Multiscale sulfate attack on sewer pipes: numerical study of a fast micro-macro mass transfer limit
Chalupecky, V.; Fatima, T.; Muntean, A.

Published: 01/01/2010

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
• A submitted manuscript is the author's version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Citation for published version (APA):

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.
• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal ?

Take down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.
Multiscale sulfate attack on sewer pipes: Numerical study of a fast micro-macro mass transfer limit

by

V. Chalupecký, T. Fatima, A. Muntean
Multiscale sulfate attack on sewer pipes: Numerical study of a fast micro-macro mass transfer limit

Vladimír Chalupecký, Tasnim Fatima, and Adrian Muntean

July 15, 2010

Abstract. We present two multiscale reaction-diffusion (RD) systems modeling sulfate attack in concrete structures (here: sewer pipes). The systems are posed on two different spatially separated scales. The only difference between them is the choice of the micro-macro transmission condition. We explore numerically the way the macroscopic Biot number \(Bi^M\) connects the two reaction-diffusion scenarios. We indicate connections between the solution of the "regularized" system (with moderate size of \(Bi^M\)) and the solution to the "matched" system (with blowing up size of \(Bi^M\)), where Henry’s law plays the role of the micro-macro transmission condition.

Keywords. Multiscale RD system, micro-macro transmission conditions, sulfate corrosion, acid attack, modeling of concrete, method of lines, finite difference scheme, convergence rates

Abbreviations. RD – reaction-diffusion; PDEs – partial differential equation(s); ODEs – ordinary differential equation(s); EOC – experimental order of convergence

1. INTRODUCTION

In this paper, we deal with the problem of corrosion of concrete sewer pipes (and other structures made of concrete) that sustain the attack of aggressive compounds like sulfuric acid. In the context of mathematical modeling of concrete corrosion, the general objective is to develop models that can give reliable predictions on the rate of corrosion and on the speed of an advancing corrosion front separating corroded and undamaged concrete.

Concrete is a material with porous structure – it can be viewed as consisting of a solid matrix and a system of interconnected pores and fissures, which are partly filled with water. Böhml et al. [4] describe this structure for the gypsum layer formed as a product of sulfatation reactions. There are two scales related inherently to the size of the air and water phase and to the chemical reactions taking place there. The network of pores allows for a fast diffusion of gaseous compounds (like \(H_2S\) in the case of sewer pipes) throughout the air phase on the macroscale. On the other hand, diffusion (and chemical reactions) in the water phase are limited by the size of pores and thus take place at a much smaller, microscopic scale. This scenario indicates that one really needs to get a sound understanding of structured transport – since this is the main mechanism responsible for a significant interplay between micro (pore level) and macro (pipe level) scales. These considerations motivate our multiscale approach to this corrosion process.

The main focus of this paper is to study the role of two micro-macro transmission conditions. In order to do this we look for the numerical solution of two multiscale partly dissipative reaction-diffusion systems modeling sulfate attack that are derived via homogenization in [9]. These systems are posed on two different spatially separated scales, the only difference between them being the choice of the micro-macro transmission condition imposed at the air-water interface. The multiscale nature of the model allows us to perform computations at macroscopic length scales that are relevant for practical applications while taking into account transport and reactions occurring at very small scales. At this point, the relevant scientific questions are: (i) How can one bridge the micro information to the macro one? (ii) Are there other alternatives? (iii) Which is the right one?

Here we choose to deal with question (i). Namely, we explore numerically the way the macroscopic Biot number \(Bi^M\) connects the two reaction-diffusion scenarios mentioned before. Furthermore, we hope to be able to find relations between the solution of the "regularized" system (with moderate size of \(Bi^M\)) and the solution to the "matched" system (with blowing up size of \(Bi^M\)), where Henry’s law plays the role of the micro-macro transmission condition.

The paper is organized as follows: Descriptions of the involved chemistry and basic geometry are given in sections 1.1 and 2.1, respectively. The two-scale model equations are outlined in 2.2 and their well-posedness is addressed in section 2.3. The bulk of the paper is contained in section 3 and section 4. We close the paper with section 5 that includes a brief discussion of a couple of open multiscale questions that we wish to address as next step.

1.1. BASIC DESCRIPTION OF THE CHEMISTRY

Sulfuric acid (\(H_2SO_4\)) is one of the most aggressive acids that can come in contact with concrete structures. It destroys the strength of the concrete completely and causes spalling and material corrosion. The chemical picture is rather simple: Active anaerobic bacteria existing in the waste water produce gaseous \(H_2S\) which moves in the air space of the pipe and goes up towards the pipe wall. Then
The modeling tool is a moving-boundary strategy. From a macroscopic PDE models to capture the motion of the Henry's law is [7].

The transfer of $\text{H}_2\text{S}$ is modeled here by means of the Henry’s law, while the production of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is incorporated in a non-standard non-linear reaction rate, here denoted as $\eta$; see (3) for a precise choice. Equation (4) indicates the linearity of the Henry’s law structure we have in mind. The standard reference for modeling gas-liquid reactions at stationary interfaces (including a derivation of the linear law, while the production of gypsum at micro solid-water interfaces.

The transfer of $\text{H}_2\text{S}$ is modeled here by means of the Henry’s law, while the production of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is incorporated in a non-standard non-linear reaction rate, here denoted as $\eta$; see (3) for a precise choice. Equation (4) indicates the linearity of the Henry’s law structure we have in mind. The standard reference for modeling gas-liquid reactions at stationary interfaces (including a derivation of the linear law, while the production of gypsum at micro solid-water interfaces.

