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A two-scale modelling approach to reaction–diffusion processes in porous materials

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Abstract

A two-scale model for a reaction–diffusion process in a porous material is developed and applied to a simplified problem related to concrete carbonation. The material is exposed to a gas which enters from the outside, diffuses through the air-filled pore space, and dissolves into the pore water where it reacts with a second solute. The problem exhibits two different spatial scales due to the great difference in diffusivities of the gas in air and water and the fine pore geometry. In contrast to common purely macroscopic models, the proposed two-scale model is capable of resolving both scales. It is shown by numerical simulations that different pore geometries lead to different macroscopic output. Results of a comparable purely macroscopic model can be recovered as a special case.

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1. Introduction

In this paper, we develop a two-scale model for a reaction–diffusion process in an unsaturated porous material. The medium is exposed to a gas which enters the medium from the outside and diffuses through the air-filled pore space. It dissolves into the pore water where it reacts with a second solute. We consider the case where the diffusivity of the gas in air is much greater than in the pore water. Consequently, the problem exhibits two spatial scales: the *macroscopic* scale, at which the gas diffuses through the air-filled pore space and the *microscopic* scale, at which the gas diffuses in the pore water and reacts.

A typical process exhibiting this feature is the degradation of reinforced concrete structures induced by *carbonation*. This process takes place in the pores of the concrete which are partially saturated with water that clings to the pore walls. Atmospheric CO_2 enters the concrete through the air-filled pores and gets dissolved in the pore water. There it reacts with dissolved constituents of the cement paste. This causes a lowering of the pH, facilitating the corrosion of the steel reinforcements, and, consequently, leads to a severe reduction of the service life of the structure. The dominant carbonation reaction is usually assumed as:

$$CO_2(aq) + Ca(OH)_2(aq) \overset{H_2O}{\rightarrow} CaCO_3(aq) + H_2O.$$

The produced $CaCO_3$ precipitates very quickly to the solid matrix. Detailed surveys on the carbonation problem were carried out, for instance, by Kropp [1], Bier [2], and Chaussadent [3].

Existing models of the carbonation process describe the mass balances of the active species only on the macroscopic scale. We refer to the approaches by Saetta et al. [4], Papadakis et al. [5], and Steffens et al. [6]. The

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drawback of such pure macromodels is that effects due to the local pore geometry are only captured via few empirical constants such as the *tortuosity* and *porosity factors*. The relatively slow diffusion of CO_2(aq) and $Ca(OH)_2$(aq) in the pore water is usually neglected. A possible delay time caused by reactants not being immediately available is therefore not taken into account. In the present paper, we propose a model which consists of a macroscopic equation coupled with a microscopic system that is solved in every point on a *representative unit cell* (RUC). Such models have been proposed, mathematically justified, and implemented for flow in naturally fractured reservoirs [7–9]. There are also various two-scale computational approaches of modelling mechanical properties of materials with microstructure [10,11]. In this area of application, two-scale simulations have already proven efficient and reliable.

As we are primarily interested in studying the principal effects of such a model, we consider a highly simplified carbonation scenario. In Section 2, we present the two-scale model incorporating the basic reaction–diffusion processes inside the concrete. As a reference, a typical purely macroscopic model based on [5] is also included. In Section 3, we present simulation results for the carbonation of a concrete piece based on ordinary Portland cement (OPC). We consider two different RUC geometries and point out the differences in the results captured by the two-scale model but not resolved in the corresponding pure macromodel. In all cases, the problems in the RUC are reduced to one space dimension for computational reasons. However, it should be emphasised that the model is conceptually capable of being extended to a more complete carbonation scenario. Finally, Section 4 collects our main results and conclusions.

2. Mathematical modelling

In order to fix ideas, we develop the two-scale model for the particular problem of concrete carbonation. In this context, our model is based on the following simplifying assumptions.

(1) The humidity is uniformly distributed in the sample and time-independent.
(2) Dissolution of solid $Ca(OH)_2$ is sufficiently fast and is therefore neglected.
(3) No matrix constituents other than $Ca(OH)_2$ react with CO_2.
(4) The pore structure does not change in time.

