A multi-level pore scale reactive transport model for the investigation of combined leaching and carbonation of cement paste

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Highlights

- A lattice Boltzmann method based multi-level pore-scale reactive transport model for simulation of carbon rich brine interacting with cement, accounting for transport in capillary and gel pores has been developed.
- Model accounts for mineral phase reactions through thermodynamic solver coupled to lattice Boltzmann method.
- The results from two dimensional simulations reveal a complex interplay between microstructure evolution and boundary solution composition, indicating that it might be necessary to recalibrate continuum scale models on case by case basis.
- Three dimensional simulations demonstrate the potential applicability of the developed methodology to realistically model the changes in microstructure evolution due to combined carbonation and leaching mechanisms.
Abstract

Cementitious materials in underground constructions are exposed to CO₂ rich ground waters which leads to combined carbonation and calcium leaching. Complex interplay between leaching, carbonation reaction and changes in transport pathways presents difficulty in parameterizing continuum scale models in a consistent way. Therefore, a novel multi-level pore-scale reactive transport model is presented to capture microstructure changes under combined carbonation and leaching. Model explicitly resolves capillary pores and phases with unresolved porosity as a porous media. Governing equations are solved using a lattice Boltzmann method based reactive transport solver with chemical reaction under thermodynamic equilibrium. The two-dimensional parametric study on idealized microstructures revealed that carbon content and pH of boundary solution strongly affects degradation rates, location and thickness of precipitated calcite layer. Furthermore, reactive surface area plays dominant role and tortuosity of media rather a secondary role. The three-dimensional simulations using virtual cement paste microstructure show that degradation rate exhibit non-linear behaviour with square root of time and time. This implies that simple empirical relations for prediction of progression of reaction fronts are not applicable and use of numerical reactive transport models is inevitable. The developed model qualitatively captures the development of carbonation, leaching fronts and zonation as observed in experiments. Good quantitative agreement between modelling and experiments is obtained for initial stages. At later times, the modelling result and experimental observations diverge significantly. This discrepancy is likely due to lack of consideration of kinetics of C-S-H dissolution and calcite precipitation.

Keywords: combined carbonation and leaching, microstructure evolution, multi-level pore-scale modelling, lattice Boltzmann methods, reactive transport modelling
1. Introduction

Critical subsurface infrastructures such as tunnels [1], CO$_2$ sequestration facilities [2,3] and deep geological disposal facilities for nuclear waste storage [4,5] contain cementitious materials in their structural elements. These structural elements are often exposed to ground water/solutions containing dissolved CO$_2$ which chemically interact with cementitious materials. Key processes manifesting from these interactions are calcium leaching leading to dissolution of crystalline phases such as portlandite and the decalcification of amorphous phases such as calcium silicate hydrate (C-S-H) and carbonation (precipitation of calcium carbonate) due to reaction of leached calcium with dissolved CO$_2$. Calcium leaching causes loss of mechanical strength and increase in transport properties of cementitious materials [6–8]. While, precipitation of calcium carbonate densifies cement matrix, it can also further accelerate or inhibit the progression of the leaching front, depending on the composition of the ingressing solution [9].

Several experimental studies have been performed to evaluate cementitious materials interactions with solutions containing dissolved CO$_2$, see Zhang and Bachu [3] for a comprehensive review. Their review highlighted that different studies have used different flow and chemical boundary conditions. This has led to considerable differences in rate of advancement of leaching front reported in literature. They further emphasise that such laboratory studies cannot act as proxy for the field studies. Hence, it is essential to develop mechanistic models which can bridge the gap between field conditions and laboratory conditions. These models should incorporate key physio-chemical processes to account for different chemical boundary conditions. In addition, the effect of pore-structure changes on constitutive relations needs to be considered.

It is challenging to predict degradation potential of cementitious materials in presence of dissolved CO$_2$ using single component models which has been popular for calcium leaching using a characteristic leaching curve [10]. Therefore, multicomponent continuum scale reactive transport models have been developed to simulate combined carbonation and leaching processes in
cementitious materials in underground structures [11–15]. The continuum scale models operate at the account for the effect of microstructure evolution through constitutive equations for reaction rates and transport parameters (diffusivity and permeability). For combined carbonation and leaching continuous competition between dissolution and precipitation leads to non-unique and non-linear evolution the constitutive relationship. Therefore, direct fitting with experimental data can significantly reduce predictive capabilities of the model. For instance, Georget et al. [11] demonstrated that use of different diffusivity models can lead to substantially different front propagation rates. Moreover, the authors note that the fitting of the diffusion coefficients to the reaction front propagation rate can be misleading, since it can result in inaccurate predictions of the solid phase assemblage. It has also been reported in literature that in case of complete clogging scenario very fine resolution of around few hundred micrometres is required due to steep chemical gradients at the locations where strong porosity reduction is occurring [16–19]. This puts applicability of continuum scale modelling for simulating such scenarios into question.

The goal of this study is to present a newly developed multi-level pore-scale model for combined carbonation and leaching. This model resolves explicitly the capillary pores and accounts for the reactive transport processes through C-S-H pores by treating it as homogenized porous media thus representing two levels of cement paste pore-structure. The developed model provides an opportunity to explore and better understand the effect of processes occurring at the fluid-mineral interface and microstructure evolution and its influence on macroscopic behaviour.

Pore-scale reactive transport modelling for cementitious systems is a relatively new and quickly evolving research field. Currently available models are limited in terms of process couplings and system complexity. Raoof et al. [20] applied a pore-network based approach to simulate the microstructure changes in cement paste in contact with boundary solution containing dissolved CO₂. Their model was able to qualitatively capture the behaviour observed experimentally e.g. formation of different zones of phase assemblage. Their model has the advantage to be able to simulate large
physical domains, however, it simplifies the pore structure of cement paste through a network of pore bodies connected via pore cylindrical pore throats which does not accurately represent pore-connectivity of the cement paste. Moreover, the study of Raoof et al. considered the same reaction rate for portlandite and C-S-H. However, decalcification of C-S-H is usually gradual and occurs after complete dissolution of portlandite as demonstrated by several continuum scale models [11,12,21] and experiments [3]. Recently, Patel et al. [22] developed a three-dimensional lattice Boltzmann method-based model for calcium leaching from cement paste in contact with deionized water. This model takes a 3D digitized microstructure as an initial phase distribution in hydrated cement paste and evolves the microstructure due to reactive transport process accounting for the reaction of both portlandite and C-S-H through an optimized implementation of geochemical reactions in the form of look-up tables. The optimized model was shown to be equivalent to reactive transport model coupled with thermodynamic solver, however it was computationally much more efficient. Such a model allows for more realistic system description compared to the pore-network model. A similar concept is followed in this study for the development of the multi-level pore-scale model for combined carbonation and leaching of cement paste. However, to account for complex reaction network in presence of dissolved carbonates and different ions we use lattice Boltzmann model coupled to an external geochemical solver PHREEQC [23].

The paper is organised as follows. Section 2 provides a detailed description of the conceptual assumptions made for the model development and the governing equations for the combined carbonation and leaching model. Section 2 concludes with the details on the lattice Boltzmann method-based modelling approach used to solve the governing equations. The results and discussions are presented in section 3. Section 3.1 presents the results of the two-dimensional parametric study which is carried out on idealized microstructures to evaluate the effects of key parameters that affect microstructure evolution under combined carbonation and leaching such as boundary solution composition, the tortuosity of the microstructure and the amount of calcium in solid phases. Section
3.2 presents the results of three-dimensional simulations of the combined carbonation and leaching based on a virtual microstructure generated using cement hydration model HYMOSTRUC [24,25] as input. Finally, conclusions of this study are presented in Section 4.

2. Model description

Section 2.1 provides details of the conceptual model considerations used in this study followed by the governing equations used for describing combined carbonation and leaching process. Section 2.2 provides details of the lattice Boltzmann method based reactive transport model used to solve these governing equations. For the sake of generality, all physical variables are described in dimensional units N, L, T which stands for moles, meter and seconds, respectively, for SI system. The specific values of these physical variables used are described with appropriate units.

