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A versatile pore-scale multicomponent reactive transport approach based on lattice Boltzmann method: Application to portlandite dissolution

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ABSTRACT

A versatile lattice Boltzmann (LB) based pore-scale multicomponent reactive transport approach is presented in this paper. This approach is intended to capture mineral phase and pore structure evolution resulting from geochemical interactions applicable, for example to model microstructural evolution of hardened cement paste during chemical degradation. In the proposed approach heterogeneous reactions are conceptualized as pseudo-homogenous (volumetric) reactions by introducing an additional source term in the fluid node located at the interface adjacent to a solid node, and not as flux boundaries as used in previously proposed approaches. This allows a complete decoupling of transport and reaction computations, thus different reaction systems can be introduced within the LB framework through coupling with external geochemical codes. A systematic framework for coupling an external geochemical code with the LB including pore geometry evolution is presented, with the generic geochemical code *PHREEQC* as an example. The developed approach is validated with a set of benchmarks. A first example demonstrates the ability of the developed approach to capture the influence of pH on average portlandite dissolution rate and surface evolution. This example is further extended to illustrate the influence of reactive surface area and spatial arrangement of mineral grains on average dissolution rate. It was demonstrated that both location of mineral grains and surface area play a crucial role in determining average dissolution rate and pore structure evolution.

1. Introduction

Coupled reaction and transport processes are dominant in varieties of natural and man-made porous materials involved in different engineering applications. This includes chemical processes in cementitious materials, such as cement hydration, degradation under chemical attacks, and sorption of contaminants. Although the scale of interest for practical purposes is often macroscopic, spanning several meters, even the transport phenomenon in these systems is affected by the microscopic pore structure. Furthermore, physico-chemical interactions between mineral phases and pore water alter the pore structure and in turn the transport properties of porous media. These "process scales" (the lower scales where processes actually occur) often remains unresolved while modelling phenomenon at the scale of interest (i.e. continuum scale). The effect of "process scales" in continuum scale models is accounted through phenomenological constitutive laws based on experimental observations (see for example, Glasser et al., 2008; Le Bescop et al., 2013).

For cementitious materials, importance of the initial pore structure and its influence on transport and mechanical properties has been long realised (Beaudoin et al., 1994). Several pore-scale cement hydration simulation approaches are being developed to

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simulate pore structure of hardened cement paste. The pore structure obtained from these models has also been used to predict physical and mechanical properties of hardened cement paste. A detailed review on the state of the art of this hydration models can be found elsewhere (Thomas et al., 2011).

For long term durability assessments of cementitious materials it is further essential to evaluate influence of different chemical degradation processes on pore structure evolution and correspondingly changing transport and mechanical properties (Glasser et al., 2008). A pore-scale reactive transport model can effectively capture these changes in pore structure during degradation. Nevertheless, the development of such approach for cementitious systems poses varieties of challenges such as mapping the initial pore structure with mineral phase distribution and development of tools with ability to model flow, transport and alterations in pore geometry due to chemical reactions (Le Bescop et al., 2013).

Qualitatively accurate initial pore geometries can be obtained from existing hydration simulation approaches (Thomas et al., 2011). However, there is lack of a robust approach to model flow, transport and alteration of pore geometry during chemical degradation in cementitious systems. Recently, a variety of approaches to model pore-scale reactive transport processes (e.g. dissolution, precipitation or adsorption) have been proposed based on different numerical schemes such as conventional computational fluid dynamics approaches (Molins et al., 2012), pore network models (Li et al., 2006; Raoof et al., 2012), smooth particle hydrodynamics (Ryan et al., 2011; Tartakovsky et al., 2007), hybrid approaches coupling different numerical methods (O'Brien et al., 2003; Verberg and Ladd, 2002; Yoon et al., 2012; Yu and Ladd, 2010) and lattice Boltzmann methods (Kang et al., 2006, 2007, 2010; Zhang et al., 2008; Sullivan et al., 2005; Verhaeghe et al., 2006, 2007; Hiorth et al., 2013). These approaches have been applied to gain insight into fundamental processes at the pore-scale and to explore ways to upscale physical properties and reaction rates to macroscopic scale.