There are many chemical reactions taking place in the pores of sewer pipes which degrade the performance of the pipe structure depending on the intensity of the interaction between the chemical reactions and the local environment. Here we focus our attention on the following few relevant chemical reactions:

\begin{align*}
(1a) & \quad 10\text{H}^+ + \text{SO}_4^{2-} + \text{organic matter} \rightarrow \text{H}_2\text{S(aq)} + 4\text{H}_2\text{O} + \text{oxidized matter} \\
(1b) & \quad \text{H}_2\text{S(aq)} + 2\text{O}_2 \rightarrow 2\text{H}^+ + \text{SO}_4^{2-} \\
(1c) & \quad \text{H}_2\text{S(aq)} \rightleftharpoons \text{H}_2\text{S(g)} \\
(1d) & \quad 2\text{H}_2\text{O} + \text{H}^+ + \text{SO}_4^{2-} + \text{CaCO}_3 \rightarrow \text{HCO}_3^- + \text{CaSO}_4 + 2\text{H}_2\text{O}.
\end{align*}

It is worth mentioning at this point, that if this is needed we can extend our multiscale models with minimal effort to more complex chemical reactions.

### 1.2. Related literature

From the modeling viewpoint, we are very much inspired by the comprehensive description of the sulfate corrosion mechanisms relevant for sewage systems as presented in [4, 12, 13]. Note that in the loc. cit. papers, the authors propose macroscopic PDE models to capture the motion of a macroscopic corrosion front penetrating sewer pipes – the modeling tool is a moving-boundary strategy. From a different perspective\(^2\), mathematically sound macroscopic approaches of sulfatation of carbonated stones (especially connected with conservation of historical heritage) are reported by Aregba-Driollet et al. in [1] and references therein. Standard reference works regarding cement chemistry are [10, 26]. For a detailed description of the mechanisms leading to sulfate corrosion in concrete, we refer the readers to standard civil engineering literature like [3, 14, 21, 25, 27], or [22]. It is worth noting that there is a lot of literature on sulphate attack. For instance, a lot of modeling work has been done by K. Scrivener and co-workers at the EPFL in Lausanne, F. Glasser in Aberdeen, F. Schmid-Döhl, E. Rigo (the software Transreac) in Hamburg. They all use a Gibbs energy minimization approach. The major issue when choosing this modeling alternative is that one cannot investigate anymore transport effects. To fill this gap, E. Beddoe, W. Dörner and collaborators from TU München use the code PHREEQC not only because it has a huge data base and is easy to use, but also because it seems that it can take diffusion of the various species into account.

None of these approaches is able to cope with the inherent multiscale geometry of the pore matrix. This is the place where we wish to contribute with our mathematical understanding of two-spatial-scale systems; compare [16, 18, 20] and also [8, 15].

## 2. Two-scale model for sulfate attack

### 2.1. Basic two-scale geometry

We consider a sewer pipe made of partially wet concrete. Focusing on the already damaged part of the concrete, we consider a single critical macroscopic region $\Omega := (0, L)$ (with $L > 0$) representing a concrete sample along a line perpendicular to the pipe surface, where corrosion initiates, and aim to follow the space-time evolution of the damage. The boundary of $\Omega$, say $\Gamma$, is composed of two disjoint parts $\Gamma^D := \{0\}$ (the inner surface of the pipe) and $\Gamma^N := \{L\}$, the Dirichlet and the Neumann boundaries. As typical microstructure (or standard cell [11]) we take $Y := (0, \ell)$ (with $\ell > 0$).

Usually cells in concrete contain a stationary water film, and air and solid fractions in different ratios depending on the local porosity. Generally, we expect that the choice of the microstructure depends on the macroscopic position $x \in \Omega$, i.e., we would then have $Y_x$; see [9] for more comments in this direction directly related to this sulfatation problem and [15] for a rather general RD setting posed in heterogeneous ($x$-dependent) domains. Here we assume that the medium $\Omega$ is made by periodically repeating the same microstructure $Y$ ($\Omega$ is a perfectly periodically paved region). Furthermore, since at the microscopic level the involved reaction and diffusion processes take place in pore water, we choose to denote by $Y$ only the wet part of the pore.

Finally, let $S$ be the time interval $(0, T)$ (with $T > 0$) during which we consider the process. As a rule $\Delta_y$ denotes the Laplacian incorporating partial derivatives only w.r.t.
the variable \( y \in Y \), while \( \Delta \) will be the Laplacian referring only to the partial derivatives w.r.t. the variable \( x \in \Omega \). A similar rule defines \( \partial_x \) and \( \partial_y \).

2.2. Outline of two-scale model equations

We consider the following two-scale system of PDEs and one ODE for unknown functions \( w_k : \Omega \times Y \times S \rightarrow \mathbb{R} \), \( k \in \{1, 2, 4, 5\} \), \( w_3 : \Omega \times S \rightarrow \mathbb{R} \), and \( w_5 : \Omega \times \{y = \ell\} \times S \rightarrow \mathbb{R} \) such that

\[
\begin{align*}
(2a) & \quad \beta_1 \partial_t w_1 - \beta_1 d_1 \Delta_y w_1 = -\Phi_1^3 k_1 w_1 + \Phi_2\kappa k_2 w_2, & \text{in } \Omega \times Y \times S, \\
(2b) & \quad \beta_2 \partial_t w_2 - \beta_2 d_2 \Delta_y w_2 = \Phi_1^3 k_1 w_1 - \Phi_2\kappa k_2 w_2, & \text{in } \Omega \times Y \times S, \\
(2c) & \quad \partial_t w_3 - d_3 \Delta w_3 = -Bi^M (H w_3 - w_2 |_{y = 0}), & \text{in } \Omega \times S, \\
(2d) & \quad \beta_4 \partial_t w_4 - \beta_4 d_4 \Delta_y w_4 = k_1 w_1, & \text{in } \Omega \times Y \times S, \\
(2e) & \quad \beta_5 \partial_t w_5 = +\Phi_2\kappa (w_1, w_5), & \text{in } \Omega \times \{y = \ell\} \times S,
\end{align*}
\]