2.1 Conceptual model and governing equations

![Figure 1: Conceptual depiction of the multi-level cement paste microstructure subjected to combined carbonation and leaching. At level I capillary pores are resolved and C-S-H matrix and calcite precipitated in capillary pores is treated as a porous media with sub-voxel porosity. Level II resolves pores in C-S-H matrix and calcite precipitated in capillary pores.](image-url)
The conceptual picture of cement paste microstructure subjected to combined carbonation and leaching is shown in Figure 1. In this study we have simplified the cement paste microstructure to consider only calcium silicate hydrate (C-S-H) matrix, portlandite and clinkers as the mineral phases in the hardened cement paste. Further, it is postulated that the clinkers do not react thus the main reactive phases in our model are portlandite and C-S-H. The rationale behind this assumption is that C-S-H and portlandite phases are the most severely affected phases and would have the strongest influence on the propagation of the reaction front [3,26]. It is also assumed that the reaction of dissolved CO$_2$ with calcium ions leads to precipitation of calcium carbonate in form of calcite which is also the main reaction product observed experimentally [3].

The heterogeneities of the cement paste microstructure are represented in two levels as shown in Figure 1. Level I represent the pore-scale level considered in this study whereas level II represents sub-voxel heterogeneities which are not explicitly resolved at the pore-scale. Voxel here refers to a volume element of the digitized microstructure. In the pore-scale model at level I only capillary porosity is explicitly resolved. The gel pores are considered to be part of C-S-H matrix at level II. Therefore, the C-S-H matrix at level I is represented as a diffusive porous media. The transport through this phase is modelled through consideration of (homogenized) sub-voxel porosity as shown in Figure 1. Moreover, we also assume that the precipitated calcite in the existing capillary pores and new capillary pores formed by portlandite dissolution have sub-voxel porosity as shown in Figure 1. This assumption is based on the experimental observations of Galan et al. [27] which suggest that the precipitated calcite layer around the portlandite, does not fully block dissolution of portlandite but can act as a barrier significantly reducing dissolution of the portlandite. They also report that the precipitated calcite layer can have diffusivity of several orders lower than in free water. Consideration of calcite precipitated at pore-scale to be diffusive with sub-voxel porosity can effectively capture this observation. Portlandite and clinkers are considered as non-diffusive mineral phases meaning
transport does not occur through these phases. Thus the microstructure representation used in this study can be conceptualized as a multi-level porous material similar to one described in Patel [28].

The microstructure evolution of cement paste due to combined carbonation and leaching is governed by reaction-diffusion process, which can be expressed as

$$\partial_t \theta C^j = -\nabla D_e \nabla C^j + \sum_{m=1}^{N^d} \nu_m R^d_m + \sum_{m=1}^{N^{nd}} I^{nd} R^{nd}_m$$  \hspace{1cm} (1)

where $C^j$ is the aqueous concentration of $j^{th}$ primary chemical species [NL^-3]. Secondary chemical species are related to primary chemical species via laws of mass action and are not transported. All primary species are transported with the same effective diffusion coefficient [L^2 T^-1], $D_e$, in order to ensure charge neutrality. Effects of ion activity and electro-kinetic effects on ion transport equation are neglected. This seems reasonable assumption at this scale for well-bore cement which considered for simulation in section 3. For well-bore cement capillary pores form main diffusion pathway. When C-S-H nano-pores are preliminary transport pathway this effect can become more significant as demonstrated by Yang et al [29].

The source-sink term due to the reaction of $m^{th}$ diffusive mineral phase for $j^{th}$ primary chemical species [NL^-3 T^-1] is represented by $R^{d,j}_m$ in Eq. (1) and the porosity of the voxel containing diffusive mineral phases [-] is represented as $\theta$. $\theta$ is equal to 1 for capillary pores. $\nu_m^j$ corresponds to the stoichiometric coefficient. The source-sink term due to the reaction of $m^{th}$ non-diffusive phase for $j^{th}$ primary chemical species [NL^-3 T^-1] in Eq. (1) is represented by $R^{nd,j}_m$ which is only applied at the capillary pore or porous mineral phase voxel in contact with the non-diffusive phase which in Eq. (1) is indicated by the indicator function $I^{nd}$. $N_{\partial \Omega_m^{nd}}$ is outward normal from non-diffusive phase and $\Delta x$ is the numerical grid spacing between voxels. The source-sink terms in the proposed model are
computed using geochemical solver *PHREEQC* [23] under the assumption of thermodynamic equilibrium and laws of mass action. Thermodynamic parameters for mineral phases stemming from the Thermodem database [30] used in this study are summarized in Table 1. Consideration of thermodynamic equilibrium as a working approximation for this study is motivated for initial experimental observation that carbonation reaction in cement systems might be diffusion controlled [3] and lack of appropriate parametrization for rate laws for cement phases pore-scale. It should be noted that developed modelling framework allows incorporation of kinetic mineral nucleation and growth rates through *PHREEQC* as demonstrated previously [31–33]. This should therefore not be seen as the limitation of modelling framework presented here.

Several models have been suggested for the dissolution of C-S-H including more advanced solid solution models (see [34] for a review). Large variations exist between the conceptualization of these models; however, the predictions of all models fall within the range of experimental uncertainty [34]. Therefore, in this study, C-S-H reaction is described using three discrete phases with fixed stoichiometry, which is computationally faster and more stable compared to solid solution model.

<table>
<thead>
<tr>
<th>Phase name</th>
<th>Reaction formula</th>
<th>log of Equilibrium constant [-]</th>
<th>Molar volume [cm$^3$/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Portlandite</td>
<td>Ca(OH)$_2 + 2H^+ → Ca^{2+} + 2H_2O$</td>
<td>22.81</td>
<td>33.06</td>
</tr>
<tr>
<td>Calcite</td>
<td>CaCO$_3 + H^+ → HCO$_3^- + Ca^{2+}$</td>
<td>1.847</td>
<td>36.934</td>
</tr>
<tr>
<td>C-S-H phases</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CSH(1.6)</td>
<td>Ca$<em>{1.6}$SiO$</em>{3.6} \cdot 2.58H_2O + 2.4H^+ → 1.6 Ca^{2+} + H_4SiO_4 + 2.18 H_2O</td>
<td>28.0</td>
<td>84.68</td>
</tr>
<tr>
<td>CSH(1.2)</td>
<td>Ca$<em>{1.2}$SiO$</em>{3.2} \cdot 2.06H_2O + 2.4H^+ → 1.2 Ca^{2+} + H_4SiO_4 + 1.26 H_2O</td>
<td>19.3</td>
<td>71.95</td>
</tr>
<tr>
<td>CSH(0.8)</td>
<td>Ca$<em>{0.8}$SiO$</em>{2.8} \cdot 1.54H_2O + 1.6H^+ → 0.8 Ca^{2+} + H_4SiO_4 + 0.34 H_2O</td>
<td>11.05</td>
<td>59.29</td>
</tr>
</tbody>
</table>

In Eq. (1) the evolution of $D_e$ for the sub-voxel porosity is accounted through Archie’s relationship as follows:

$$D_e = D_0(\theta)^n$$ (2)
Where, \( D_0 \), in the above equation is the diffusivity in pure water and is set to \( 2.2 \times 10^{-9} \) m\(^2\)/s for all species corresponding to the diffusion coefficient of calcium ion in the free water [35]. For diffusive C-S-H phase, \( n \) is determined as 8.23 from a continuum micro-mechanics based model for C-S-H diffusivity [36]. For diffusive calcite phase precipitated in capillary pores, there is no experimental data available on the evolution of diffusivity as a function of porosity. Therefore, in this study \( n \) is set to 1 as an approximation based on values of diffusivity of precipitated calcite layer reported by Galan et al. [27]. For capillary pores \( D_e \) is equal to \( D_0 \).

