Simulating cement microstructural evolution during calcium leaching

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Abstract

Calcium leaching is one of the important degradation mechanisms causing dissolution of the crystalline phases such as, AFm, portlandite increasing capillary porosity. Further it leads to decalcification of an amorphous C-S-H phase causing increase in the gel porosity and in turn degrading the long term performance of concrete structures. In this paper a lattice Boltzmann based pore-scale reactive transport approach in the context of simulating the evolution of microstructure of a hardened cement paste during calcium leaching is presented. This approach is based on fundamental principles of chemical thermodynamics and mass transport. The example presented illustrates influence of location of mineral grains and surface area on overall dissolution rate and pore structure evolution.

1 Introduction

Durability of concrete is affected by a wide range of complex physico-chemo-mechanical phenomena causing changes in the underlying microstructure which affects its macroscopic behaviour [1–3]. Calcium leaching is an important degradation mechanism causing severe damage to the concrete structures such as dams, pipes or conduits [4,5]. Calcium leaching is also of an importance for the long-term safety assessment of the nuclear waste disposal systems [3, 4]. Calcium leaching initiates dissolution of the crystalline phases such as portlandite, AFM and leaching of calcium from amorphous C-S-H phases which causes increase in a porosity and pore connectivity. This in turn causes increase in the permeability, diffusivity and loss of strength [1,2]. Performing calcium leaching under natural conditions is a slow process and often the experiments are accelerated using aggressive low pH solutions such as deionized water or ammonium nitrate solution. However, these solutions may have different effects on the dissolution behaviour of mineral phases and microstructure of cement paste[6,7]. Hence experimental results obtained under accelerated conditions are often difficult to be extrapolated for behaviour under natural conditions.An alternative approach to experimentation under accelerated condition is to develop a computer model to simulate the changes in the microstructure of cement paste (essentially dissolution of portlandite and AFM phases and leaching of calcium in C-S-H phases) and to derive the effective parameters through homogenization principles.

Different microstructural models for simulating the hydration and early stage microstructure of the cement paste have been developed (for a detailed review refer [8]). These models can be the starting point for a pore scale model to simulate the degradation phenomena under calcium leaching. Bentz and Garboczi [1] were first to simulate the influence of dissolution of portlandite from microstructure of hydrated cement paste on pore structure, percolation and diffusivity. The dissolution of portlandite in their model was carried out by the random removal of portlandite pixels in contact with water but ion transport was not simulated at the microstructural level. This model has been further coupled with a finite volume based reactive transport approach to simulate the degradation over larger domains [9]. Gaitero et al. [10] developed a microstructural based reactive transport model for calcium leaching with ammonium nitrate solution. However their model simplifies the cement chemistry and effects of ion activities on dissolution are not considered in their model.

Recently, a pore-scale reactive transport model was developed keeping in mind its application to simulate evolution of hardened cement paste microstructure under chemical degradation [11,12]. This model combines the mass transport and fundamental principles of chemical thermodynamics to model microstructural evolution. The mass transport of chemical species is carried out using Lattice Boltzmann (LB) method. The LB transport model is coupled with the *PHREEQC* [16] speciation code to compute geochemical reactions occurring in cement system and with a geometry update algorithm which updates the pore-structure due to dissolution or precipitation of mineral phases. The flowchart of the model is illustrated in Fig 1. Particular details of the model with context to calcium leaching are described in section 2. Finally in section 3, an example illustrates the potential of our model to be a plausible approach to simulate the changes in microstructure under calcium leaching.

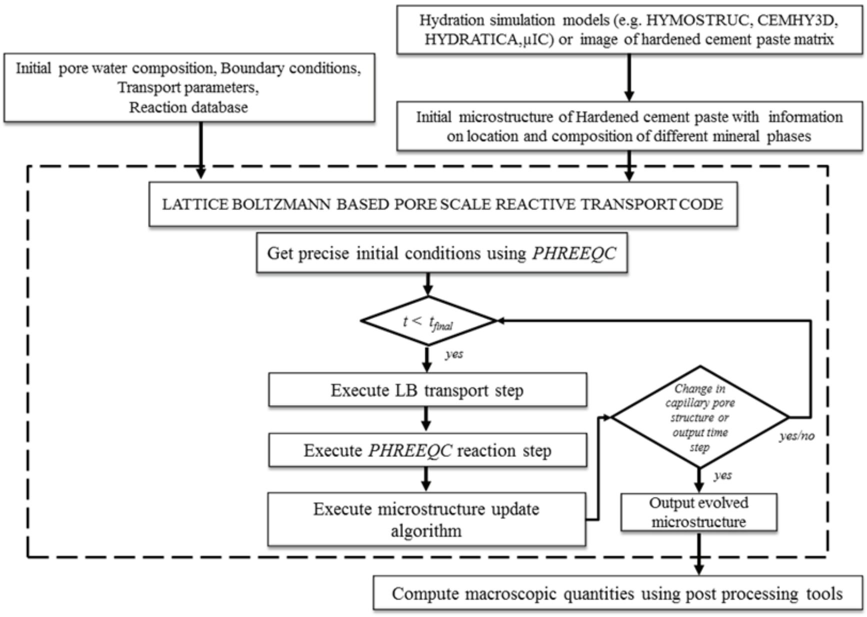


Fig. 1 Illustrative flow chart for the pore scale model to simulate degradation of hardened cement pate under chemical effects