where \( \beta_k > 0, k \in \{1, 2, 4, 5\} \), are parameters, \( d_k > 0, k \in \{1, 2, 3, 4\} \), are the diffusion coefficients, \( Bi^M \) is a dimensionless Biot number [28], and \( k_k : Y \rightarrow \mathbb{R}, k \in \{1, 2, 3\} \), are functions modeling the rate "constants". We assume the reaction rate \( \eta \) takes the form

\[
(3) \quad \eta(\alpha, \beta) = \begin{cases} \\
\ \ k_3 \alpha^p (\hat{c} - \beta)^q, & \text{if } \alpha > 0, \ \beta > 0, \\
0, & \text{otherwise},
\end{cases}
\]

where \( \hat{c} \) is a known equilibrium constant concentration and \( p \geq 1, q \geq 1 \) are the partial orders of reaction. The \( \Phi_k^2, k \in \{1, 2, 3\} \), are Damköhler numbers [28] corresponding to three distinct chemical mechanisms (reactions). They are dimensionless numbers that compare the characteristic time of the fastest transport mechanism (here: the diffusion of \( H2S \) in the gas phase) to the characteristic timescale of the \( k \)-th chemical reaction. It is worth noting that terms like

\[
(4) \quad Bi^M (H w_3(t, x) - w_2(t,x, y = 0))
\]

are usually referred to in the literature as production terms by Henry’s or Raoult's law; see [7]. \( H > 0 \) is the Henry's constant. The special feature of our scenario is that now the term (4) bridges two distinct spatial scales: one macro with \( x \in \Omega \) and one micro with \( y \in Y \).

The system (2) is supplemented with initial and boundary conditions, which read as

\[
(5a) \quad -d_1 \partial_y w_1 = 0, \quad \text{on } \Omega \times \{y = 0\} \times S, \\
(5b) \quad -d_1 \partial_y w_1 = +\Phi_3^{\gamma_3}(w_1, w_3), \quad \text{on } \Omega \times \{y = \ell\} \times S, \\
(5c) \quad -d_2 \partial_y w_2 = -Bi^M (H w_3 - w_2), \quad \text{on } \Omega \times \{y = 0\} \times S, \\
(5d) \quad -d_2 \partial_y w_2 = 0, \quad \text{on } \Omega \times \{y = \ell\} \times S, \\
(5e) \quad w_3 = w_3^0, \quad \text{on } \Gamma^D \times S, \\
(5f) \quad -d_3 \partial_x w_3 = 0, \quad \text{on } \Omega \setminus \Gamma^D \times S, \\
(5g) \quad -d_4 \partial_y w_4 = 0, \quad \text{on } \Omega \times \{y = 0\} \times S, \\
(5h) \quad -d_4 \partial_y w_4 = 0, \quad \text{on } \Omega \times \{y = \ell\} \times S.
\]

Note that the "information" at the microscale is connected to the macroscale situation via the right-hand side of (2e) and via the micro-macro transmission condition (5c). Remark that all involved parameters (except for \( H, d_1 \) and \( Bi^M \)) contain microscopic information. The coefficients \( d_3 \) and \( Bi^M \) are effective ones (see [9] for a way of calculating them), while \( H \) can be read off from existing macroscopic experimental data. For more modeling details, we refer the reader to [4, 9] and references cited therein.

We refer to (2a)–(5h) as problem \((P)\).

2.3. Well-posedness of problem \((P)\)

Let us assume the following restrictions on data and parameters:

- (A1) \( d_i > 0 \) \( (i \in \{1, \ldots, 4\}) \), \( \beta_j > 0 \) \( (j \in \{1, 2, 4, 5\}) \), \( \Phi_2 > 0 \) \( (i \in \{1, 2, 3\}) \).
- (A2) The reaction term \( \eta : \mathbb{R} \times \mathbb{R} \rightarrow \mathbb{R}_+ \) is globally Lipschitz with respect to both variables;
- (A3) \( w_3^0 \in H^1(S, H^2(\Omega)) \cap H^2(S, L^2(\Omega)) \cap L_\infty^\gamma(S \times \Omega), w_3 |_{\Omega} \in H^2(\Omega) \cap L^\infty(\Omega), w_{30} = w_3^0 |_{\Omega} \in H_0^1(\Omega), w_{30} |_{\Omega} \in L^p(\Omega, H^2(\Omega)) \cap L_\infty^\gamma(\Omega \times Y) \) for \( p \in \{1, 2, 4\} \), and \( w_{50} \in L^2(\Omega \times \{y = \ell\}) \cap L_\infty^\gamma(\Omega \times \{y = \ell\}) \).

Let us introduce the set of indices \( \mathcal{I} := \{1, 2, 4\} \) as well as the functions \( F_i : \mathbb{R}^3 \rightarrow \mathbb{R} \) defined by

\[
(6) \quad F_1(r) := -\Phi_1^2 k_1 r_1 + \Phi_2^2 k_2 r_2, \\
(7) \quad F_2(r) := \Phi_1^2 k_1 r_1 - \Phi_2^2 k_2 r_2, \\
(8) \quad F_3(r) := k_1 r_1, 
\]

for all \( r := (r_1, r_2, r_3) \in \mathbb{R}^3 \).

