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# Modeling of a self-healing process in blast furnace slag cement exposed to accelerated carbonation

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**Abstract.** In the current research, a mathematical model for the post-damage improvement of the carbonated blast furnace slag cement (BFSC) exposed to accelerated carbonation is constructed. The study is embedded within the framework of investigating the effect of using lightweight expanded clay aggregate, which is incorporated into the impregnation of the sodium mono-fluorophosphate (Na-MFP) solution. The model of the self-healing process is built under the assumption that the position of the carbonation front changes in time where the rate of diffusion of Na-MFP into the carbonated cement matrix and the reaction rates of the free phosphate and fluorophosphate with the components of the cement are comparable to the speed of the carbonation front under accelerated carbonation conditions. The model is based on an initial-boundary value problem for a system of partial differential equations which is solved using a Galerkin finite element method. The results obtained are discussed and generalized to a three-dimensional case.

## 1. Introduction

Blast furnace slag cement (BFSC) is the most important product of the cement industry in the northern European countries, particularly in the Netherlands, Belgium and Germany. Apart from the low-heat application, the superior durability of BFSC against aggressive environment makes this material a suitable binder for the concrete exposed to chloride, acid and sulfate attack.

In general, the microstructure of Portland-slag cement pastes is not too different from that of ordinary Portland cement (OPC) [1]. However, it has been found that cements containing a high amount of BFS have a poor resistance against carbonation. It is generally known that the content of calcium hydroxide ($Ca(OH)_2$) in concrete plays an important role for carbonation resistance. Calcium carbonate ($CaCO_3$), which is a major product of $Ca(OH)_2$ carbonation, blocks the capillary pore in concrete leading to the reduction of gas diffusivity, thereby reducing the rate of carbonation. However, BFSC concrete tends to suffer much more from carbonation than the OPC mixture does due to its significantly lower $Ca(OH)_2$ content. One way to improve this disadvantage of BFSC concrete is to use sodium-monofluorophosphate (Na-MFP) as an addition to the cement mixture [2].

The solution of Na-MFP is encapsulated by use of cement paste to produce a *self-healing* system in the BFSC. The content of the capsule (Na-MFP) dissolves and diffuses through water which occupies the pores of both uncarbonated and carbonated parts of the cement specimen. The chemical reaction between Na-MPF and certain components of the carbonated cement matrix takes place such that fluoroapatite ($Ca_5(PO_4)_3F$) forms according to the following reaction equation:

$$5Ca(OH)_2 + 3Na_2PO_3F \quad \rightarrow \quad Ca_5(PO_4)_3(F, OH) + 4NaOH + 2NaF + 3H_2O \ .$$

Fluoroapatite is a highly insoluble compound which improves the micro-structure of BFSC and increases its tensile resistance.

In this paper we are going to consider a mathematical model for the post-damage improvement of the carbonated BFSC using expanded clay spherical capsules filled with Na-MFP.

## 2. The mathematical model

To construct a mathematical model of the healing process, we consider one spherical capsule of radius $R$ within a cement cube with side length $L \in [4R, 10R]$. The following assumptions are used:

- the cement cube is subject to carbonation and the ingress of gaseous carbon dioxide into the cement matrix takes place through the upper edge of the cube;
- the reaction of carbonation takes place in the narrow zone which can be approximated by a surface (a plane) referred to as *the carbonation front*; so, after some definite time, the cube is supposed to be divided by the carbonation front into two rectangular cuboids consisting respectively of carbonated and uncarbonated cement;
- both parts of the cement cube are penetrable for water to a different extent;
- the pores of both parts of the cement cube are filled with water, which facilitates diffusion of Na-MFP from the capsule through pores; we further neglect diffusive transport through solid cement particles;
- the carbonation front position $l$ is assumed to move downwards according to the relation $l(t) = L/2 - \kappa\sqrt{T+t}$ [4], where $l(0)$ is the initial $z$-coordinate of the horizontal carbonation front and $T$ is the known time of carbonation process which is necessary to reach the position $l(0)$.

The vertical rectangular section of the cement cube passing through the center of the capsule provides us with a representation for the two-dimensional mathematical model (Fig. 1 (*left*)). Due to symmetry reasons, we consider half of this cross-section (Fig. 1 (*right*)).

The domain of computation $\Omega$ consists of three parts, $\Omega_1$, $\Omega_2$, and $\Omega_3$ representing, respectively, the carbonated cement matrix, the capsule and the uncarbonated part of the cement matrix. The boundary $\partial\Omega$ of $\Omega$ is a rectangle of dimensions $L/2 \times L$.