In this paper we propose a lattice Boltzmann (LB) based reactive transport approach for simulating pore-scale physico-chemical phenomena in cementitious systems. The LB method is efficient and due to its inherent local computation parallelizable and scalable for computationally intensive applications. Applicability of LB method has been successfully demonstrated for dissolution and precipitation reactions (Kang et al., 2006, 2007, 2010; He et al., 2000; Verhaeghe et al., 2006, 2007). This formulation has been further extended to incorporate ion-exchange reactions (Hiorth et al., 2013). However, in these approaches the heterogeneous reactions at mineral grain boundary are conceptualized as flux from the boundary which makes it difficult separate the transport and reaction calculations and consequently coupling of external geochemical codes. As a result, the applicability of LB method till date has been demonstrated only on fixed chemical systems. To eliminate this short coming an alternate treatment for heterogeneous reactions in LB method is proposed in this paper. In our approach the heterogeneous reactions are treated as pseudo homogenous reactions and corresponding additional source-sink terms are imposed in fluid nodes next to the solid boundary. This approach allows sequential operation of transport and reaction step which facilitates coupling of LB transport solver with the external geochemical code. In this paper a detailed approach to couple LB transport solver with *PHREEQC* (Parkhurst and Appelo, 2013) is presented. *PHREEQC* has capabilities for simulating a broad range of equilibrium reactions between water and minerals, ion exchangers, surface complexes, solid solutions, and gases. It also has a general kinetic formulation that allows modelling of non-equilibrium mineral dissolution and precipitation, microbial reactions, decomposition of organic compounds, and other kinetic reactions. Thus, coupling with *PHREEQC* provides access to this wide range of geochemical models which is lacking in the existing LB framework. In case of cementitious system it enables incorporation of a range of geochemical reactions involved in cementitious materials (Jacques et al., 2010; Lothenbach, 2010), using a pre-compiled thermodynamic database (Jacques, 2009).

This coupling approach has been previously demonstrated on 1D examples (Patel et al., 2013). It is further extended for two dimensional systems in this paper. The two dimensional approach is then benchmarked and applied to portlandite mineral grain dissolution which is an important mineral phase in hardened cement paste.

Section 2 discusses the governing equations and assumptions involved in the proposed pore-scale modelling approach and the LB method for multicomponent reactive transport and the coupling procedure with *PHREEQC*. For the sake of clarity, the conversion between LB unit system and physical unit system is described. In Section 3.1, coupling of *PHREEQC* with a two dimensional LB solver is first benchmarked for a portlandite reaction system through quasi one dimensional setup. Finally, the developed approach is applied to dissolution of a portlandite grain to illustrate the influence of pH, reactive surface area and local equilibrium on the average dissolution rate (average dissolution rate in this paper refers to the reaction rate derived from average concentrations over the entire domain) and on the mineral grain surface evolution in Sections 3.2 and 3.3. Conclusions and outlook are discussed in Section 4.

2. Theory and model description

2.1. Governing equations

Multi-component mass transport at the pore-scale is usually described using the advection–diffusion equation given by Eq. (1) under the assumptions that electro kinetic effects due to charged species are neglected and mass transport is considered as a passive scalar (i.e. feedback from change of molar concentration to fluid flow is neglected) (Dentz et al., 2011).

$$\begin{aligned}\frac{\partial C^j}{\partial t} &= -\vec{\nabla}\cdot\vec{J}^j + R^j \\ \vec{J}^j &= (-D^j\vec{\nabla}C^j) + \vec{u}C^j\end{aligned} \tag{1}$$

where C^j is the molar concentration of jth species [N L^{-3}], $\vec{J}^j$ is the flux for jth species [N L^{-2} T^{-1}], D^j is the molecular diffusion coefficient of jth species in water [L^2 T^{-1}], $\vec{u}^j$ is the velocity vector field for fluid flow [L T^{-1}] and R^j represents the sink-source term due to geochemical reactions for jth species [N L^{-3} T^{-1}]. This general sink-source term represents both homogenous equilibrium and non-equilibrium reactions. The velocity vector field (advection-driven) is not used in our benchmarks and examples; however this term is retained in following equations for the sake of generality.

The heterogeneous surface reactions occurring at the fluid solid interface can be expressed in terms of mass balance of jth species at the solid fluid interface as

$$\vec{J}^j\cdot\hat{n}|_{\Gamma=\Gamma_s} = R^j_{surf} \tag{2}$$

where $\hat{n}$ is the unit normal vector to the solid boundary Γ_s, and R^j_{surf} is the surface reaction source sink term for jth component.

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 (Steefel and Macquarrie, 1996).