Our concept of weak solution is as follows:

**Definition 1.** The vector of functions

\[
(9) \quad (w_1, w_2, w_3, w_4, w_5)
\]

with \( w_3 - w_3^0 \in L^2(S, H_0^1(\Omega)), \partial_t w_3 \in L^2(S \times \Omega), w_i \in L^2(S, L^2(\Omega, H^1(\Omega))), \partial_t w_i \in L^2(S \times \Omega \times Y) \) for all \( i \in \mathcal{I} \), and \( w_{50}(., x, y) \in H^1(S) \) for a.e. \((x, y) \in \Omega \times Y\), is called weak solution to problem \((P)\) if for a.e. \( t \in S \) the following identities hold:

\[
\int_\Omega \partial_t w_3 \varphi_3 + d_3 \int_\Omega \nabla w_3 \nabla \varphi_3 = -\int_\Omega \nabla_y w_2 |_{y = 0} \varphi_3,
\]
\[ \sum_{i \in I} \beta_i \int_{\Omega} \int_Y \partial_t w_i \varphi_i + \sum_{i \in I} \beta_i d_i \int_{\Omega} \int_Y \nabla_y w_i \nabla_y \varphi_i = \int_{\Omega} \sum_{i \in I} F_i(w) \varphi_i, \]

and

\[ \beta_5 \partial_t w_5 = + \Phi_5^2 \eta(w_1, w_5), \]

for all \( \varphi := (\varphi_1, \varphi_2, \varphi_3, \varphi_4) \in \left[ L^2(\Omega; H^1(Y)) \right]^2 \times H^1_0(\Omega) \times L^2(\Omega; H^1(Y)) \).

**Lemma 2.** Let the assumptions (A1)–(A3) be satisfied. Then the weak solutions in the sense of Definition 1 are positive and bounded a.e. in \( \Omega \) or, following the case, in \( \Omega \times Y \).

**Proof.** The conclusion of this result is obtained by choosing special test functions in Definition 1 in combination with a suitable application of Gronwall’s lemma. \( \square \)

**Theorem 3** (Global existence and uniqueness). Let the assumptions (A1)–(A3) be satisfied and let \( \tau > 0 \) be arbitrarily chosen. Then problem (P) admits a unique positive and bounded (weak) solution such that

1. \( w_3 \in w_3^2 + L^2([0, \tau] ; H^1_0(\Omega)), \)
2. \( \partial_t w_3 \in L^2([0, \tau] \times \Omega), \)
3. \( (w_1, w_2, w_4) \in \left[ L^2([0, \tau] ; L^2(\Omega ; H^1(Y))) \right]^3, \)
4. \( (\partial_t w_1, \partial_t w_2, \partial_t w_4) \in \left[ L^2([0, \tau] \times \Omega \times Y) \right]^3, \)
5. \( w_5 \in H^1([0, \tau] ; L^3(\Omega \times \{ y = \ell \})). \)

**Sketch of the proof.** We obtain the existence of weak solutions to problem (P) relying on the two-scale Galerkin scheme developed in [20]. The idea is to exploit the special structure of the PDE system. In this way, the function spaces to be used for the (two-scale) Galerkin approximation of the solution can be chosen as tensor product of spaces on the macroscopic domain \( \Omega \) and microstructure (local cell) \( Y \). Sufficient uniform estimates for the finite dimensional approximations permit the convergence of the approximating sequence. Additionally, we can also prove the uniqueness of positive and bounded weak solutions to (P). \( \square \)

**Remark 4.** It is worth noting that there are at least three other strategies than that sketched above, which are able to analyze this class of multiscale reaction-diffusion scenarios.

(i) Problem (P) can also deal with in a more direct way, i.e., without a derivation via homogenization from a lower spatial scale. More precisely, it can be formulated as a Cauchy problem in a Hilbert space and resolved by holomorphic semigroups in the spirit of [24].

(ii) Trusting [15, 23], a suitable construction of a fixed-point operator can also provide the existence of weak solutions to (P).

2.4. **Two-scale model with fast Henry-type transfer limit**

We are interested in understanding the behavior of solutions to problem (P) as the mass-transfer Biot number \( Bt_M \) goes to infinity. In particular, we expect the solution \( (w_1', w_2', w_3', w_4', w_5') \) of problem (P) to converge as

\[ \epsilon := \frac{1}{Bt_M} \to 0 \]

to the solution \( (u_1, u_2, u_3, u_4, u_5) \) of the following problem, say \((\tilde{P})\):

\[ \begin{align*}
(15a) \quad & \beta_1 \partial_t u_1 - \beta_1 d_1 \Delta_y u_1 = -\Phi_1^2 k_1 u_1 + \Phi_2^2 k_2 u_2, \\
& \quad \text{in} \; \Omega \times Y \times S, \\
(15b) \quad & \beta_2 \partial_t u_2 - \beta_2 d_2 \Delta_y u_2 = \Phi_1^2 k_1 u_1 - \Phi_2^2 k_2 u_2, \\
& \quad \text{in} \; \Omega \times Y \times S, \\
(15c) \quad & \partial_t u_3 - d_3 \Delta u_3 = 0, \quad \text{in} \; \Omega \times S, \\
(15d) \quad & \beta_4 \partial_t u_4 - \beta_4 d_4 \Delta_y u_4 = k_1 u_1, \quad \text{in} \; \Omega \times Y \times S, \\
(15e) \quad & \beta_5 \partial_t u_5 = + \Phi_5^2 \eta(u_1, u_5), \\
& \quad \text{in} \; \Omega \times \{ y = \ell \} \times S,
\end{align*} \]

with

\[ \begin{align*}
(16a) \quad & -d_1 \partial_y u_1 = 0, \quad \text{on} \; \Omega \times \{ y = 0 \} \times S, \\
(16b) \quad & -d_1 \partial_y u_1 = + \Phi_1^2 \eta(u_1, u_5), \quad \text{on} \; \Omega \times \{ y = \ell \} \times S, \\
(16c) \quad & u_2 = H u_3, \quad \text{on} \; \Omega \times \{ y = 0 \} \times S, \\
(16d) \quad & -d_2 \partial_y u_2 = 0, \quad \text{on} \; \Omega \times \{ y = \ell \} \times S, \\
(16e) \quad & u_3 = u_3^D, \quad \text{on} \; \Gamma^D \times S, \\
(16f) \quad & -d_3 \partial_x u_3 = 0, \quad \text{on} \; \Omega \setminus \Gamma^D \times S, \\
(16g) \quad & -d_4 \partial_y u_4 = 0, \quad \text{on} \; \Omega \times \{ y = 0 \} \times S, \\
(16h) \quad & -d_4 \partial_y u_4 = 0, \quad \text{on} \; \Omega \times \{ y = \ell \} \times S,
\end{align*} \]

Note that (16c) is actually the well-known Henry’s law. Following the terminology of Cook and Showalter [6], problem \((\tilde{P})\) is a matched microstructure model.