Additionally, at the boundary of non-diffusive phases (\( \partial \Omega_m^{nd} \)) a zero-concentration gradient condition is imposed

\[
\vec{V} C^i \cdot \hat{N}_{\partial \Omega_m^{nd}} \bigg|_{\partial \Omega_m^{nd}} = 0
\]

(3)

The change in mineral volume due to dissolution or precipitation for non-diffusive minerals and diffusive mineral phase can be computed as

\[
\partial_t V_m^d = -V_m R_m^d
\]

(4)

\[
\partial_t V_m^{nd} = -\bar{V}_m R_m^{nd}
\]

Where, \( V_m^{nd} \) and \( V_m^d \) is the volume of \( m^{th} \) diffusive and non-diffusive phases [L\(^3\)], respectively. \( \bar{V}_m \) is the molar volume of \( m^{th} \) mineral phase [L\(^3\)N\(^{-1}\)] which is tabulated in Table 1. The change in the volume of diffusive phase translates to the change in \( \phi^d \) as

\[
\partial_t \theta = 1 - \frac{1}{V} \partial_t V_m^d
\]

(5)

In above equation \( V \) is volume of the discretised element [L\(^3\)]. For the non-diffusive phase, the change in volume leads to movement of the boundary which in this study is accounted through static update rules detailed in [37]. The initial porosity of C-S-H phase (\( \theta^{C-S-H} \)) is obtained from the total porosity computed using Power’s model [38] as
\[
\theta_{c-s-h} \bigg|_{t=0} = \frac{1}{\phi_{c-s-h} \bigg|_{t=0}} \left( \frac{w/c - 0.17\alpha}{w/c + 0.317} - \phi_{cp} \right)
\]

where \(\phi_{c-s-h}\) is the volume fraction of C-S-H in cement paste microstructure, \(w/c\) is the water to cement ratio \(\alpha\) is the degree of hydration and \(\phi_{cp}\) is the capillary porosity in cement paste microstructure.

2.2 Lattice Boltzmann method for modelling multi-level pore-scale reactive transport problem

The lattice Boltzmann (LB) method solves the simplified form of the discrete Boltzmann equation which describes the evolution of a particle distribution function \(f_i(x, t)\) [NL^{-3}] corresponding to discrete lattice velocity \(e_i\) [LT^{-1}] in \(i\)th direction. In this study, we use a two relaxation time (TRT) formulation of the LB method [39]. The evolution of the distribution function according to the TRT-LB equation for \(j\)th species in the case of multi-component multi-level pore-scale reactive transport is given as

\[
f_i^j(x + \tilde{e}_i \Delta t, t + \Delta t) = f_i^j(x, t) + \Delta t Q_i^{TRT,j}(x, t) + \Delta t Q_i^{rxn,j}(x, t)
\]

\[
Q_i^{TRT,j}(x, t) = -\frac{1}{\tau_+} \left(f_i^{+, j}(x, t) - f_i^{eq+, j}(x, t)\right) - \frac{1}{\tau_-} \left(f_i^{-, j}(x, t) - f_i^{eq-, j}(x, t)\right)
\]

\[
f_i^+ = \frac{f_i + f_{i+}}{2}, f_i^- = \frac{f_i - f_{i-}}{2}, f_i^{eq,+} = \frac{f_i^{eq} + f_{i+}}{2}, f_i^{eq,-} = \frac{f_i^{eq} - f_{i-}}{2} \text{ with } \tilde{e}_{i-} = -\tilde{e}_i
\]

\[
Q_i^{rxn,j}(x, t) = w_i \left( \sum_{m=1}^{N^d_m} v_m^j R_m^a + \sum_{m=1}^{N^{nd}_m} I_m^j R_m^{nd} \right)
\]

where \(f_i^{eq}\) is the equilibrium distribution function [NL^{-3}]. \(\tau_+\) and \(\tau_-\) are relaxation parameters for the symmetric and anti-symmetric part respectively [T^{-1}]. The above equation is discretized on a uniform grid with its center representing a volume element of the microstructure and \(\Delta t\) [T] as discrete time step and grid spacing \(\Delta x = e \Delta t\) [L] with \(e\) being lattice speed [LT^{-1}]. Additionally, a constraint is laid on the zero moment of \(f_i(x, t)\) to ensure mass conservation:
Orthogonal lattices are used for discretising velocity space. That is, for a two-dimensional lattice with 4 directions and one rest velocity denoted as zero, commonly referred as D2Q5 and in three dimensions lattice with 6 directions and one rest velocity denoted as 0 commonly referred as D3Q7 is used. The following equilibrium distribution function is sufficient to recover the multi-level pore-scale diffusion-reaction equation from Eq. (7) using Chapman-Enskog analysis [28,40].

\[
f_{i}^{eq,j} = c_{\theta} C_{j}^{i} \]

(9)

\[
f_{0}^{eq,j} = \theta C_{j}^{i} - \sum_{i \neq 0} f_{i}^{eq} \]

where \(c_{\theta}\) is the positive adjustable parameter. The equation recovered from multi-scale Chapman-Enskog analysis of Eq. (7) yields

\[
\partial_{t} \theta C_{j}^{i} = -\nabla \cdot (\tau_{-} - \frac{\Delta t}{2}) \cdot \nabla \theta C_{j}^{i} + \sum_{m=1}^{N_{d}} v_{m}^{d} R_{m}^{d} + \sum_{m=1}^{N_{nd}} f_{m}^{nd} v_{m}^{nd} \]

(10)

Comparing Eq. (10) with Eq. (1) the effective diffusion coefficient \(D_{e}\) relates to the relaxation parameter \(\tau_{-}\) as

\[
D_{e} = c_{\theta} \left( \tau_{-} - \frac{\Delta t}{2} \right) \]

(11)

\(c_{\theta}\) has to be set constant throughout the domain to ensure correct formulation of Eq. (1) and is set to \(c_{\theta} \leq \frac{\min(\theta)}{3}\) for D2Q5 lattice and \(c_{\theta} \leq \frac{\min(\theta)}{3.5}\) to ensure non-negativity of the zero velocity particle distribution function. \(\tau_{+}\) is the free parameter in TRT scheme and is set such that

\[
\left( \tau_{-} - \frac{1}{2} \right) \left( \tau_{+} - \frac{1}{2} \right) = \frac{1}{4} \]

(12)

which ensures optimal stability for a wide range of values of \(\tau_{-}\) and \(\tau_{+}\) [41].
The distribution functions are initialized as equilibrium distribution functions with the value of concentration equal to initial concentration. The zero-flux boundary condition on arbitrary domain boundary is implemented using a bounce back scheme, which essentially implies that the unknown incoming $f_i$'s at a given voxel are set to the outgoing $f_i$'s in opposite lattice direction.

$$f_i^j = f_{-i}^j$$  \hspace{1cm} (13)

The constant concentration boundary is implemented on the domain boundary by setting the unknown inward distribution function $f_i$ as

$$f_i = c_\theta C^j - \sum_{j \neq i} f_j$$  \hspace{1cm} (14)

The LB simulations are performed by extending and adapting the open source code *Yantra* version 1.0.0-dev [28,42]. The reactions are computed in *Yantra* using *PHREEQC*’s IPhreeqc interface [43]. *IPhreeqc* and LB transport solver is coupled with algorithm for pore-structure evolution due to dissolution and precipitation, with details as given in [28,32,44]. Furthermore, in order to dynamically adjust the time step based on concentration change, adaptive time-stepping scheme for LB method, developed by Patel [28] is used.

