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LATTICE BOLTZMANN BASED MULTICOMPONENT REACTIVE TRANSPORT MODEL COUPLED WITH GEOCHEMICAL SOLVER FOR PORE SCALE SIMULATIONS

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Abstract. A Lattice Boltzmann (LB) based reactive transport model intended to capture reactions and solid phase changes occurring at the pore scale is presented. The proposed approach uses LB method to compute multi component mass transport. The LB multi-component transport model is then coupled with the well-established geochemical reaction code *PHREEQC* which solves for thermodynamic equilibrium in mixed aqueous-solid phase system with homogenous and heterogeneous reactions. This coupling enables us to update solid phases volumes based on dissolution or precipitation using static update rules which, on pore scale, affects the change of potentially pore network geometry. Unlike conventional approach, heterogeneous reactions are conceptualized as volumetric reactions by introducing additional source term in the fluid node next to solid node, and not as flux boundaries. To demonstrate the validity of this approach several examples are presented in this paper.

1 INTRODUCTION

Multicomponent reactive transport modelling is an important tool for analysing different applications involving coupled physical-chemical processes such as chemical degradation of cementitious materials, transport and sorption of radionuclides, environmental contaminant transport, bioremediation and geologic sequestration of carbon dioxide. Advancements in geochemical reaction modelling and reactive transport modelling have led to development of

several geochemical reaction modelling codes [1-4] and efficient reactive transport codes to simulate coupled continuum scale physical-chemical processes [5-7]. Continuum scale models do not account explicitly for heterogeneities present at pore scale; rather these effects are often lumped up in macroscopic parameters. However, reactions such as precipitation, dissolution or surface reactions occurs at mineral surfaces which in turn changes properties of porous media, affecting flow and transport at both pore and continuum scale [8]. Pore scale modelling can be used to resolve these heterogeneities at lower scale to understand the mechanism governing up scaling of parameters to continuum scale. A number of pore scale reactive transport approaches have been presented in recent years based on conventional computational fluid dynamics approaches [8], pore network models [9], smooth particle hydrodynamics [10], hybrid approaches [11], and Lattice Boltzmann (LB) methods [12-15]. LB methods are easy to implement, efficient and due to its inherent local computation easily parallelizable and scalable for computationally intensive applications. However application of LB methods has been restricted to reaction systems with simple kinetics and geochemistry [14, 15]. In this paper we present an approach to couple LB method with the well-established geochemical modelling tool *PHREEQC* [1] which allows LB based methods to be applied to variety of geochemical systems with different set of complexities. Additional mass given to or taken out of the aqueous phase due to dissolution and precipitation processes is modelled as a source term in this study, as opposed to the more commonly used boundary flux formulation which simplifies the coupling with external geochemical codes.

First, the standard LB method with Bhatnagar-Gross-Krook (BGK) collision operator [16] for multi-component solute transport is briefly described. For more detailed information, reader is referred to specialized textbooks [17-21]. Next, the principles of the coupling procedure with *PHREEQC* and rules for updating pore geometry are outlined. Finally, benchmark results and example cases are discussed.

2 LATTICE BOLTZMANN METHOD FOR MULTI COMPONENT MASS TRANSPORT

Multicomponent mass transport at pore scale mainly occurs through pore water and is governed by advective-diffusive transport equation given by equation (1), if the electro kinetic effects due to presence of charged species is not considered and if mass transport is considered as passive scalar i.e. feedback of change of concentration to change in density is neglected.

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

where, C^j is the Concentration of j^{th} species [N L^{-3}], $\vec{J}^j$ is the flux for j^{th} species [N L^{-2} T^{-1}], D^j is the isotropic diffusion tensor of j^{th} species in water [L^2 T^{-1}], $\vec{u}$ is the velocity vector field for fluid flow [L T^{-1}] and R^j represents reaction term for j^{th} species [N L^{-3} T^{-1}].

Further simplification is made by reducing the number of species to be transported to be equal to number of primary species [22] and by having same diffusion coefficient for all species[8], thus reducing the computational burden.