**Remark 5.** The analysis of problem \((\tilde{P})\) can be done in the same spirit as indicated in section 2.3.

3. **Numerical scheme**

In this section, we describe a semi-discrete numerical scheme for the problem (P) based on finite-difference discretization in space.
Let \( h_x := L/N_x \) and \( h_y := \ell/N_y \) be the spatial step sizes, where \( N_x \) and \( N_y \) are positive integers. Let \( \Omega_h := \{ x_i := ih_x \in \Omega \mid i = 0, \ldots, N_x \} \) and \( Y_h := \{ y_j := jh_y \in Y \mid j = 0, \ldots, N_y \} \) be uniform grids of nodes on \( \Omega \) and \( Y \), respectively. Also, let \( \omega_h := \Omega_h \times Y_h \) and \( \omega'_h := \Omega_h \times \{ y_{N_y} \} \). We define sets of grid functions on \( \Omega_h \), \( \omega_h \) and \( \omega'_h \) as \( G_h := \{ u_h \mid u_h : \Omega_h \to \mathbb{R} \} \), \( G^2_h := \{ \Phi_h \mid \Phi_h : \omega_h \to \mathbb{R} \} \) and \( G^3_h := \{ \Phi_h \mid \Phi_h : \omega'_h \to \mathbb{R} \} \), respectively, such that \( u_i := u_h(x_i), \) \( u_h \in G_h \), \( \omega'_h \) and \( v_{ij} := v_h(x_i, y_j), \) \( v_h \in G^3_h \). Finally, we define the discrete Laplacian operators as \( \Delta_h u_i := (u_{i-1} - 2u_i + u_{i+1})/h_x^2 \), for \( u_i \in G_h \), and as \( \Delta_Y v_{ij} := (v_{i,j-1} - 2v_{i,j} + v_{i,j+1})/h_y^2 \), for \( v_h \in G^3_h \).

A quintuple \( \{ w^k_h \mid k = 1, \ldots, 5 \} \) with \( w^k_h \in C^1([0, T], G^3_h) \), \( k \in \{ 1, 2, 4 \} \), \( w^0_h \in C^1([0, T], G_h) \), \( w^5_h \in C^1([0, T], G^3_h) \) is called a semi-discrete solution of the problem \( (P) \), if it satisfies the following system of ODEs

\[
\begin{align*}
(17a) & \quad \beta_1 \frac{dw^1_{ij}}{dt} = \beta_1 d_1 \Delta_Y h w^1_{ij} - \Phi^3_h k_1 w^1_{ij} + \Phi^2_h k_2 w^2_{ij}, \\
(17b) & \quad \beta_2 \frac{dw^2_{ij}}{dt} = \beta_2 d_2 \Delta_Y h w^2_{ij} + \Phi^3_h k_1 w^1_{ij} - \Phi^2_h k_2 w^2_{ij}, \\
(17c) & \quad \frac{dw^3_i}{dt} = d_3 \Delta_h w^3_i - B_i^M (H w^3_i - w^2_{i,0}), \\
(17d) & \quad \beta_4 \frac{dw^4_{ij}}{dt} = \beta_4 d_4 \Delta_Y h w^4_{ij} + k_1 w^1_{ij}, \\
(17e) & \quad \beta_5 \frac{dw^5_{ij}}{dt} = \Phi^3_h \beta_5 (w^1_{i,N_y} w^3_{ij}), \quad i = 0, \ldots, N_x,
\end{align*}
\]

for \( t > 0 \), together with the initial conditions

\[
(17f) \quad w^k_h(0) = \mathcal{P}^k_h w_{k0}, \quad k = 1, \ldots, 5,
\]

where \( \mathcal{P}^k_h \) denotes projection operators that project conti-
Valued functions $w_{40}$ on the corresponding grids.

Values of grid functions on nodes outside the grids, that arise in (17), are eliminated using centered difference approximations of the boundary conditions (5). Thus, for these values and for the Dirichlet boundary condition we obtain the following relations

\[(18a)\] \[w_{1,-1}^i = w_{1,1}^i, \quad i = 0, \ldots, N_x,\]
\[(18b)\] \[w_{1,N_y+1}^i = w_{1,N_y-1}^i - \frac{2h_y \Phi_i^2}{d_1} \eta(w_{1,N_y}^i, w_i^5), \quad i = 0, \ldots, N_x,\]
\[(18c)\] \[w_{2,1}^{i-1} = w_{2,1}^i + \frac{2h_y Bi M}{d_2} \left(H w_i^3 - w_i^2(0)\right), \quad i = 0, \ldots, N_x,\]
\[(18d)\] \[w_{2,N_y+1}^i = w_{2,N_y-1}^i, \quad i = 0, \ldots, N_x,\]
\[(18e)\] \[w_3^0 = w_3^4,\]
\[(18f)\] \[w_{3,N_y+1}^i = w_{3,N_y-1}^i, \quad i = 0, \ldots, N_x,\]
\[(18g)\] \[w_{4,1}^{i-1} = w_{4,1}^i, \quad i = 0, \ldots, N_x,\]
\[(18h)\] \[w_{4,N_y+1}^i = w_{4,N_y-1}^i, \quad i = 0, \ldots, N_x,\]

for $t > 0$.

In this section we present numerical results illustrating the behavior of solutions to the problem (P). The numerical results for the problem (P) were obtained by integrating the initial value problem (17), (18) in time by means of the toolbox CVODE [5].