### 3. Results and discussions

In section 3.1 the results from the two-dimensional parametric study are first presented. The goal of this parametric study is to qualitatively analyse the effect of boundary solution composition and microstructure features such as solid calcium content, reactive surface area and tortuosity, on the evolution of the system. For the parametric study a two-dimensional idealized microstructure with only portlandite as a reactive mineral are generated using the QSGS algorithm [45]. The use of this idealized microstructure, which at this stage neglects the C-S-H phase is chosen since it yields similar qualitative behaviour as that observed in experiments for cementitious systems as previously reported by Raoof et al. [20] for pore-network modelling approach. In addition, such idealized microstructures
have previously used as substitute for actual representation [46–48] because they allow variation of microstructure features in a controlled way e.g. keeping portlandite volume fraction same but changing surface area or tortuosity. In section 3.2 simulations are carried out using 3D dimensional virtual microstructure of ordinary Portland cement (OPC) paste generated from HYMOSTRUC [24,25] (modified to consider portlandite nucleation and growth [49]) as input.

3.1. Two-dimensional parametric study on idealized microstructures

![Generated stylized microstructure used for the parametric study (a) coarse microstructure (b) fine microstructure. Red represents portlandite and blue pore phase. White volume elements were assigned to pores, portlandite or an inert phase to simulate six different initial mineral assemblages for the 2D parametric study.](image)

**Table 2: Key characterization parameters of generated two-dimensional microstructure.**

<table>
<thead>
<tr>
<th>Name</th>
<th>Description</th>
<th>(\phi_{\text{port}})</th>
<th>(\phi_{\text{inert}})</th>
<th>(A_{\text{port}}) ((\mu\text{m}^{-1}))</th>
<th>(D_e/D_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coarse</td>
<td>Coarse microstructure with white volume elements as pore</td>
<td>0.30</td>
<td>0</td>
<td>0.6329</td>
<td>0.2521</td>
</tr>
<tr>
<td>PortCoarse</td>
<td>Coarse pore structure with white volume elements as portlandite</td>
<td>0.45</td>
<td>0</td>
<td>0.7630</td>
<td>0.1102</td>
</tr>
<tr>
<td>InertCoarse</td>
<td>Coarse pore structure with white volume elements as inert mineral</td>
<td>0.30</td>
<td>0.15</td>
<td>0.5162</td>
<td>0.1102</td>
</tr>
<tr>
<td>Fine</td>
<td>Fine pore structure with white volume elements as pore</td>
<td>0.30</td>
<td>0</td>
<td>0.9039</td>
<td>0.18057</td>
</tr>
<tr>
<td>PortFine</td>
<td>Fine pore structure with white volume elements as portlandite</td>
<td>0.45</td>
<td>0</td>
<td>1.1794</td>
<td>Not percolated</td>
</tr>
</tbody>
</table>
Two different types of microstructures are generated for performing the parametric study as shown in Figure 2. Figure 2 (a) and (b) represents coarse and fine microstructures, containing coarse sized grains and fine size grains, respectively, while maintaining the same volume fraction of portlandite (red volume elements in Figure 2) which is equal to 0.3. This value is close to calcium bearing solid volume fraction in 3D microstructure considered later in this study. Further, in order to vary the microstructure for different simulations in a controlled way, the volume indicated with white colour in Figure 2 was assigned the properties of a pore, portlandite or inert mineral. This procedure resulted in six different microstructures. Key characterization parameters for these microstructures viz.,
portlandite volume fraction ($\phi_{\text{port}} [-]$), inert phase volume fraction ($\phi_{\text{inert}} [-]$), the reactive surface area of portlandite ($A_{\text{port}} [\mu\text{m}^{-1}]$) and relative diffusivity ($D_e/D_0 [-]$) are summarized in Table 2. The volume fraction in this study are computed as the volume of a given phase divided by total volume of the domain unless and otherwise specified. Reactive surface area here refers to the area of portlandite grains in contact with pores normalized with the total volume of the domain. The relative diffusivity is the ratio of diffusivity of a tracer in porous material with respect to its diffusivity in pure water and is computed using computational homogenization approach detailed in [36]. The finer microstructures lead to higher surface area and lower relative diffusivity for same fractions of portlandite. The concentration of primary species and pH for boundary solutions used for the parametric study are summarized in Table 3. BC1 and BC2 represents the conditions corresponding to the cement paste in contact with sandstone formation and limestone formation for CO$_2$ sequestration as used in experiments by Duguid and Scherer [26] at 20 °C. The exact composition of these solutions is taken as the one used by Huet et al. [12] in their continuum scale simulations. BC3 maintains the same pH as solution 2 but is equilibrated by adjusting the concentration of Na ions. These three cases are repeated in BC4 to BC6 but with one order lower total carbon concentration. In total with these variations 36 simulations were carried out. These simulations during later discussion are referred to with solution name followed by short name assigned to the microstructure. For example, BC3InertFine refers to simulation results corresponding to fine microstructure with white pixel considered as inert and exposed to BC3 boundary solution. The simulation results are discussed in two subsections, section 3.1.1 and 3.2.2, discussing the influence of boundary solution composition and microstructure, respectively. The results are discussed in terms of key parameters such as the time evolution of portlandite and calcite volume fractions, and profiles of calcite, portlandite and pH.

3.1.1. Influence of boundary solution composition
Figure 3: Time evolution of InertFine microstructures: (a) normalized volume fraction of dissolved portlandite with respect to initial value and (b) volume fraction of precipitated calcite.

Figure 3 shows the time evolution of the dissolved portlandite volume fraction normalized with respect to its initial value in the domain, as well as the precipitated calcite volume fraction ($\phi_{\text{calc}}$) for different boundary solution compositions for the set of InertFine microstructure. Figure 3 indicates that portlandite dissolution and calcite precipitation does not have constant slope with respect to square root of time and exhibit non-linear behaviour. This can be attributed to the fact that at certain point the calcium leaching is controlled by precipitation of calcite and diffusion through the newly formed precipitated calcite layer, which leads to the change in slope. For the boundary solutions with total carbon concentration equal to 0.057 M the amount of portlandite dissolved as shown in Figure 3 (a) for most cases is higher than that for boundary solutions with total carbon concentration equal to 0.0057 M. However, in some cases (BC1InertFine and BC4InertFine) the amount of portlandite dissolved for boundary solution with total carbon concentration equal to 0.0057 M is higher at certain time instances. On the contrary, the amount of calcite precipitated is always higher for boundary solution with total carbon concentration equal to 0.057 M. This indicates that the dissolved calcium is leached out of the domain in the cases where portlandite dissolution is same or higher, for the solutions with total carbon concentration equal to 0.0057 M, due to lack of the availability of dissolved carbon to precipitate calcite. The reason for the acceleration of portlandite dissolution
which is observed in most of the cases for boundary solutions with total carbon concentration equal to 0.057 M, is the larger consumption of calcium due to higher amount of calcite precipitating, which in turn is a consequence of higher availability of dissolved carbon, which maintains the system constantly out of equilibrium. Similar observations can be made after examining the simulations results for other microstructures (see supplementary information Figure A.1-A.6).