2 Modelling approach

2.1 Governing equations and model assumptions

The reactive mass transport of the chemical species in microstructure of the hardened cement paste in absence of electro kinetic effects can be given by the advective-diffusion-reaction equation. Same diffusion coefficient is assumed for all aqueous species to limit the number of transport equations to be solved to primary species. The transport equation is then expressed in terms of total concentration as the stoichiometric sum of the concentrations of all primary and secondary species of this component.

$$\frac{\partial \theta C^j}{\partial t} = -\vec{\nabla} \cdot \vec{J}^j + R^j \qquad (1)$$

$$\vec{J}^j = \left(-\xi \theta D_0 \vec{\nabla} C^j\right) + \vec{u} C^j$$

where C^j is the total concentration for j^{th} primary species [N L^{-3}], $\vec{J}^j$ represents the mass flux of j^{th} species [N L^{-2} T^{-1}], D_0 is the isotropic diffusion tensor of j^{th} species in water [L^2 T^{-1}], $\vec{u}$ is the Darcy velocity field of fluid containing chemical species, R^j is the general sink-source term representing both homogenous equilibrium and non-equilibrium reactions which is computed using *PHREEQC* [N L^{-3} T^{-1}], θ is the porosity and ξ represents the tortuosity factor.

In capillary pores, θ and ξ would be 1 reducing Eq. (1) to mass transport in pure water. The C-S-H phase is treated here as a porous media and the transport of species is given by Eq. (1) where θ and ξ represents porosity and tortuosity of C-S-H respectively. Initial porosity of C-S-H phase can be assumed to be equal to around 0.28 [5]. Due to the lack of experimental data, tortuosity factor ξ is assumed to be given by a power function $\theta^{3.707}$ analogous to Archie's law, which fits two known diffusivity values viz., initial diffusivity of C-S-H with porosity of 0.28 which can be approximated as $D_o/400$ as proposed by [13] and D_o when θ is 1. Note that the tortuosity factor and porosity of C-S-H are input parameters and can be easily changed with evidence from new experimental data.

Crystalline phases such as portlandite, AFM are considered as pure solids (no mass transport through this phases) and the heterogeneous reactions corresponding to this mineral phases are treated as pseudo-homogenous reaction by addition of an extra source-sink term in Eq. (1) at the boundary of mineral phase. The dissolution of mineral phases further causes movement of mineral boundaries.

2.2 Lattice Boltzmann based pore scale reactive transport method

The Lattice Boltzmann (LB) method is the efficient tool to model the flow and transport at pore scale and has been previously applied to compute permeability of hardened cement paste using microstructure from cement hydration model[14,15]. The advantage of lattice Boltzmann method is the inherent local computations at each lattice node which can be parallelized easily for computationally intensive applications compared to other numerical methods. In our model LB method is coupled with a generic speciation code *PHREEQC* [16] which allows incorporation of cement chemistry based on equilibrium approach using reaction parameters from thermodynamic database CEMDATA07 [17,18] for *PHREEQC* [19].The flow of algorithm in a given time step consists of three distinct steps as shown in Fig. 1 viz., the LB transport step, the reaction step executed by *PHREEQC* and a microstructure update algorithm (details can be found elsewhere [11,12]). In previous studies the LB transport algorithm consisted of mass transport in pure water. To incorporate the mass transport in porous media described by Eq. (1), the diffusion velocity formulation has been used [20,21]. Thus mass transport Eq. (1) in terms of the LB method can be expressed as,

$$f_i^j(\vec{r}+\vec{e}_i\,\Delta t, t+\Delta t) = f_i^j(\vec{r},t) + \Omega^{BGK,j}(\vec{r},t) + \Omega^{rxn,j}(\vec{r},t) + \Omega^{P,j}(\vec{r},t) \qquad (2)$$

