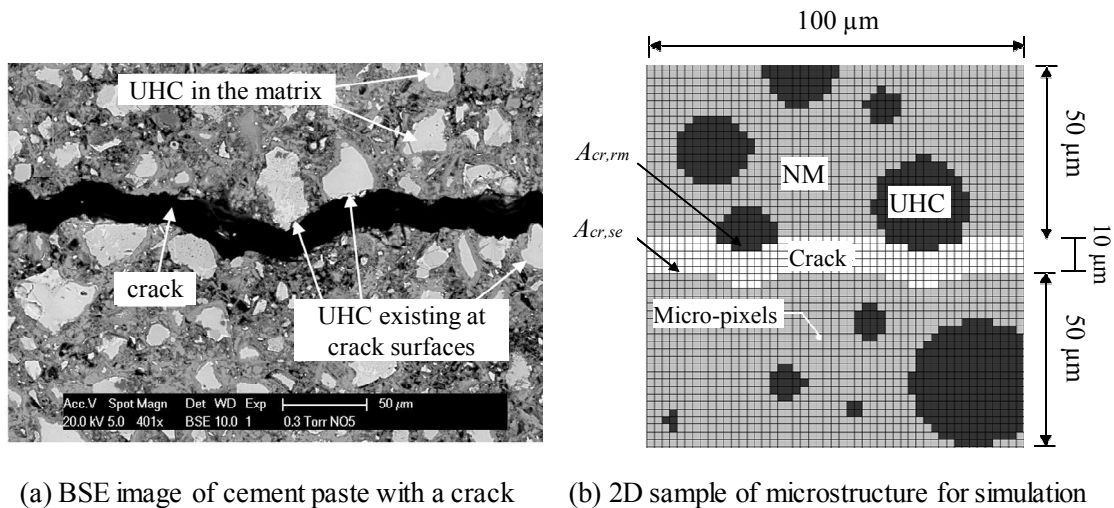
Figure 1: Microstructure from BSE image and the comparable 2D sample for simulation (UHC refers to unhydrated cement particles).

Table 2: Information about microstructure of Portland cement paste determined by means of BSE image analysis, compared to that from modeling with HYMOSTRUC3D (in brackets). The w/c ratio is 0.3.

Age (days)	Capillary porosity (-)	Fraction of unhydrated cement (%)	Fraction of unhydrated cement at crack surfaces in the sample for simulation (%)
7	0.141 (0.124)	19.1 (18.5)	5.7
14	0.124 (0.104)	17.8 (16.4)	4.8
28	0.108 (0.087)	16.3 (14.7)	3.4

2.2 Parameters of the coupled transport-reaction model
2.2.1 Basic reaction rate of cement R_0

As described in part I, the rate of phase-boundary reactions can be described as:

$$\frac{d\delta_P}{dt} = \varepsilon_1 \cdot \varepsilon_2 \cdot R_0 \tag{1}$$

where δ_P [m] is the penetration depth of the reactive material, which is the thickness of the layer of material that has reacted (as illustrated in Figure 2); R_0 [m/s] is the basic reaction rate of reactive material, which depends on the chemical composition; ε_1 [-] is the parameter used to describe the "induction period" of the reaction as affected by the large amount of water in the crack; ε_2 [-] is the parameter used to described the acceleration of the reaction due to the seeding effect of previously formed hydrates at the crack surfaces. The rate of diffusion-controlled reaction can be calculated by the formula:

$$\frac{d\delta_P}{dt} = \frac{\varepsilon_1 \cdot \varepsilon_2 \cdot R_0}{\left|\delta_P \times 10^6\right|} \qquad \left(\delta_P \geq \delta_{P,tr}\right) \tag{2}$$

where $\delta_{P,tr}$ [m] is the transition thickness particularly for the reaction of reactive material at crack surfaces.