We perform the numerical experiments on $\Omega = (0, 10)$ and $\Gamma = (0, 1)$. The computational grid is chosen so that $N_x = N_y = 128$, unless stated otherwise. The relative and absolute tolerance for the CVODE solver is set to the value of 10$^{-9}$. We assume zero constant initial conditions for $w_k^0(0)$, $k = 2, 4, 5$ (i.e., there is no initial concentration of H$_2$S, moisture and gypsum, respectively), while we assume $w_k^0(0) = 0.01$ (i.e., low initial concentration of H$_2$SO$_4$). The value of the initial concentration $w_k^0(0)$ is chosen to be compatible with the Dirichlet boundary condition $w_3^0 = 0.011$. The values of the remaining parameters which are common to all presented numerical experiments are summarized in Table 1.
and meshes, i.e., meshes with the spatial step sizes
of approximate solutions obtained on two successive
Then we measure the convergence by comparing the er-
Finally, we consider a set of gradu-
As there is no analytical solution available against which
In this paragraph we present results of measuring the ex-
4.1. Rate of convergence of the scheme (17) for

In this paragraph we present results of measuring the ex-

As there is no analytical solution available against which

To quantify the error, we define the following discrete

for $k \in \{3, 5\}$ and

for $k \in \{1, 2, 4\}$.
for \( k \in \{3, 5\} \) and

\[
\|e_k^h\|_2 := \frac{h_x h_y}{4} \sum_{i=0}^{N_x-1} \sum_{j=0}^{N_y-1} \left( (e_{ij}^k)^2 + (e_{i+1,j}^k)^2 \right) + (e_{i,j+1}^k)^2 + (e_{i+1,j+1}^k)^2,
\]

\[
\|e_k^h\|_{\infty} := \max_{x \in G^N} |e_{ij}^k|,
\]

for \( k \in \{1, 2, 4\} \).

Finally, we define the experimental order of convergence \( EOC^h_p \) of \( w^k_h \) as

\[
EOC^h_p := \log_2 \left( \frac{\|e_k^h\|_p}{\|e_{k/2}^h\|_p} \right).
\]

Using these definitions we performed the analysis of the rate of convergence for \( w^k_h, k = 1, \ldots, 5 \). We set \( L_x = L_y = 1 \) to obtain equal spatial step sizes in both directions and we evolved the solution until \( T = 80 \). Also, to minimize the influence of the truncation error from the time integration, we set the relative and absolute tolerance to a stringent value of \( 10^{-13} \). The Biot number \( Bi^M \) was set equal to 86.4 and the values of the remaining parameters are given in Table 1. The results of the EOC computations are given in Table 2 where the error is measured in \( L^2 \)-norms (21), (23) and in Table 3 where the error is measured in maximum norms (22), (24). In the first column the number of mesh nodes \( N \) in one direction is shown (the corresponding spatial step size is thus \( h_x = h_y = 1/2^N \)). In the following columns we show the norm of the error function for each \( w^k_h, k \in \{1, \ldots, 5\} \) together with the EOC.

From the obtained results we can conclude that, with very high probability, the scheme converges with second-order accuracy.

### 4.2. Illustration of Concentration Profiles for \( \epsilon > 0 \)

We next present several computations in order to demonstrate the behavior of the system \((P)\) for various values of the parameter \( \epsilon \) defined in (14), that is for various values of \( Bi^M \). We used parameter values as described at the beginning of this Section and in Table 1. We evolved the solution until \( T = 800 \).

The numerical solutions are presented in the figures in the following way. In the columns, the time evolution of each of the functions \( w_k \) is shown and each row corresponds to one time moment (displayed at left) with the top row showing the initial conditions. We plot functions \( w_k, k \in \{1, 2, 4\} \), defined on \( \Omega \times Y \) as functions of \( y \) for four fixed values of \( x \in X := \{1, 3, 5, 9\} \) (i.e., we plot the profiles of these functions at pores located at the specified \( x \) positions). The position of these values of \( x \) is shown in the third and fifth column as colored vertical dotted lines and the color of each dotted line matches the color of the graph of the functions \( w_k(x, \cdot), k \in \{1, 2, 4\} \), \( x \in X \), in the first, second and fourth column.

The result of the first computation is shown in Fig. 1 where \( Bi^M = 0.00864 (\epsilon \approx 115.741) \). We also use this example to describe a typical behavior of the solution of the system (2). Starting with the middle column displaying the evolution of \( w_3 \) we see that at the onset of the simulation, the initially constant concentration of \( H_2S \) in the air phase decreases rapidly as it enters through the air-pore water interface into the water phase at each pore unsaturated by \( H_2S \). The concentration of \( H_2S \) in the sewer atmosphere is assumed constant and is modelled by the Dirichlet boundary condition at \( x = 0 \). After entering the water phase, \( H_2S \) diffuses and undergoes a reaction that converts it into \( H_2SO_4 \). This evolution is depicted in the second column. The \( w_2 \) attains higher values at lower \( x \) position (closer to the inner surface of the pipe) copying at \( y = 0 \) the profile of \( w_3 \).

The concentration of \( H_2SO_4 \) (i.e., \( w_4 \)) is plotted in the first column. At first \( w_4 \) has a nearly linear profile for each fixed \( x \) decreasing to almost zero at the water-concrete interface \((y = \ell)\) where it is consumed by the chemical reaction (1d) that converts concrete into gypsum. This conversion can be seen in the fifth column which shows the evolution of the gypsum concentration \( w_5 \). At the beginning, the concrete is not damaged and \( w_5 = 0 \). Increased concentration of \( w_4 \) at \( y = \ell \) results in growing concentration of \( w_5 \), this process being at first more noticeable closer to the surface of the pipe. The \( w_5 \) continues to grow until it reaches a critical value \( \bar{w} = 0.9 \) which can be interpreted as an indication of complete conversion of concrete into gypsum.