Comparing the set of simulations with variable boundary solution compositions with total carbon concentration equal to 0.057 M (BC1-BC3), it can be observed from Figure 3 that for low pH boundary solutions (BC1) the amount of calcite precipitated is lower compared to the high pH boundary solutions (BC2 and BC3). There were some exceptions to these observations e.g. comparison of BC1Fine and BC3Fine (See supplementary information Figure A.4). However, the amount of portlandite dissolved was observed to be higher or comparable in case of BC1 compared to the other two cases. It can be thus concluded that the amount of calcium leached out of the domain is higher in case of BC1. This can be attributed to a combination of multiple factors; first, low pH leads to more portlandite dissolution, and secondly the boundary solution is undersaturated with respect to calcite, which leads to dissolution of the precipitated calcite. It can be also observed in Figure 3 that in the case where the boundary solution is equilibrated with respect to calcite (BC2) the amount of calcite precipitated is much larger compared to the other boundary solutions (BC1 and BC3). For all simulations expect in case BC2PortFine and BC1PortFine (see Figure A.5 in supplementary information) this observation holds. Since the boundary solutions which are equilibrated with Na (BC3) and low pH boundary solution (BC1) are undersaturated with respect to calcite, in the later stage the precipitated calcite is further dissolved to re-equilibrate the pore solution. This can be clearly seen in Figure 4, which shows simulation snapshots of the evolution of the pore-structure at 30 s and 1000 s for the BC3Fine case. This mechanism is not occurring in the case of BC2 and hence leads to higher amounts of precipitated calcite. Thus, it is also expected that in case of BC2 at later stages clogging would occur due to formation of protective layer of calcite. In contrast,
for the solutions with total carbonation concentration equal to 0.0057 M, the amounts of dissolved
portlandite and of precipitated calcite is higher in case of low pH boundary solution (BC4) than in
the cases of high pH boundary solutions (BC5 and BC6). This is due to the fact that BC4 has tendency
to dissolve portlandite faster than BC5 and BC6 which has a close to neutral pH. This also leads
higher precipitation amounts of calcite. The comparison of solutions with same pH equilibrated with
Ca (BC5) and with Na (BC6), in Figure 3, shows that the amount of portlandite dissolved and calcite
precipitated is lower for the former compared to latter. However, this observation is not consistent
for all types of microstructures (See supplementary material), and for some cases either the opposite
observation is made or similar amount of portlandite dissolved and calcite precipitated is observed
for BC5 and BC6.

Figure 4: Evolution of BC3Fine simulation at the 30s and 1000 s. Portlandite, calcite, and pores are shown in red, green
and black, respectively. Shading of colour is proportional to the volume fraction of the phase. Figure shows that at the
later stage the precipitated calcite can further dissolve when solution is not in equilibrium with calcite
Figure 5: Spatial profile of normalized portlandite volume fraction with respect to the initial volume fraction for InertFine microstructure. The spatial profile obtained by averaging along a direction perpendicular to diffusion (y-direction).

The profiles of portlandite are of interest for determining the extent of degradation. Figure 5 shows the spatial profiles of the normalized portlandite volume fraction for the set of InertFine microstructure simulations. The spatial profiles are obtained by averaging volume fraction in a direction perpendicular to the applied concentration gradient (i.e. along the y-axis). From Figure 5 it is clear that portlandite dissolution front advances further for the boundary solution with total carbon concentration equal to 0.057 M (BC1-BC3) compared to the boundary solution with total dissolved carbon concentration equal to 0.0057 M (BC4-BC6) at the end of simulation. In early stages of system evolution this observation may not hold as shown in Figure 5. In Figure 6, the profiles of the mean location of portlandite dissolution front with respect to different boundary solutions at 1000 s are plotted. The mean location of portlandite dissolution front is obtained by taking an average of the location of the points where portlandite volume fraction is greater than 0.01 in the direction perpendicular to applied concentration gradient (along the y-axis). Figure 6 also highlights that the dissolution front advances further for boundary solutions with total carbon concentration equal to 0.057 M compared to the boundary solution with total dissolved carbon solution equal to 0.0057 M.
irrespective of microstructure. Comparing the simulations for boundary solution with high pH (equilibrated with Na or Ca) (BC2, BC3, BC5, BC6) and low pH (BC1, BC4), shown in Figure 5, we can infer that the portlandite dissolution front extents further for the boundary solution with low pH compared to the boundary solutions with high pH irrespective of microstructure and this is more clear in Figure 6. This observation however does not hold in early times of the evolution of the system as seen in Figure 5. Comparing the cases for boundary solutions with total carbon concentration equal to 0.057 M and same pH adjusted by addition of Ca (BC2) and Na (BC3), the location of mean portlandite dissolution front progresses further in case of former compared to latter at 1000 s as evident in Figure 5 and Figure 6. However, for boundary solution with total carbon equal to 0.0057 M (BC5 and BC6) this was not observed as seen more clearly in Figure 6, and the portlandite dissolution front had similar location at the end of simulations for the two solutions. Note that in the experiments of Duguid and Scherer [26] no major degradation was observed in conditions equivalent to these of BC2. They only observed a light grey layer of around 580 microns light grey layer appearing at the end of the first day. The simulation results presented here represents early onset of degradation processes and therefore for BC2 we still observe dissolution of portlandite and porosity is not fully clogged. However, it can be expected that at later stage the precipitated calcite (which does not dissolve further) would form a few microns thick protective layer which can inhibit or slow the further propagation of the reaction front.

![Figure 6: Mean location of portlandite dissolution front with respect to different boundary solutions at 1000 s.](image)
Figure 7: Spatial profiles of calcite volume fraction for InertFine microstructure. The spatial profile obtained by averaging along a direction perpendicular to diffusion (y-direction).

The spatial profiles of the calcite volume fraction for InertFine microstructure for different boundary conditions are shown in Figure 7. Spatial calcite profiles are obtained by taking average along the direction perpendicular to the concentration gradient (y-direction). Figure 8 plots the mean thickness of calcite layer for different simulations at 1000 s. From Figure 7 it can be seen that at 1000 s the peak volume fraction of calcite for all boundary solutions is found to be more or less similar for these simulations. However, the thickness of the precipitated calcite layer differs substantially as visible in Figure 8. It is also evident that in the case of boundary solution with total carbon concentration equal to 0.0057 M (BC4-BC6) the calcite precipitation occurs more towards the boundary and the precipitated calcite layer is thin. Moreover, the spatial peak of calcite precipitated is higher for this case which indicates that this case might have much more potential to clog the surface. In the case of boundary solutions with total carbon concentration equal to 0.057 M (BC1-BC3), the calcite front penetrates deeper and the precipitated calcite layer is thicker. This is due to instantaneous calcite precipitation near the location where portlandite dissolves. For boundary solutions with total carbon...
concentration equal to 0.057 M and undersaturated with calcite (BC1 and BC3), Figure 7 shows that the precipitated calcite further dissolves and the front moves inwards. For a solution with total carbon concentration equal to 0.057 M the calcite layer thicker in the case of boundary solution in equilibrium with calcite (BC2) compared to the rest of the cases. This is due to the fact that in the case of BC1 and BC3 the precipitated calcite further dissolves. For solution with low carbon concentration such a correlation is not observed.

Figure 8: Mean thickness of precipitated calcite layer with respect to different boundary solutions at 1000 s.

Another parameter of interest is the pH profile which is plotted in Figure 9. Figure 9 further complements the observations drawn from portlandite and calcite profiles. pH profiles in later stages show three distinct zones viz., a) a zone where portlandite is present where pH is same as initial condition, b) a zone where portlandite is dissolved and calcite has precipitated and pH is gradually reducing and c) a zone where pH is same as that for boundary solution. For boundary solutions with total carbon concentration equal to 0.057 M (BC1-BC3) the pH front moves further in the domain compared to the boundary solutions with the total carbon concentration equal to 0.0057 M (BC4-BC6). This complements the observation from Figure 5 on faster advancements of the portlandite dissolution front for BC1-BC3. From Figure 9 it can be also inferred that for BC4-BC6 the pH front remains close to the boundary, which explains the calcite precipitation layer forming near the boundary for the respective simulations (See Figure 7). From Figure 9 further observations can be made for the boundary solutions with different pH and containing total carbon concentration equal to
0.057 M. The pH front has advanced most for the solution with low pH, followed by the solution with high pH equilibrated with calcite, followed by the solution equilibrated with Na. This observation was valid for all microstructures. For boundary solutions with total carbon concentration equal to 0.0057 M such general observations cannot be deduced.

Figure 9: Spatial profiles of pH for InertFine microstructure. The spatial profile obtained by averaging along a direction perpendicular to diffusion (y-direction).