For cement clinker, the basic dissolution rate is related to the chemical composition of the clinker [4]. To simulate hydration of C_3S, a good fit of the simulation results with the experimental results is obtained for $R_0 = 0.065$ μm/h [4]. In comparison, to simulate hydration of C_2S, a good fit of simulation results with the experimental results is obtained for $R_0 = 0.01$ μm/h [4]. As recommended by van Breugel [4], R_0 value ranges from 0.025 μm/h to 0.055 μm/h for different types of Portland cement, depending on the percentages of C_3S and C_2S. For Portland cement CEM I 42.5N, the basic dissolution rate R_0 in Equation 1 can be assumed to be 0.045 μm/h [4].

2.2.2 Diffusion coefficients for ions

In the healing process, ion diffusion takes place between the solution in the crack and the solution in the matrix. This ion diffusion can be described by Fick's second law [5]:

$$\frac{\partial c_i}{\partial t} = \nabla \cdot (D_i \nabla c_i) \tag{3}$$

where c_i [mol/m^3] is the concentration of the ith ion and D_i [m^2/s] is the diffusion coefficient in the solution in the crack for the ith ion.

In this section, the ion diffusion coefficients used in the model are discussed. Before the reaction products start to form in cracks and thus fill it partially or completely, the diffusion

coefficient $D_{i,c}$ of the pixels representing the crack can be assumed to be equal to the ion diffusion coefficients in free water. The ion diffusion coefficients in free water used in the simulation are listed in Table 3.

Table 3: Diffusion coefficients of ions in free water at 25°C [6]

Species	Ca^{2+}	Al^{3+}	Mg^{2+}	OH^-	SO_4^{2-}	$H_2SiO_4^{2-}$
Diffusion coefficient (10^{-9} m^2/s)	0.72	0.60	0.71	5.28	1.01	0.70

When reaction products are formed in cracks, the ion diffusion coefficients inside the crack decrease gradually. Zhang [7] determined the relationship between the diffusion coefficient of cement paste for chloride ions and the effective porosity by using lattice Boltzmann method. The mathematic expression of diffusion coefficient of cement paste as a function of the porosity ($0.05 < \varphi < 0.55$) could be obtained by fitting the data in [7]. Moreover, the diffusion coefficient almost linearly decreases with the decrease of porosity ranging from 0.55 to 0.65 [7]. Based on this, it is assumed that the diffusion coefficient almost linearly decreases with the decrease of porosity for $0.55 \leq \varphi \leq 1$. The diffusion coefficient $D_{i,C}(\varphi)$ in the crack is written as:

$$D_{i,C}(\varphi) = \begin{cases} 1.8\left(D_{i,C0} \cdot \varphi^2\right) & (0.05 < \varphi < 0.55) \\ D_{i,C0} \cdot \varphi & (0.55 \leq \varphi \leq 1) \end{cases} \tag{4}$$

where $D_{i,C0}$ [m^2/s] is the initial diffusion coefficient of the solution in the crack before the healing process. In this case, $D_{i,C0}$ is equal to the ion diffusion coefficient in free water; After reaction products are formed in the crack, the crack is partially filled and φ [-] is the volume fraction of the crack not filled by reaction products. It must be mentioned that in the coupled transport-reaction model φ should not be smaller than 0.05, otherwise Equation 4 is not valid.

Regarding the ion diffusion in the bulk paste, the diffusion coefficient $D_{i,B}$ can also be calculated with the capillary porosity of the bulk paste in Table 2 with Equation 4. The results are presented in Table 4.

Table 4: Diffusion coefficient $D_{i,B}$ for Ca^{2+}, $H_2SiO_4^{2-}$ and OH^- ions in the bulk paste

Age (days)	Diffusion coefficient of Ca^{2+} (10^{-11} m^2/s)	Diffusion coefficient of $H_2SiO_4^{2-}$ (10^{-11} m^2/s)	Diffusion coefficient of OH^- (10^{-11} m^2/s)
7	2.58	2.51	18.89
14	1.99	1.94	14.61
28	1.51	1.47	11.09

2.2.3 Effect of large amount of water on the "induction period" of the reaction of reactive material - ε_1

Regarding the hydration of cement four stages can be considered: pre-induction, induction, acceleration and deceleration [8]. During the "induction" period, t_{ind}, the reaction rate of cement is almost 0. Therefore ε_1, the parameter used to describe the "induction period" of the reaction in Equation 1, can be written as:

$$
\varepsilon_1 = \begin{cases} 0 & \left(t \le t_{ind} \right) \\ 1 & \left(t > t_{ind} \right) \end{cases} \tag{5}
$$