Where

$$\Omega^{BGK,j}(\vec{r},t) = -\frac{\Delta t}{\tau}\left[f_i^j(\vec{r},t) - f_i^{eq,j}(\vec{r},t)\right]$$

$$f_i^{eq,j}(\vec{r},t) = w_i C^j\left[1 + \frac{\vec{e}_i\cdot\vec{u}}{e_s^2}\right]$$

$$\Omega^{P,j}(\vec{r},t) = \left(1-\theta(\vec{r},t)\right)\frac{C^j(\vec{r},t)-C^j(\vec{r},t-\Delta t)}{\Delta t} + C^j(\vec{r},t)\frac{\theta(\vec{r},t)-\theta(\vec{r},t-\Delta t)}{\Delta t}$$

where f_i^j is the particle's distribution function for j^{th} species along i^{th} lattice direction [N L^{-3}], $\vec{e}_i$ is the discrete velocity vector in i^{th} direction for i =1-5 in case of D2Q5 lattice [L T^{-1}], τ is relaxation time [T] and $f_i^{eq,j}$ is the particle's equilibrium distribution function [NL^{-3}] which is given by the Maxwellian distribution, $\vec{r}$ is the position vector of a given point, Δt is the discrete time step [T], w_i are the weights for particle's distribution function along the i^{th} direction (w_i = 2/6 for i = 0 and w_i = 1/6 for i = 1 – 4) ,e_s is the lattice internal speed($e_s = e/\sqrt{3}$) [L T^{-1}] , $e = \Delta x/\Delta t$ [L T^{-1}] and Δx is the lattice spacing [L].

The macroscopic parameters and diffusivity in terms of LB parameters can be defined as,

$$C^j(\vec{r},t) = \textstyle\sum_i f_i^j(\vec{r},t) \qquad (3)$$

$$\vec{J}^j(\vec{r},t) = \textstyle\sum_i f_i^j(\vec{r},t)\,\vec{u}(\vec{r},t) - \left(1-\frac{\Delta t}{2\tau}\right)\left[\sum_i f_i^j(\vec{r},t)\,\vec{u}(\vec{r},t) - \sum_i f_i^j(\vec{r},t)\vec{e}_i\right]$$

$$D_0 = e_s^2\left(\tau - \frac{\Delta t}{2}\right)$$

From the above equation it can be noted that the parameter τ corresponds to diffusivity of primary species in pure water. To account for the variability of diffusivity as in Eq. (1) due to the porosity and tortuosity, according to diffuse velocity formulation the flux of this fluctuating diffusivity is transferred to advective term and while computing $f_i^{eq,j}$ additional term $\vec{u}_{diff}$ is added to Darcy velocity which can be calculated using Eq. (4)

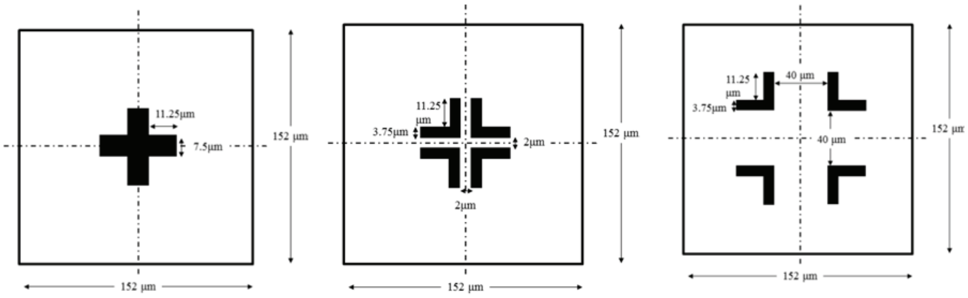
$$\vec{u}_{diff}^j(\vec{r},t) = \frac{\widetilde{D}(\vec{r},t)/\tau\, e_s^2}{1+\widetilde{D}(\vec{r},t)/\tau\, e_s^2}\left(\frac{\sum_i f_i^j\vec{e}_i}{C^j} - \vec{u}\right) \qquad (4)$$

$$\widetilde{D}(\vec{r},t) = (\xi(\vec{r},t)\theta(\vec{r},t) - 1)D_0$$

More details on derivation and validation of above formulation can be found elsewhere [20,21].

3 Application

The ability of our model to study influence of calcium leaching on pore structure evolution was illustrated with a simple example involving portlandite dissolution for a fictitious grain shape [11]. Three different setups were considered as shown in Fig 2. In case 2 and case 3 the surface area of portlandite grain is twice as that of case 1. Compared to case 2 four ‘L’ grain are located fairly apart for case 3. The dissolution of portlandite was carried out in an 8mM NaOH solution.



(a) (b) (c)

Fig. 2 Setup for the example a) case 1, b) case 2 and c) case 3

It was found that for case 2, the narrow channel between the grains quickly reaches local equilibrium (concentration gradient inside the narrow channel is close to zero) soon after the start of portlandite dissolution. This inhibits further dissolution of the inner surfaces. Thus, even though the total surface area is twice than that in case 1, the accessible reactive surface area is almost the same as in case 1. Therefore, only small differences in average dissolution rate and total Ca concentration are observed between cases 1 and 2 (see Fig. 3 which shows variations of average total *Ca* concentration over time). When the grain surfaces are sufficiently apart from each other (as in case 3), concentration gradients exist in all directions, and hence all faces dissolve faster. This result in a higher average dissolution rate and shorter time to reach equilibrium for case 3 compared to cases 1 and 2 as shown in Fig 3.