Experiments show that, in reality, the pore structure is altered by the carbonation process itself. Moreover, the humidity entering the sample from outside or being produced by reaction can have a strong influence on the carbonation [6]. Nevertheless, we neglect these processes in this first approach and concentrate on the basic features of the two-scale model.

2.1. The two-scale model

We start with the representation of the local pore geometry. Let $x = (x_1, x_2, x_3)$ be a point of the concrete sample Ω. We assume the local pore geometry at x to be described by a *representative unit cell* (RUC) contained in a cuboid Y, as depicted in Fig. 1. In Y, a local coordinate system $y = (y_1, y_2, y_3)$ is introduced. We refer to y as the *microscopic* variable, in contrast to the *macroscopic* variable x. Three different phases are considered: the air-filled pore space Z^a, the water-filled pore space Z^w and the solid matrix Z^s. The air–water and water–solid interfaces are denoted by Γ^a and Γ^s, respectively.

The transport of the dissolved species in the pore water is comparably slow and therefore restricted to the local RUC. We denote the mass concentration of CO_2(aq) by $u_2(x, y, t)$ and that of $Ca(OH)_2$(aq) by $u_3(x, y, t)$. The mass balances read as:

$$\partial_t u_2 - D_2 \Delta_y u_2 = -m_2 R(u_2)^p (u_3)^q, \quad x \in \Omega, \quad y \in Z^w, \tag{1a}$$

$$\partial_t u_3 - D_3 \Delta_y u_3 = -m_3 R(u_2)^p (u_3)^q, \quad x \in \Omega, \quad y \in Z^w, \tag{1b}$$

where the diffusivities D_2 and D_3 are of the same magnitude. Here Δ_y denotes the Laplace operator where the derivatives are taken with respect to y. The macroscopic variable x serves only as a parameter in (1a) and (1b). To describe the reaction kinetics, we adopt a generalised form of the law used in [6]. The quantities $m_2 = 44$ g/mol and $m_3 = 74$ g/mol are the molar weights of CO_2 and $Ca(OH)_2$, respectively, whereas R, p, and q are empirical constants, Typical values are $p = q = 1$ and $R = 160\ \mathrm{mol\,cm^3/(g^2\,d)}$ [6].

The exchange of CO_2 with the air phase in the pores is described by Henry's law. This leads to the boundary condition at the air–water interface Γ^a:

$$-D_2 \nabla_y u_2 \cdot \nu = -K(H u_1 - u_2), \quad y \in \Gamma^a, \tag{1c}$$

where $u_1(x,t)$ is the mass concentration of CO_2(g) in air, $H = 0.81$ is the Henry constant for CO_2 in water [12], and ν is the outward unit normal at Γ^a. Therefore, the microscopic system is closed by the no-flux conditions:

$$\begin{aligned} &-D_2 \nabla_y u_2 \cdot \nu = 0, \quad y \in \Gamma^s; \\ &-D_3 \nabla_y u_3 \cdot \nu = 0, \quad y \in \Gamma^a \cup \Gamma^s \end{aligned} \tag{1d}$$

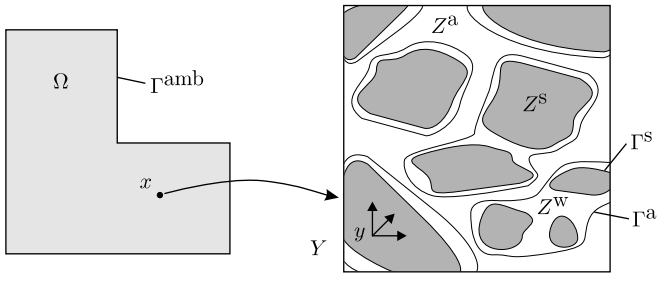

Fig. 1. A cross-section of a corner of a concrete structure, together with a typical RUC around a point x of the medium.