However, for mixture with w/c ratio of 50.0, there is no "induction" stage during the hydration, whereas for the mixture with w/c ratio of 0.5, the "induction period" lasts for about 5 hours [9]. For self-healing of cracks, there is much water in the crack compared to the volume of cement clinker present at the crack surfaces and some hydrates are already present acting as seeds. Therefore, in case of self-healing ε_1 in Equation 1 can be written as:

$$
\varepsilon_1 = 1 \quad \left(t \ge 0 \right) \tag{6}
$$

2.2.4 Seeding effect of the crack surfaces on the dissolution kinetics of reactive materials - ε_2 and $\delta_{P,tr}$

Parameter ε_2 in Equation 1 describes the seeding effect of the crack surfaces on the dissolution rate of reactive material in the coupled transport-reaction model. Parameter $\delta_{P,tr}$ is the transition thickness describing the change from a phase-boundary reaction to a diffusion-controlled reaction. The simulation results obtained for different values of these two parameters are compared with the experimental results.

For simulation of hydration of cement CEM I in bulk paste, the transition thickness defined in cement hydration model HYMOSTRUC3D approximates 1.5 μm [10]. No seeding effect is present for the hydration of cement in bulk paste, therefore $\varepsilon_2 = 1.0$. In case of simulation of self-healing, with the same values for ε_2 and $\delta_{P,tr}$, the filling fraction of cracks calculated by the coupled transport-reaction model is much lower than the experimental results (see Figure 2). When ε_2 and $\delta_{P,tr}$ are increased to 2.6 and 4.0 respectively, the simulated results are in
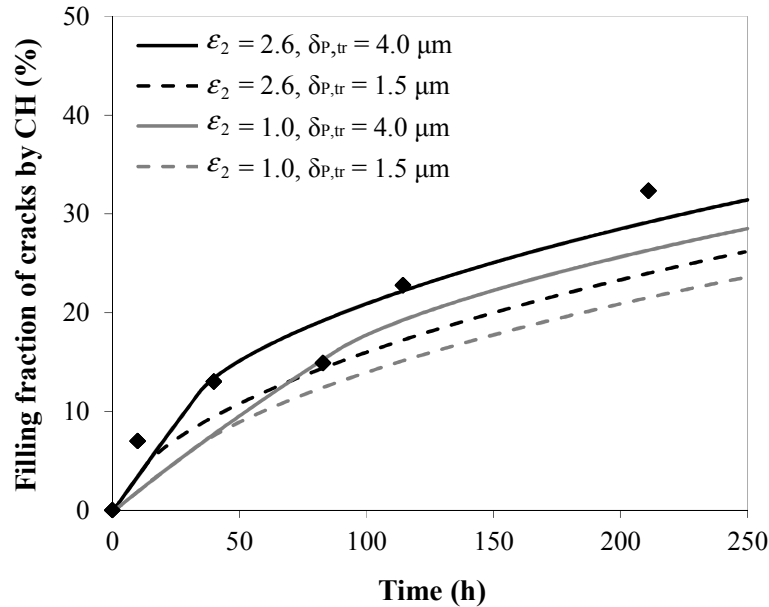

Figure 2: Filling fraction of a crack with portlandite for different values of ε_2 and $\delta_{P,tr}$ in Equations 1 and 2. Self-healing starts at the age of 28 days of the paste. The experimental results from [11] are shown with solid squares in the figure. The crack width is 10 μm.

good agreement with the experimental results from [11]. These values of ε_2 and $\delta_{P,tr}$ indicate that the seeding effect of the crack surfaces accelerates the cement hydration and delays the transition from a phase-boundary reaction to a diffusion-controlled reaction, i.e. taking place at higher degree of hydration of cement. Two mechanisms are thus likely to be involved: first, a distribution of the solid reaction products on both previously formed solid reaction products and unhydrated cement at the cracks surface leading to slower formation of a covering layer at the unhydrated cement surface. Second, a less dense layer of solid reaction products is leading to a transition from a phase-boundary reaction to a diffusion-controlled reaction that occurs at higher degree of hydration of cement.