In LB methods, a discrete velocity Boltzmann equation is solved instead of solving

equation (1) directly which is further discretised in space and time domain (equation (2)). The collision term of Boltzmann equation in equation (2), is simplified using BGK assumption [16] and the resulting LB-BGK method [23] is represented as

$$\begin{aligned} g_i^j(\vec{r} + \vec{e}_i\Delta t, t + \Delta t) &= g_i^j(\vec{r}, t) + \Omega^{BGK,j}(\vec{r}, t) \\ \Omega^{BGK,j}(\vec{r}, t) &= \frac{\Delta t}{\tau}\left[g_i^{eq,j}(\vec{r}, t) - g_i^j(\vec{r}, t)\right] \end{aligned} \tag{2}$$

where, $\vec{r}$ is position vector, g_i^j represents the particle's distribution function along lattice i^{th} direction for j^{th} species [N L^{-3}], $\vec{e}_i$ is the velocity vector in i^{th} direction which depends on type of lattice [L T^{-1}], Δt is the time step [T], τ is relaxation time [T], and $g_i^{eq,j}$ is the particle's equilibrium distribution function for j^{th} species [N L^{-3}] given by equation (3).

$$g_i^{eq,j}(\vec{r}, t) = w_i C^j \left[1 + \frac{\vec{e}_i \cdot \vec{u}}{e_s^2}\right] \tag{3}$$

where, w_i are the weights for particle's distribution function along i^{th} direction and e_s is the speed of sound on lattice [L T^{-1}].

Orthogonal lattices are isotropic enough to recover equation (1) [18] and one of the most commonly used lattices are *D1Q3* (equation (4)) for 1-D with 3 lattice directions and *D2Q5* (equation (5)) for 2-D with 5 lattice directions as shown in Figure 1.

D1Q3,

$$\begin{aligned} \vec{e}_i &= 0 && i = 0 \\ \vec{e}_i &= \left(\cos\frac{(i-1\ )\pi}{2}\right)e && i = 1,3 \end{aligned} \tag{4}$$

D2Q5,

$$\begin{aligned} \vec{e}_i &= 0 && i = 0 \\ \vec{e}_i &= \left(\cos\frac{(i-1\ )\pi}{2}\ , \sin\frac{(i-1\ )\pi}{2}\right)e && i = 1,2,3,4 \end{aligned} \tag{5}$$

where $e = \Delta x/\Delta t$ [L T^{-1}] and Δx is the distance between two lattice nodes [L]. For these lattices, weights and speed of sound for equation (3) are given by $w_i = \frac{4}{6}, \frac{1}{6}$ and $\frac{1}{6}$ for i =0, 1 and 3 respectively in case of *D1Q3* and $w_i = \frac{2}{6}, \frac{1}{6}, \frac{1}{6}, \frac{1}{6}$ and $\frac{1}{6}$ for i = 0-4 for *D2Q5*. Speed of sound on lattice is $e_s = e/\sqrt{3}$ for both cases.

It can be shown that equation (2) together with the particle's equilibrium distribution function given by equation (3), and lattices described by equation (4) or equation (5) it is possible to recover equation (1) using multiscale Chapman-Enskog expansion [21, 24]. Moreover, from multiscale Chapman-Enskog expansion, the relation between diffusion coefficient and relaxation time for *D1Q3* and *D2Q5* lattice is given as

$$D = e_s^2\left(\ \tau - \ \frac{\Delta t}{2}\right) \tag{6}$$

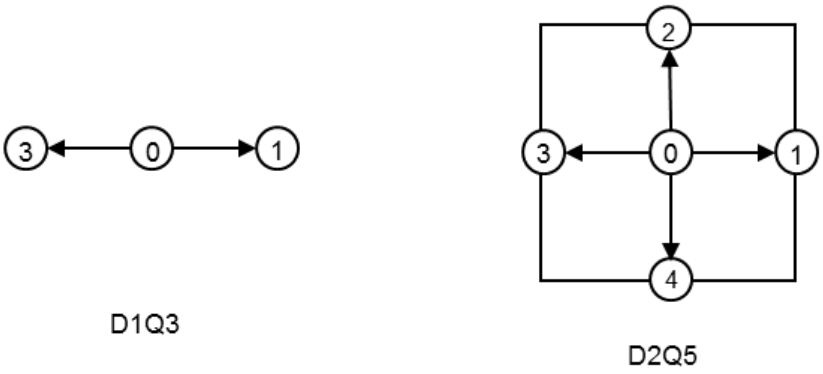


Figure 1: Lattices for mass transport equation

The macroscopic quantities such as concentration (C^j) and flux (J^j_α) in terms of particle's distribution functions is given as