3.1.2. Influence of microstructure

Figure 10: Time evolution of (a) normalized portlandite volume fraction dissolved with respect to initial value and (b) calcite volume fraction for different microstructures for simulations with BC1 as boundary composition.
Figure 10 shows the time evolution of normalized portlandite volume fraction dissolved and calcite volume fraction precipitated for different microstructures for simulations with BC1 as boundary solution. It clearly shows that fine microstructures lead to higher dissolution and correspondingly more precipitation of calcite compared to coarse microstructures even though the former has lower diffusivities that the later. These results are in contrast with the results for leaching simulations under deionized water performed previously using the same model by Patel et al. [48]. In the case of leaching under deionized water, microstructures with lower relative diffusivity led to the slower dissolution of portlandite and the reactive surface area did not have an influence to the dissolution behaviour. In the present study, the reactive surface plays a more dominant role compared to the initial tortuosity of the material, due to competition between reactive transport process and precipitation of calcite. Higher reactive surface area leads to faster dissolution of portlandite, which is immediately consumed by calcite precipitation thus leading to self-sustaining mechanism which tries to drive system continuously towards equilibrium. In terms of different variations of coarse microstructures, Figure 10 shows that the Coarse microstructure has the highest amount of portlandite dissolved followed by InertCoarse microstructure and PortCoarse microstructure. The amount of calcite precipitated is highest for Coarse microstructure followed by PortCoarse microstructure and InertCoarse microstructure. This observation can be attributed to the higher initial relative diffusivity in case of Coarse microstructure compared to other two variations. On contrary, for variations of Fine microstructures, portlandite dissolution rate is similar for Fine and PortFine microstructure and is higher compared to InertFine microstructure. The amount of calcite precipitated is highest for PortFine microstructure followed by Fine microstructure and InertFine microstructures. This can be attributed to more dominant behaviour of the increase of the reactive surface area in the case of PortFine. Further, from supplementary information (Figures B.1-B.6) it can be seen that these observations are not consistent for all boundary solution composition indicating strong intercoupling
between the effect of boundary solutions and the microstructure properties such as reactive surface area and tortuosity.

Figure 11: Spatial profile of normalized portlandite volume fraction with respect to the initial volume fraction for different microstructures with BC1 as boundary solution composition. The spatial profile obtained by averaging along a direction perpendicular to diffusion (y-direction).

Figure 11 shows the spatial profiles of the normalized portlandite volume fraction for different microstructures for simulations with BC1 as boundary conditions. It can be seen from Figure 11 that the extent of portlandite dissolution is much larger for fine microstructures compared to the coarse microstructure for a given time, even though the initial relative diffusivity of former is higher than the later. Correspondingly, the mean location of portlandite dissolution front plotted in Figure 12 at the end of 1000 s is found to be further for fine microstructure than for coarse microstructure. Comparing the variations in Fine microstructures, it can be seen from Figure 11 that for PortFine microstructure is furthest followed by Fine microstructure and InertFine microstructure at later times. This suggest that in case of PortFine microstructure, the increase in tortuosity and the increase in reactive surface area has a counter-balancing effect. However, these observations are not consistent for all boundary solutions as seen in Figure 12 and Figures B.7-B.12 in supplementary information.

For variations of coarse microstructures, it can be seen from Figure 11 that for Coarse microstructure
the portlandite dissolution front has moved further compared to PortCoarse and InertCoarse microstructures for which profiles are almost coinciding. However, again from Figure 12 and Figures B.7-B.12 it can be seen that this behaviour is not same for all boundary solutions. This indicates that a competition between boundary solution composition, tortuosity and reactive surface area collectively dictates the macro-scale behaviour.

![Figure 12: Mean location of portlandite dissolution front with respect types of microstructure at 1000 s.]

![Figure 13: Spatial profiles of calcite volume fraction for different microstructures with BC1 as boundary solution composition. The spatial profile obtained by averaging along a direction perpendicular to diffusion (y-direction).]
Figure 13 shows the spatial profiles of calcite volume fraction. It can be seen that the peak volume fraction of calcite is higher for fine microstructures than coarse microstructures. Secondly, the extent of dissolution of calcite is more for fine microstructure compared to coarse microstructures. Figure 14 shows the thickness of calcite layer with respect to microstructure at 1000 s. From Figure 14 it can be deduced that the thickness of calcite layer is larger for fine microstructures compared to coarse microstructures for boundary solution with higher carbon concentration (BC1-BC3). For boundary conditions with lower carbon concentration (BC3-BC6) the thickness of calcite layer is almost same for all microstructures. Considering variations of coarse microstructures, Figure 14 shows that the coarse microstructure has highest thickness followed by PortCoarse microstructure and InertCoarse microstructure for boundary conditions with higher carbon concentration as carbon diffuses much further in the case of the coarse microstructure.

Figure 15 shows the spatial profiles of pH for different microstructures with BC1 as boundary solution composition. Clearly, for finer microstructures the pH front moves faster compare to coarse microstructure. This is complementary to observations shown in Figure 11 and Figure 13. In terms of variations of Fine microstructure, the pH front moves faster for PortFine microstructure compared to other variations. Whereas pH front almost coincides for all variations of Coarse microstructure at 1000s. However, these observations are not consistent for all boundary conditions (See Figures B.19-
B.24 in supplementary information) indicating that the boundary solution composition, the reactive surface area and the tortuosity collectively govern the pH profiles and no individual parameter is dominant for all cases.

![Graph showing pH profiles for different microstructures with BC1 as boundary solution composition. The spatial profile obtained by averaging along a direction perpendicular to diffusion (y-direction).]

**Figure 15**: Spatial profiles of pH for different microstructures with BC1 as boundary solution composition. The spatial profile obtained by averaging along a direction perpendicular to diffusion (y-direction).

### 3.2 Three-dimensional simulations using virtual cement paste microstructure for carbonated brine cement interactions.

**Table 4**: Composition of cement for Duguid and Scherer [26] experiments in wt% taken from Huet et al. [12].

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>SO₃</th>
<th>Alkali (Na₂O)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>21.66</td>
<td>2.78</td>
<td>4.41</td>
<td>63.8</td>
<td>3.18</td>
<td>2.96</td>
<td>0.21</td>
</tr>
</tbody>
</table>

**Table 5**: Volume fraction of different phases in the generated cement paste microstructure.

<table>
<thead>
<tr>
<th>Phases</th>
<th>Volume fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capillary pores</td>
<td>0.415</td>
</tr>
<tr>
<td>Portlandite</td>
<td>0.116</td>
</tr>
<tr>
<td>C-S-H solid</td>
<td>0.24183</td>
</tr>
<tr>
<td>Gel pores</td>
<td>0.15693</td>
</tr>
<tr>
<td>Unreacted clinker</td>
<td>0.069</td>
</tr>
</tbody>
</table>
To demonstrate the applicability of the developed model to a more realistic scenario the results from three-dimensional simulation are presented for comparison with experimental study of Duguid and Scherer [26]. Previous simulations of these experiments have been performed using continuum scale models [12–14]. The shortcomings of continuum modelling approach include the needs to calibrate or adjust key model parameters such as diffusion coefficient, porosity relationships or reaction rates to match experimental results. Therefore, it is interesting to apply the developed pore-scale modelling approach to these experiments to explore the possibility of alleviating some of these shortcomings. For this study, we consider the experimental dataset reported for sandstone like reservoir exposure condition at 20 °C for ordinary Portland cement paste with water cement ratio (w/c) equal to 0.7. The detailed boundary solution composition is given in Table 3 as BC1.