Once \( w_4 \) reaches \( \bar{w} \), \( w_4 \) is not consumed anymore in the concrete corrosion and the boundary condition at \( y = \ell \) changes into no-flux condition. At \( t = 640 \) this change has taken place at \( x = 1 \) and is about to take place at \( x = 3 \). As can be seen in the first column, as a consequence of this change, \( w_4 \) starts to grow at \( x = 1 \) gradually approaching a constant value over all \( Y \). At \( t = 800 \) the corrosion front has nearly arrived to \( x = 5 \): the profiles of \( w_4 \) corresponding to \( x = 1 \) and \( x = 3 \) have already grown and the one corresponding to \( x = 5 \) is now starting to grow. The growth of \( w_4 \) results in the growth of \( w_2 \) which in turn results in a slow growth of \( w_3 \). Finally, the fourth column shows the evolution of \( w_4 \) - moisture as a product of reaction decomposing \( H_2SO_4 \). As the time increases, the corrosion tends to be complete and apparently the system wants to reach a constant steady state.

In Fig. 2, we show a computation with a Biot number much lower than in the previous numerical experiment - here \( Bi^M = 0.000864 (\epsilon \approx 1157.407) \). Consequently, the coupling between the equations for \( w_3 \) and \( w_4 \) becomes looser. As a result, \( w_3 \) does not decrease as much as in the previous experiment due to a barrier for \( H_2S \) in the air hindering its entrance into the water phase. Hence \( w_2 \) and \( w_1 \) attain lower values and their profiles tend to be uniform along the \( x \)-axis. Eventually, this leads to a slow, gradual corrosion of the pipe wall simultaneously along the whole domain and we do not observe the same progress of the
corroding front as in the previous case (there is nearly no motion of the corrosion front).

Fig. 3 shows a computation with a much larger Biot number compared to both previous experiments. Here we used $Bi^M = 864$ ($\epsilon \approx 0.00116$), which means that the boundary condition for $w_2$ at $y = 0$ is essentially a Dirichlet one. We can observe that in this case the concentrations of $w_2$ and $w_3$ are higher than in the previous numerical experiments. Additionally, the corrosion process seems to be much faster exhibiting a prominent corroding front (observable in the fifth column) advancing into the concrete.

<table>
<thead>
<tr>
<th>$M$</th>
<th>$|e_1|_2$</th>
<th>$EOC_1$</th>
<th>$|e_1|_2$</th>
<th>$EOC_2$</th>
<th>$|e_1|_2$</th>
<th>$EOC_3$</th>
<th>$|e_1|_2$</th>
<th>$EOC_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>32</td>
<td>0.01929</td>
<td>1.85669</td>
<td>0.00216</td>
<td>1.85466</td>
<td>0.00009</td>
<td>1.80801</td>
<td>0.98538</td>
<td>1.83429</td>
</tr>
<tr>
<td>64</td>
<td>0.00533</td>
<td>1.96049</td>
<td>0.00060</td>
<td>1.96036</td>
<td>0.00003</td>
<td>1.94844</td>
<td>0.27633</td>
<td>1.95547</td>
</tr>
<tr>
<td>128</td>
<td>0.00137</td>
<td>1.98988</td>
<td>0.00015</td>
<td>1.98986</td>
<td>0.00001</td>
<td>1.98686</td>
<td>0.07125</td>
<td>1.98865</td>
</tr>
<tr>
<td>256</td>
<td>0.00034</td>
<td>0.91004</td>
<td>0.00000</td>
<td>0.91000</td>
<td>0.00000</td>
<td>0.9795</td>
<td>0.00026</td>
<td></td>
</tr>
</tbody>
</table>

Table 2: Results of our convergence rate study (measured in the discrete $L^2$-norm).

<table>
<thead>
<tr>
<th>$N$</th>
<th>$|e_h|_{\infty}$</th>
<th>$EOC_1$</th>
<th>$|e_h|_{\infty}$</th>
<th>$EOC_2$</th>
<th>$|e_h|_{\infty}$</th>
<th>$EOC_3$</th>
<th>$|e_h|_{\infty}$</th>
<th>$EOC_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>32</td>
<td>0.04280</td>
<td>1.98990</td>
<td>0.00417</td>
<td>1.99067</td>
<td>0.00012</td>
<td>1.80827</td>
<td>1.27092</td>
<td>1.83487</td>
</tr>
<tr>
<td>64</td>
<td>0.01078</td>
<td>2.00096</td>
<td>0.00105</td>
<td>2.00400</td>
<td>0.00003</td>
<td>1.94850</td>
<td>0.35626</td>
<td>1.95564</td>
</tr>
<tr>
<td>128</td>
<td>0.00269</td>
<td>2.00047</td>
<td>0.00026</td>
<td>2.00091</td>
<td>0.00001</td>
<td>1.98687</td>
<td>0.09185</td>
<td>1.98869</td>
</tr>
<tr>
<td>256</td>
<td>0.00067</td>
<td>0.99997</td>
<td>0.00000</td>
<td>0.99997</td>
<td>0.00000</td>
<td>0.9795</td>
<td>0.00026</td>
<td></td>
</tr>
</tbody>
</table>

Table 3: Results of our convergence rate study (measured in the discrete maximum norm).

\[
\log_4 Bi^M \quad \|H w_h^0 - w_h^0\|_{\Omega} \quad EOC_E
\]