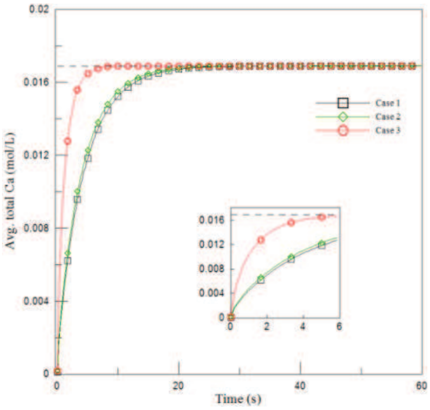
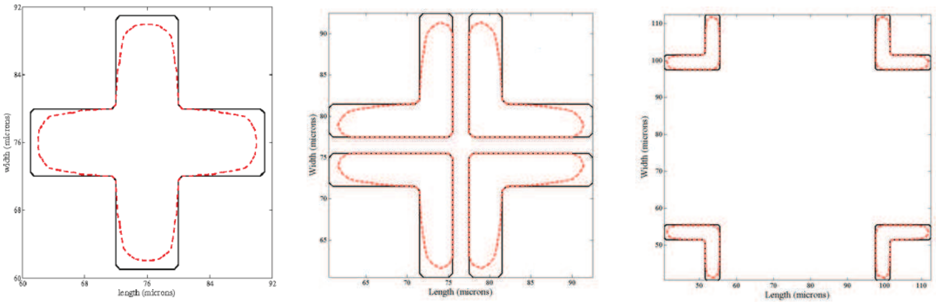


Fig. 3 Average total Ca concentration profiles. The first 6 sec of profile is magnified in inset. Dashed line indicates equilibrium computed using *PHREEQC*

Fig. 4 shows the altered grain shapes for cases 1, 2 and 3 at end of simulation. Fig. 5 magnifies the top-left ‘L’ shaped grains for case 2 and 3. Fig. 5 clearly shows that inner surfaces do not tend to dissolve in case 2 whereas all surfaces are affected by dissolution in case 3.

This example effectively demonstrates the influence of surfaces area, spatial arrangement of grains and role of mass transport at microstructural level on the average dissolution rate and suggests that in case of complex pore structure which is the case for hardened cement paste heterogeneities might play an important role in determining the average dissolution rate and pore structure evolution which in turn affects behaviour of hardened cement paste.



(a) (b) (c)

Fig. 4 Final shape of portlandite grains at the end of simulation a) case 1 b) case 2 and c) case 3. Solid black line represents initial shape and red dash line indicates the final shape at the end of simulation

4 Outlook

In this paper a pore scale reactive transport model for microstructural evolution under calcium leaching based on fundamental principles of chemical thermodynamics and transport phenomena is proposed. The applicability of this approach was illustrated through a simple example. In particular, this example demonstrates the ability of our model to tackle different complexities involved in modelling microstructural evolution under calcium leaching. It also highlights influences of mineral locations and surface area on the pore structure evolution. In future the developed model would be applied to study the significance of different pore network characteristics on evolution of microstructure, average reaction rates and macroscopic properties during calcium leaching.

Acknowledgements

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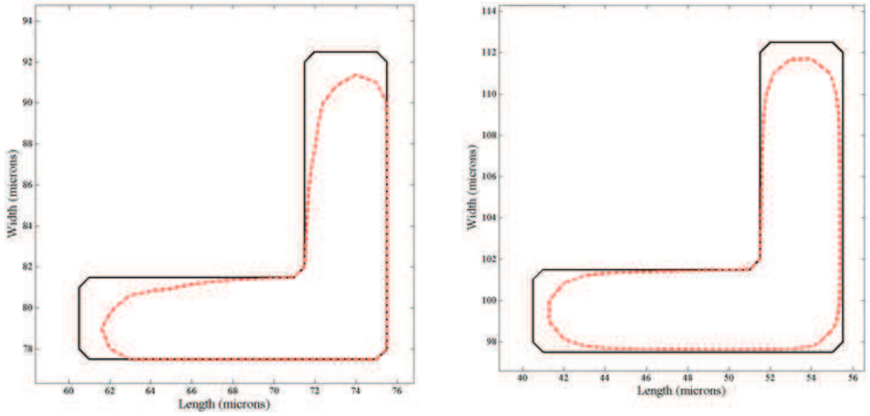

(a) (b)

Fig. 5 Final shape of top left portlandite grain at the end of simulation a) case 2 and b) case 3. Solid black line represents initial shape and red dash line indicates the final shape at the end of simulation

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