2.2.5   Summary of study of parameters in the coupled transport-reaction model

For autogenous self-healing in Portland cement paste (w/c=0.3) starting after the age of 28 days, values of the parameter R_0, ε_1, ε_2 and $\delta_{P,tr}$ of the coupled transport-reaction model are summarized in Table 5.

Table 5: Parameters for simulating self-healing in Portland cement paste immersed in water. The w/c ratio is 0.3. Self-healing starts after the age of 7 days.

Parameters	R_0 (µm/h)	ε_1 (-)	ε_2 (-)	$\delta_{P,tr}$ (µm)
Values	0.045	1.0	2.6	4.0

3.   PREDICTION OF AUTOGENOUS SELF-HEALING WITH THE COUPLED TRANSPORT-REACTION MODEL

In case of self-healing in Portland cement paste, the seeding effect of the crack surfaces depends on the area of the previously formed hydrates at the crack surfaces ($A_{cr,se}$ in Figure 1).

Table 2 shows that for Portland cement paste with w/c ratio of 0.3 the fraction of unhydrated cement in the cement paste hardly changes after the age of 7 days (from 19.1% to 16.3%). Therefore, when cracks occur at any time after the age of 7 days, the ratios $A_{cr,rm}/A_{cr}$ of the crack surfaces can be almost the same ($A_{cr,rm}$ is the area of reactive material at the crack surfaces; A_{cr} is the area of the crack surfaces, see Figure 1). Hence, $A_{cr,se}/A_{cr}$ can be assumed to be a constant for the case that cracks occur after the age of 7 days in Portland cement paste with w/c ratio of 0.3. The same values of ε_2 and $\delta_{P,tr}$ can be used for this particular case.

The parameter values of the coupled transport-reaction model determined above (summarized in Table 5) are used for simulating autogenous self-healing starting at the age of 7 days and 14 days of Portland cement paste. As shown in Figure 3 and Figure 4, the calculated filling fraction of cracks by portlandite is in good agreement with the experimental results from [11]. Moreover, Figures 3 and 4 show that the filling fraction of cracks with C-S-H is much lower than with portlandite. This is consistent with the experimental results in [11], demonstrating that the fraction of portlandite in the reaction products formed in cracks accounts for about 80% by mass, while C-S-H accounts for less than 15%.