Since the vast majority of the reacting chemicals in the cement is calcium hydroxide ($Ca(OH)_2$), we neglect the contribution of other cement components.

We denote the density of Na-MFP and $Ca(OH)_2$ by $c_1 = c_1(r, z, t)$ and $c_2 = c_2(r, z, t)$, respectively. The following differential equations hold for $c_1$ and $c_2$:

$$\frac{\partial c_1}{\partial t} = \nabla \cdot (D \, \nabla c_1) - 3 \, k \, c_1 \, \frac{1000 \, c_2}{\mathrm{M}_{\mathrm{Ca(OH)_2}}}, \ (r, z) \in \Omega, \ t > 0 \ , \tag{1}$$

$$\frac{dc_2}{dt} = -5 \, k \, c_2 \, \frac{1000 \, c_1}{\mathrm{M}_{\mathrm{Na_2PO_3F}}}, \ (r, z) \in (\Omega_1 \cup \Omega_3), \ t > 0 \ , \tag{2}$$

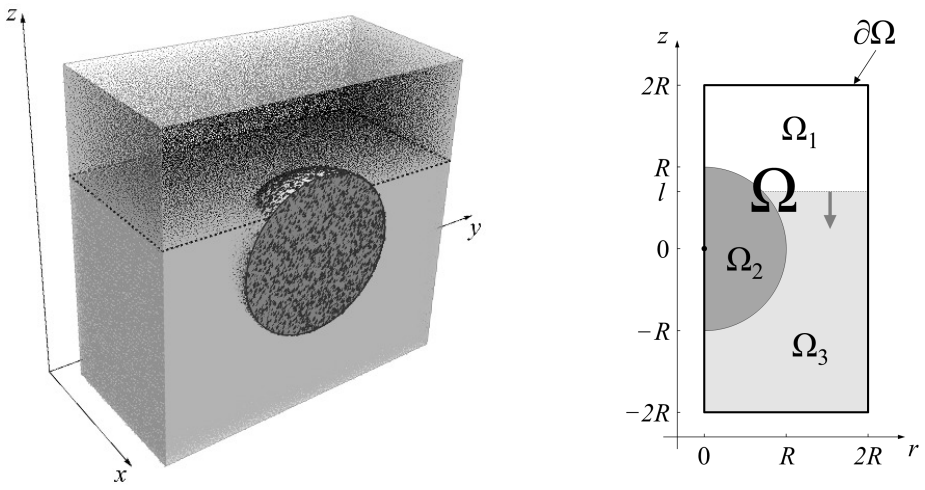


**Figure 1.** (*left*) Representation of a half of the concrete cube containing the capsule and consisting of uncarbonated (below) and carbonated (above) parts. (*right*) Computational domain for a two-dimensional mathematical model.

where $M_X$ are molar masses of corresponding chemicals, $k$ is a proportionality factor which determines the reaction rate, and the diffusion coefficient $D$ changes over space and time:

$$D = D(r, z, t) = D_0\, \varepsilon_i/\tau_i,\ (r, z) \in \Omega_i,\ t > 0,\ i = 1, 2, 3\ .$$

Here, $D_0$ is the actual diffusion coefficient of Na-MFP in water, $\varepsilon_i = \varepsilon_i(r, z, t)$ and $\tau_i = \tau_i(r, z, t)$ are, respectively, the effective porosity and tortuosity of the $i$-th medium. The capsule and both parts of the cement cube are penetrable for water to a different extent: the carbonated cement possesses a higher porosity which implies, according to the Kozeny-Carman equation [3], a higher permeability, whereas the porosity and, hence, permeability of the uncarbonated cement is much lower. The values of $\tau_i$ can be defined empirically or one can invoke the approximation $\tau_i \approx 1 - (\ln \varepsilon_i)/2$ described in [5], which we use in our calculations.

No transport of Na-MFP is assumed through the boundary of $\Omega$, hence we have a zero flux boundary condition.

The initial densities of Na-MFP and $Ca(OH)_2$ are defined as follows:

$$c_1(r, z, 0) = \begin{cases} c_1^{\max}, & (r, z) \in \Omega_2\,; \\ 0\,, & (r, z) \in \Omega_1 \bigcup \Omega_3 \end{cases} \quad \text{and} \quad c_2(r, z, 0) = \begin{cases} c_2^{\max}, & (r, z) \in \Omega_1\,; \\ 0\,, & (r, z) \in \Omega_2\,; \\ c_2^{\min}, & (r, z) \in \Omega_3\ . \end{cases} \tag{3}$$

Equations (1), (2), zero flux boundary condition, and initial conditions (3) form an initial boundary value problem in $\Omega$ and for $t > 0$.