Input microstructure needed for our model is generated using HYMOSTRUC, which requires cement composition, Blaine fineness and rate parameters for hydration as key inputs. The cement composition is taken from Huet et al. [12] which is summarized in Table 4. Blaine fineness is taken as 228 m²/kg as reported in [50] for a similar type of cement. The rate parameters are kept to default settings of HYMOSTRUC as they have been well calibrated for OPC. The 28-day hydrated microstructure is used for these simulations and the hydration degree at 28 days was 0.74. Several simplifications where made in setting up numerical simulations. Instead of cylindrical columns used for experiment we considered a cuboid domain. Further we truncate the simulation domain to 450 µm × 250 µm × 250 µm. Note that these simplifications are reasonable as we are simulating early onset of degradation processes and making comparisons with the location of fronts which is considered to be uniform for cylindrical samples in the experimental results. The vector microstructure was mapped on computational domain resolution of 7.5 µm resolution which was possible due to high w/c of cement paste while allows preserving the volume fraction of different phases and degree of percolation of capillary pores at this resolution. The coarsening of microstructure allowed us to attain realistic time scale for direct comparison with experiments. The
generated microstructure is shown in Figure 16. The volume fraction of different phases in the microstructure is summarized in Table 5. The boundary solution is introduced on the left-hand side of the domain by the addition of an additional fluid layer (x=0).

Figure 16: Generated microstructure using HYMOSTRUC used for simulations.

Figure 17 and Figure 18 provide visualization model output for aqueous phases and solid phases, respectively. Figure 17 shows aqueous molal concentrations of primary species Ca and C and pH at 24 hr. Figure 18 shows molal concentration of calcite and portlandite. For this plot only the volume elements containing portlandite and calcite higher than 0.5 M are shown. Figure 17 and Figure 18 demonstrates the capability of the developed model to capture the complete picture of 3D microstructure evolution and changes in pore solution due to combined carbonation and leaching of cement paste. From Figure 17 and Figure 18 it can be seen that maximum calcite precipitation is observed at the point at which the calcium leaching out meets ingressing dissolved carbon from the boundary. Figure 18 clearly shows formation of separate zones of calcite precipitation where portlandite is completely leached and an intact zone with unreacted portlandite which is consistent with the experimental observations of Duguid and Scherer [26].
Figure 17: Visualization of aqueous molal concentrations of Ca and C and pH at 24 hr. All solid phases are transparent in this visualization.
Figure 18: Visualization of calcite and portlandite molal concentrations at different time. Only volume elements containing calcite and portlandite higher than 0.5 M are shown in figure and all other volume elements are transparent.

Figure 19 shows the time evolution of macroscopic quantities viz., percentage calcium leached from solid phases and volume fraction of calcite precipitated. In Figure 19 (a) the percentage of calcium leached is computed by change of calcium content in solid phase normalized with initial calcium content in the solid phase. Figure 19 (a) shows that the amount of calcium leached from the portlandite is higher compared to that from C-S-H. Figure 19 (b) shows the volume fraction of calcite precipitated in the microstructure. Additionally, in Figure 19 (b) the volume fraction of calcite precipitated is further decomposed in the amount precipitated in capillary pores initially present or generated from
portlandite dissolution and amount precipitated in gel pores. It can be clearly seen in Figure 19 (b) that the amount of calcite precipitated in capillary pores is much higher compared to that in gel pores. This leads to reduction of fluxes through capillary pores thus in later time reducing the amount of calcium leached as shown in Figure 19 (a). Figure 19 shows that the amount of calcium leached does not follow a linear relationship with respect to square root of time as well as which usually observed in case of pure leaching [6,10]. This can be attributed to the complex interplay between diffusion process and calcite precipitation. For instance, in Figure 19 it can be seen that up to 2 hr amount of calcium leached has linear relationship with respect to square root of time. At this point the volume fraction of calcite precipitated reaches a value of 0.01. After 2 hr the calcite start dissolving which leads to further opening of pores and thus promoting leaching but with a different slope with respect to square root of time and correspondingly calcite precipitation. Hence, such deduction of linear rates with respect to square-root of time or time should from limited experimental data points should be avoided.

Figure 19: (a) Percentage calcium leached from C-S-H and portlandite in the microstructure with respect to square root of time (b) Volume fraction of calcite ($\phi_{\text{calc}}$) precipitated in the microstructure, C-S-H and initial capillary pores and capillary pores created by portlandite dissolution with respect to square root of time.
Figure 20: Phase assemblage at different simulation times. All quantities are averaged along the plane perpendicular to the ingress of boundary solution (YZ-plane). For colour figure refer to online version. Four different zones can be identified viz., intact zone, portlandite depletion zone, calcite precipitation zone and C-S-H dissolution zone.

Figure 21: Profile of pH at different simulation times. Profile is obtained by averaging pH along the plane perpendicular to the ingress of boundary solution (YZ-plane).
Figure 20 shows the phase assemblage at different time for this simulation. The phase volume fractions are averaged along the plane perpendicular to solution ingress i.e. YZ-plane. From Figure 20 four different zones can be identified viz., intact zone, portlandite depletion zone, calcite precipitation zone and C-S-H dissolution zone. In the intact zone portlandite concentration is same as initial concentration. The portlandite concentration is gradually decreasing in the portlandite depletion zone and at the end of this zone portlandite is completely dissolved. In the calcite precipitation zone portlandite is completely dissolved, C-S-H 1.6 is partly dissolved and large amount of calcite has been precipitated. Note that the calcite in this zone does not fully fill the pore-space. However, precipitated calcite can lead to significant reduction in propagation of reaction fronts. Finally, in C-S-H dissolution zone, C-S-H has very low calcium to silicon ratio and a small trace of calcite and amorphous silica precipitation can be observed. The zonation with different phases observed is consistent with the experiments of Duguid and Scherer [26]. The dark grey zone, grey zone, white zone and brown zone in their experiments can be considered to correspond to intact zone, portlandite depletion zone, calcite precipitation zone, and C-S-H dissolution zone, respectively, providing qualitative validation of the model. Figure 21 shows the pH profiles at different time. It can be seen from Figure 21 that pH remains constant to initial value where portlandite is present i.e. in intact zone and portlandite depletion zone. It gradually drops in calcite precipitation zone and C-S-H dissolution zone and reaches to the pH of boundary solution. Figure 20 shows that from 2 hr to 12 hr the portlandite dissolution progresses faster compared to from 12 hr to 24 hr where phase assemblage profiles are almost identical. This can be also seen in Figure 21 where pH profile for 12 hr and 24 hr are very close to each other. This can be attributed to the reduction of diffusive flux of ions through capillary pores caused by precipitation of calcite. This is clearly visible in Figure 19 (b) and Figure 20. Also note that the peak of calcite volume fraction in Figure 20 is at the location where C-S-H is still present in significant amounts. Thus, even though the boundary solution is undersaturated with respect to calcite, calcite in the capillary pores is stable and its volume fraction continues to increase due to calcium available from dissolution of C-S-H. At the later stage when C-S-H has depleted, the
precipitated calcite eventually dissolves, leading to progress of portlandite dissolution front from 24 hr to 120 hr but at lower rate.