For the cement pastes with a higher w/c, there is less cement directly exposed to the crack surfaces. $A_{cr,rm}/A_{cr}$ *is lower.* $A_{cr,se}/A_{cr}$, hence, is higher. A larger value of ε_2 should be used for describing the seeding effect of the crack surfaces in the simulation of autogenous self-healing.
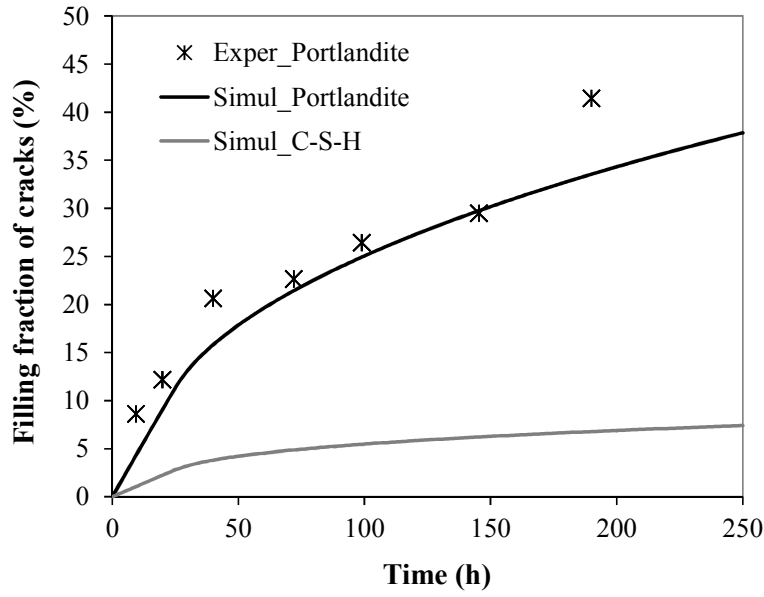
Figure 3: Filling fraction of a crack in Portland cement paste starting at the age of 7 days. "Exper_Portlandite" refers to the filling fraction of cracks with portlandite determined experimentally in [11]. "Simul_Portlandite" refers to the calculated filling fraction of cracks with portlandite, while "Simul_C-S-H" refers to the calculated filling fraction of cracks with C-S-H. The initial crack width is 10 μm.
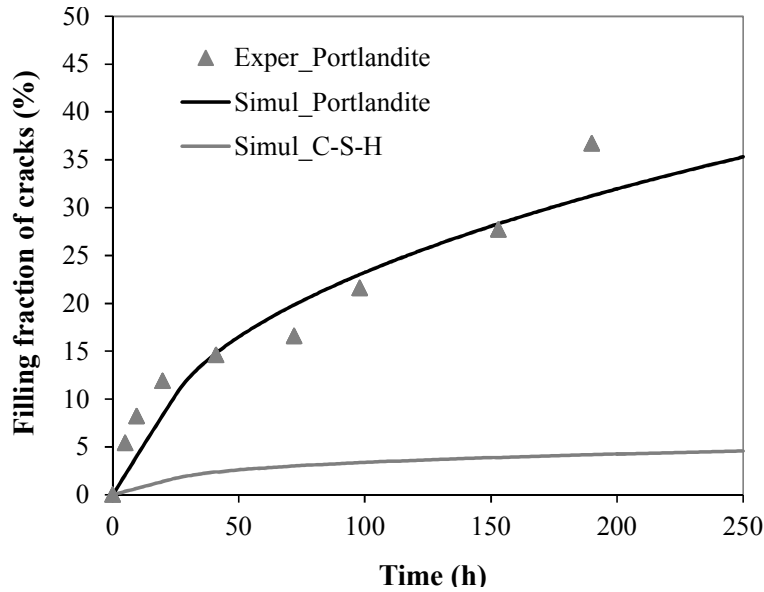

Figure 4: Filling fraction of a crack in Portland cement paste starting at the age of 14 days. "Exper_Portlandite" refers to the filling fraction of cracks with portlandite determined experimentally in [11]. "Simul_Portlandite" refers to the calculated filling fraction of cracks with portlandite, while "Simul_C-S-H" refers to the calculated filling fraction of cracks with C-S-H. The initial crack width is 10 μm.

For the cement paste made of coarser cement particles, the degree of hydration of cement is lower than finer cement particles. Hence, more cement will be directly exposed to the crack surfaces. *$A_{cr,rm}/A_{cr}$ is higher. $A_{cr,se}/A_{cr}$*, hence, is lower. A smaller value of ε_2, therefore, is used for simulating autogenous self-healing.

4. CONCLUSIONS

In this paper, parameters of the coupled transport-reaction model for simulating autogenous self-healing are determined by fitting the filling fraction of a crack with CH for a given cement paste. From the parameter study, it is found that the effect of large amount of water in the crack on the dissolution rate of cement should be taken into account. Because of the seeding effect of the crack surfaces, the dissolution rate of the cement exposed to the crack surfaces is accelerated. The transition from a phase-boundary reaction to a diffusion-controlled reaction is delayed, i.e. taking place at higher degree of hydration of cement.

With these parameter, the coupled transport-reaction model is used to predict the efficiency of self-healing of that given cement paste but at different ages. The simulation results are comparable with the experimental results. Therefore, the coupled transport-reaction model is validated. The model can be used to predict the initial step of the autogenous self-healing affected by the finesse of cement particles, w/c ratio and blended materials. Moreover, some phases, such as C-S-H, are hardly identified as newly formed reaction products in the healing process. By modelling, filling fraction of the crack with these phases can be determined as well. Subsequent steps of autogeneous self healing mostly induced by carbonation can be then readily modelled by adding carbonate in the simulation.

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