After solving the boundary value problem on each time step, the density and the volume of fluoroapatite formed in $\Omega_1$ and $\Omega_3$ as well as values of $\varepsilon_1$ and $\varepsilon_3$ are corrected with regard to amounts of reacted chemicals.

## 3. Results and discussion

Equations (2) and (1) are solved using Galerkin finite element method over a structured triangle grid. Some results obtained through a computer simulation are presented in figure 2. In this example, we consider a half of the capsule section with the radius of 1 mm.

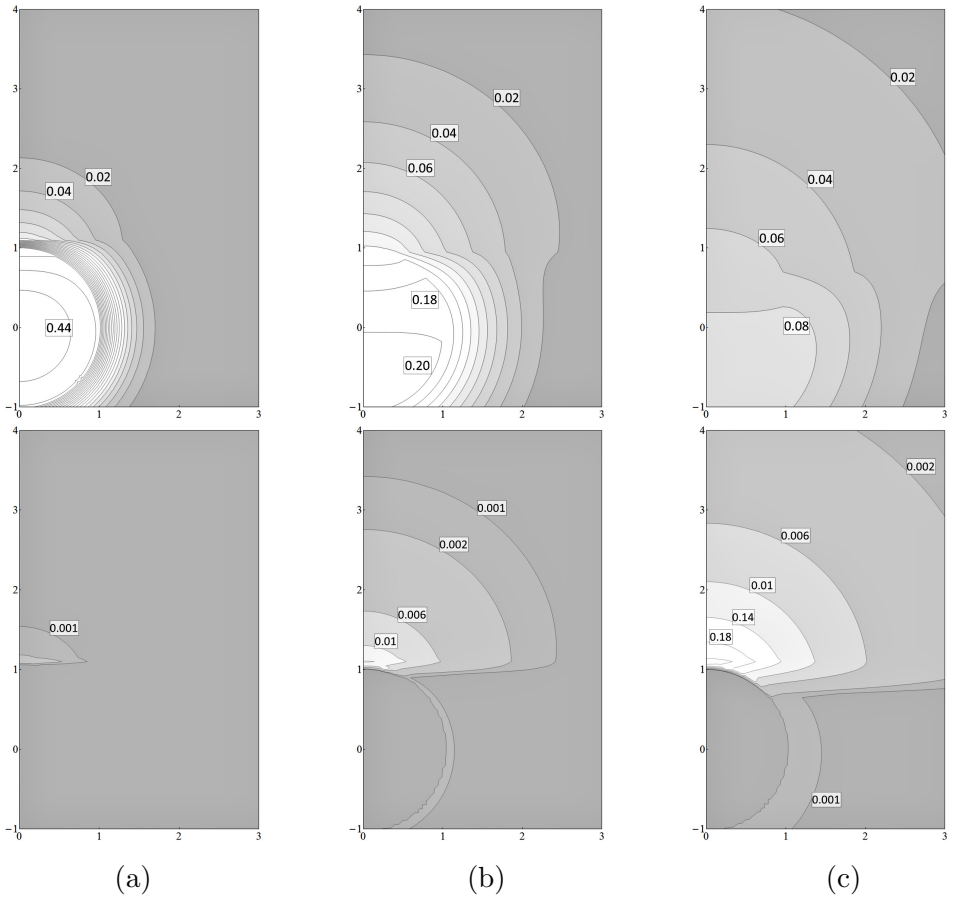


**Figure 2.** Concentration profile of Na-MFP (above) and density profile of fluoroapatite (below) after (a) 10, (b) 40 and (c) 80 days of healing process; $\varepsilon_1 = 0.15$, $\varepsilon_2 = 0.21$, $\varepsilon_3 = 0.02$.

In figure 2, the first row of illustrations represents the evolution of the Na-MFP concentration profile, whereas the second row shows the corresponding changes of fluoroapatite density around the capsule. The columns (a), (b) and (c) correspond to the state of both profiles at the certain moments of the healing process: after 10, 40 and 80 days, respectively.

It can be seen how the movement of the carbonation front influences the process of diffusion of Na-MFP and, hence, forming of fluoroapatite. It is possible also to retrace the process of growing of the fluoroapatite layer and, in particular, the layer in which the density of the reaction product exceeds 0.01 g/cm$^3$. This density is considered as sufficient to improve the cement structure. According to the results observed, one can make definite conclusions about necessary amount and concentration of Na-MFP in the capsule and the number of capsules per unit volume of cement.

A three-dimensional representation of this model can be obtained from symmetry considerations in a straight-forward manner.

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