Table 6 summarizes the starting locations of different zones observed in Figure 20. The starting locations of intact zone and portlandite depletion zone are defined as the first point where portlandite volume fraction is greater than 0.99 times the initial volume fraction and 0.1 time the initial volume fraction, respectively. The starting point of calcite precipitation zone is defined as the location where C-S-H 1.6 is greater than 0.5 times the initial volume fraction. Furthermore for comparison purpose, Table 6 also provides location of outer edge of different layers observed by Duguid and Scherer [26]. These locations are computed from the rate of advancement reported by them considering linear progression of fronts with respect to time. These layers in experimental studies have been identified visually based on the colours as brown, white, grey and dark grey. Based on chemical analyses using XRD and EMPA on samples at the end of the experiments it was further deduced that the orange zone and brown layers represent the leached zone, the white layer represents a carbonating zone containing large amounts of calcite, the light grey layer represents a calcium hydroxide dissolution zone and the dark grey layer represents intact cement. Comparing the values from multi-level pore-scale model and experiments shows that up to 24 hr the model compares reasonably well with experimental observations. The differences between the model and experimental observations can be attributed to model simplifications such as use of virtual microstructure, simplification of cement paste mineral composition, diffusion process and consideration of chemical equilibrium at pore-scale. Additionally, the empirical interpretation of linear rate with time for advancement of reaction fronts by Duguid and Scherer [26] may not hold true as demonstrated in our simulations. At 120 hr of reaction time, there are striking differences between model predictions and observed location of fronts. This as explained above is due to the stable precipitated calcite layer in presence of C-S-H leading to slow down of the progression of degradation. Additionally, we observe large discrepancy between C-S-H leaching zone observed in model and experiments at these times. This suggest that kinetic considerations of C-S-H
dissolution and calcite precipitation might be needed to further improve predictions at later stage of system evolution. As mentioned above our modelling framework is flexible to account for mineral nucleation and growth kinetics. However, the parameters for reaction kinetics for cement phases at pore-scale are not well-established at this stage. Note that consideration of kinetics would also impact the evolution of diffusion in sub-voxel porosity. For instance, Liu and Jacques [51] has demonstrated this in case of continuum scale model while considering nano-scale effects. Alternatively, the porosity-diffusivity relationship for calcite in capillary pores can be further adjusted to match experiments. However, this would also lead to change in the thickness of precipitated calcite layers. For instance if precipitated calcite layer is consider non-diffusive then the calcite layer will be single voxel layer thick (see results reported in [52]). It will also impact phase assemblage of the system as reported for continuum scale modelling by Georget et al. [11]. Therefore, calibration of kinetic rates and transport properties of precipitated layer would require experiments that can be directly simulated at pore-scale and can provide detailed quantitative characterization of the mineralogy. Hence, further refinement of model considering incorporation of the aforementioned elements in absence of comprehensive experimental data is considered out of scope for present study.

<table>
<thead>
<tr>
<th>Time(hr)</th>
<th>Calcite precipitation zone</th>
<th>Portlandite depletion zone</th>
<th>Intact zone</th>
<th>Brown</th>
<th>White</th>
<th>Grey</th>
<th>Dark grey</th>
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<tbody>
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<td>33.75</td>
<td>108.75</td>
<td>131.25</td>
<td>0.083</td>
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<td>198.75</td>
<td>236.25</td>
<td>5</td>
<td>230</td>
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<td>1675</td>
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</table>

4. Conclusions

In this study a new multilevel pore-scale reactive transport model taking into account sub-voxel un resolved porosity has been proposed to simulate the microstructure evolution of cement paste
subjected to coupled carbonation and leaching processes. The governing equations are solved using a robust lattice-Boltzmann method-based pore-scale solver. The pore-scale solver allows us to directly take the three-dimensional digitized cement paste microstructure as input and model its evolution under the combined effect of leaching and carbonation subjected to different boundary conditions. For this study digitized microstructure generated using hydration model, HYMOISTRUC has been used. However, modelling framework is flexible to use microstructure from computer tomography. In addition to the three-dimensional simulations a detailed parametric study has been carried out to explore the influence of microstructure (tortuosity, reactive surface area and calcium content of solid phases) and boundary solution compositions (dissolved carbon content, calcium content and pH) on and apparent extent of the degradation. The two-dimensional parametric study yields similar qualitative behaviour as observed in 3D model. Key conclusions from these studies are presented below:

Two-dimensional parametric study

- Portlandite dissolution and calcite precipitation exhibit non-linear behaviour with respect to time and square root of time.
- For boundary solutions with total carbon concentration equal to 0.0057 M the amount of calcite precipitated is lower for the cases where as the amount of portlandite dissolved is comparable to boundary solutions with total carbon concentration equal to 0.057 M. This suggests more calcium leaching out of the domain in the case of former compared to latter.
- The portlandite dissolution front progresses faster for boundary solutions with total carbon concentration equal to 0.057 M compared to solutions with 0.0057 M carbon concentration. This is because the calcium in pore solution due to dissolution of portlandite is immediately consumed by the dissolved carbon to precipitate calcite thus driving the system constantly away from the chemical equilibrium. Consequently, the amount of calcite precipitated for is also higher.
• The portlandite dissolution front progresses faster for Low pH boundary solutions than at higher pH boundary solutions.

• For simulations with boundary solution containing the total carbon concentration equal to 0.0057 M the calcite precipitates close to the injection boundary, whereas for simulations with boundary solutions containing total carbon concentration equal to 0.057 M, the precipitation of calcite occurs in the vicinity of the portlandite dissolution. Consequently, the precipitated calcite layer is thicker in case of latter compared to former. Moreover, the spatial peak of calcite precipitated is higher for 0.0057 M boundary solution which indicates that this case might have much more potential to clog the surface.

• It was observed that the reactive surface area has more dominant effect on the progress of degradation. The tortuosity of the media plays secondary role. In the simulations with fine microstructures the cumulative dissolution of portlandite was faster and the amount of calcite precipitated was higher compared to coarse microstructure. This was due to the competition between diffusion through the media and calcite precipitation reaction.

• The calcium content of microstructure does not have clear correlation to the degree of degradation and rather collective effects of boundary solution and microstructure seems to overall control of the system evolution.

• The increase in tortuosity caused by inert mineral lead to slower rate of degradation for same microstructure features.

The simulations from 2D parametric study shows that the boundary solution compositions and microstructure strongly affect degradation rates which may not be fully accounted for in continuum scale models. This also explains need for recalibrating model for each and every experimental case.

Three-dimensional simulations
• Calcium leached and calcite precipitation exhibit non-linear behaviour with respect to time and square root of time. This implies that simple empirical models may not be useful and use of numerical reactive transport model is inevitable for practical predictions.

• The amount of portlandite dissolved is much higher compared to C-S-H dissolution.

• The amount of calcite precipitated in capillary pores is higher than that in gel pores and, at the later stages of the system evolution, the diffusion through the calcite precipitated in capillary pores is the limiting factor controlling the progression of degradation front. It should be noted that the precipitated calcite does not fully occupy both the gel pores and the capillary pores, meaning that the pore space is not fully clogged.

• The simulation is able to capture four distinct zones observed due to combined action of carbonation and leaching viz., the intact zone, the zone where portlandite is gradually dissolving, zone where calcite is precipitated in large volume fractions and zone where C-S-H has severely decalcified. These zones are consistent with the one observed in experiments thus providing qualitative validation of the model.

• The model prediction quantitatively agrees with experimental observations at the early stage of the system evolution. Minor differences between experimental and modelling results can be attributed to model simplifications such as use of virtual microstructure, simplification related to model setup and diffusion process and simplified representation of cement paste mineral composition. It is worth mentioning that the measurement of the degradation front thickness in the experimental study was conducted visually and thus may contain significant uncertainties. Moreover, in experimental study simple linear relationship has been used to define the rate of advancement of this layer as function of time which does not hold true.

• At later time large differences are observed between model and experiments. During this time the diffusion through the calcite precipitated in capillary pores which is also chemically stable due to presence of C-S-H in this zone governs the progression of degradation front. Therefore,
in order to correctly capture the progression of long-term degradation of the system kinetics of C-S-H dissolution and calcite precipitation might be needed to be accounted. However, the kinetic parameters of these phases in such exposure conditions are largely unknown. Additionally, the diffusivity of calcite phase in capillary pore might be also recalibrated.

- In order to correctly capture the progression of long-term evolution of the system, kinetics of C-S-H dissolution and calcite precipitation needs to be considered within the model. For this purpose, new experimental studies are needed which can help to back calculate appropriate kinetic rates for the C-S-H dissolution and calcite precipitation in cementitious system and diffusivity of calcite layer. These experimental studies should focus on detail pore structure analysis and quantitative chemical characterization at different time interval for systematic variation of boundary solution exposures which will enable a better quantitative comparison with the model.

Finally, the development of multiscale framework taking into account information from pore-scale models such as on presented in this study will enable us to develop predictive models for cement exposed to CO₂ rich ground water. The present model represents a significant step in this direction.
5. Supplementary information

Additional figures from two-dimensional parametric study has been provided in two sections in supplementary information

A. Supplementary figures for section 3.1.1 influence of boundary solution composition

B. Supplementary figures for section 3.1.2 influence of microstructure

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7. References


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