<table>
<thead>
<tr>
<th>$\log_4 Bi^M$</th>
<th>$|H w_h^0 - w_h^0|_{\Omega}$</th>
<th>$EOC_E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-2</td>
<td>6.95208 \cdot 10^{-2}</td>
<td>0.98907</td>
</tr>
<tr>
<td>-1</td>
<td>1.76455 \cdot 10^{-2}</td>
<td>0.98806</td>
</tr>
<tr>
<td>0</td>
<td>4.48495 \cdot 10^{-3}</td>
<td>0.99612</td>
</tr>
<tr>
<td>1</td>
<td>1.12728 \cdot 10^{-3}</td>
<td>0.99896</td>
</tr>
<tr>
<td>2</td>
<td>2.82225 \cdot 10^{-4}</td>
<td>0.99973</td>
</tr>
<tr>
<td>3</td>
<td>7.05819 \cdot 10^{-5}</td>
<td>0.99993</td>
</tr>
<tr>
<td>4</td>
<td>1.76471 \cdot 10^{-5}</td>
<td>0.99998</td>
</tr>
<tr>
<td>5</td>
<td>4.1187 \cdot 10^{-6}</td>
<td>0.99999</td>
</tr>
<tr>
<td>6</td>
<td>1.10297 \cdot 10^{-6}</td>
<td></td>
</tr>
</tbody>
</table>

Table 4: Experimental order of convergence of $E$, as $\epsilon \to 0$.

4.3. ILLUSTRATION OF THE CONVERGENCE SCENARIO: $\epsilon \to 0$

In this paragraph we are concerned with the behavior of solutions to $(P)$ as $\epsilon \to 0$. The main result here is that we show numerically that

\[
\|H w_1 - w_2\|_{\Omega} \to 0 \text{ as } \epsilon \to 0,
\]

i.e., as $Bi^M \to \infty$. We show this by simply measuring the experimental order of convergence. We plan to prove rigorously this behavior elsewhere. We proceed as follows: We compute solutions of (17) at $T = 800$ for gradually increasing values of $Bi^M = 4^i$, $i \in \{1, \ldots, 6\}$. For each choice of $\epsilon$, we measure the quantity $E_\epsilon := \|H w_h^0(T) - w_h^0(T)\|_{\Omega}$ in terms of the discrete $L^2$-norm; see (21). Finally, we define the experimental order of convergence of $E_\epsilon$ as

\[
EOC_{E_\epsilon} := \frac{\log(E_{\epsilon_1}) - \log(E_{\epsilon_2})}{\log(\epsilon_1) - \log(\epsilon_2)}.
\]

The results shown in Table 4 indicate that $E_\epsilon$ behaves as $O(\epsilon)$.

5. DISCUSSION

The results of section 4.3 encourage us to ask the questions:

(Q1) Do the concentration profiles corresponding to $(P)$ approach those corresponding to $(\tilde{P})$ as $\epsilon$ goes to zero? If yes, then in which sense?

(Q2) For suitable parameter regimes, have the solutions to problems $(P)$ and $(\tilde{P})$ have the same large-time behavior?

Trust the analysis by Cook and Showalter reported in [6], we expect a positive answer to the question (Q1). However, we need to take into account the specifics of $(P)$ and check which regularity of data and parameters is required for the limit $Bi^M \to \infty$ to make sense.

To reply to (Q2), we would need to do more numerical experiments. From the analysis point of view, we expect the existence of constant steady states. Again, it remains to investigate what are the necessary and sufficient conditions that both problems have the same constants as steady states.

Following the line open by [19, 20], we are very much interested in analyzing from a rigorous perspective the effect of the choice of micro-macro transmission conditions on the quality of the multiscale FD scheme described in section 3. More precisely, we will address elsewhere questions related to finding a priori and a posteriori error estimates for such
class of two-scale reaction-diffusion systems.

ACKNOWLEDGMENTS

We acknowledge fruitful discussions with Maria Neuss-Radu (Heidelberg), Toyohiko Aiki (Gifu), Omar Lakkis (Sussex), Jens Kruschwitz (Bochum), and Robin Beddoe (München). A. M. thanks Michael Böhm (Bremen) and the researchers team involved in the DFG priority program SPP 1122 for introducing him to the modeling of concrete-based materials. V. Ch. was supported by Global COE Program Education and Research Hub for Mathematics-for-Industry from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

REFERENCES


Vladimír Chalupecký
Faculty of Mathematics, Kyushu University, Fukuoka, Japan
E-mail: chalupecky@math.kyushu-u.ac.jp

Tasnim Fatima
CASA – Centre for Analysis, Scientific computing and Applications, Department of Mathematics and Computer Science, Technical University Eindhoven, Netherlands
E-mail: t.fatima@tue.nl

Adrian Muntean
CASA – Centre for Analysis, Scientific computing and Applications, Institute for Complex Molecular Systems (ICMS), Department of Mathematics and Computer Science, Technical University Eindhoven, Netherlands
E-mail: a.muntean@tue.nl
## PREVIOUS PUBLICATIONS IN THIS SERIES:

<table>
<thead>
<tr>
<th>Number</th>
<th>Author(s)</th>
<th>Title</th>
<th>Month</th>
</tr>
</thead>
</table>
| 10-36  | M. Pisarenco  
J.M.L. Maubach  
I. Setija  
R.M.M. Mattheij | The aperiodic Fourier modal method in contrast-field formulation for simulation of scattering from finite structures | June ‘10 |
| 10-37  | A. Bergant  
J.M.C. van ‘t Westende  
T. Koppel  
J. Gale  
Q. Hou  
Z. Pandula  
A.S. Tijsseling | Water hammer and column separation due to accidental simultaneous closure of control valves in a large scale two-phase flow experimental test rig | July ‘10 |
| 10-38  | A.S. Tijsseling  
Q. Hou  
B. Svingen  
A. Bergant | Acoustic resonance in a reservoir-pipeline-orifice system | July ‘10 |
| 10-39  | A. Keramat  
A.S. Tijsseling  
A. Ahmadi | Investigation of transient cavitating flow in viscoelastic pipes | July ‘10 |
| 10-40  | V. Chalupecký  
T. Fatima  
A. Muntean | Multiscale sulfate attack on sewer pipes: Numerical study of a fast micro-macro mass transfer limit | July ‘10 |