$$C^j = \sum_i g_i^j \; ; \; \vec{J}^j = \sum_i g_i^j \, \vec{u} - \left(1 - \frac{\Delta t}{2\tau}\right)\left[\sum_i g_i^j \, \vec{u} - \sum_i g_i^j \vec{e}_i\right] \tag{7}$$

Reaction term of equation (1) is obtained in LB model by addition of an additional collision term [25-27] in equation (2) as follows

$$g_i^j(\vec{r} + \vec{e}_i \Delta t, t + \Delta t) = g_i^j(\vec{r}, t) + \Omega^{BGK,j}(\vec{r}, t) + \Omega^{reaction,j}(\vec{r}, t)$$
$$\Omega^{reaction,j}(\vec{r}, t) = \Delta t \cdot w_i \cdot R^j \tag{8}$$

3 COUPLING LATTICE BOLTZMANN MASS TRANSPORT SOLVER WITH *PHREEQC*

Previously, LB method has been used to solve reactive mass transport equations and mimic dissolution and precipitation reactions. A short review on developments of LB for reactive transport modelling has been made by Kang et al. [28]. However, application of LB methods has been restricted to predefined simple chemical systems [14, 15] and recently further developed for incorporating exchange reactions [29]. Furthermore, existing approaches of applying heterogeneous reaction in LB method does not allow use of external geochemical reaction codes directly thus restricting application of developed solver to predefined chemical systems. In this section we show methodology to couple a LB mass transport solver with a generic geochemical solver viz., *PHREEQC*, to overcome this barrier.

PHREEQC is a widely used geochemical reaction modelling code with capabilities to seek thermodynamic equilibrium for solution speciation and redox reactions, mineral dissolution and precipitation reactions, ion exchange reactions, surface complexation based on diffused double layer model, gas phase exchange, (non)ideal solid solutions or mixed-equilibrium reaction networks with user-defined rate equations depending on solution speciation, temperature or moisture content [1].

An RD time splitting approach [30] for equation (8) is used to couple reactions with LB which is equivalent to Sequential Non-Iterative Approach used for continuum scale finite

element/finite difference numerical methods [22], e.g. [31] when coupling with *PHREEQC*. The LB advective-diffusive transport solver written in *MATLAB* in this study calls the recently released *PHREEQC* COM version of *PHREEQC-3* [32, 1] to obtain the reaction collision term of equation (8). Similar to the approach of Wissmeier & Barry [33], a LB model is set up by assigning initial and boundary conditions through *PHREEQC* speciation calculations at the beginning of simulation. After setting up the model, a typical calculation step consists of

a.) Executing transport step as in equation (2)

b.) Transferring concentrations at the end of transport time step $t + \Delta t'$ to *PHREEQC*

c.) Executing reaction calculation using *PHREEQC* and obtain new concentrations at the end of reaction time step $t + \Delta t''$

d.) Correcting the particle's distribution function using equation (9) for time step $t + \Delta t$

$$g_i^j(\vec{r}, t + \Delta t) = g_i^{j,transport}(\vec{r}, t + \Delta t') + \Omega^{reaction,j}(\vec{r}, t + \Delta t'') \tag{9}$$

$$\Omega^{reaction,j}(\vec{r}, t + \Delta t'') = \Delta t \cdot w_i \cdot \left[C^j_{phreeqc}(\vec{r}, t + \Delta t'') - C^j_{transport}(\vec{r}, t + \Delta t')\right]$$

where, $C^j_{phreeqc}$ is the concentration for j^{th} species obtained from *PHREEQC* after executing reaction step and $C^j_{transport}$ is the concentration for j^{th} species obtained at the end of transport step.

Unlike, previous approaches where heterogeneous reactions were implemented using flux boundary, we implemented heterogeneous reactions as an additional reaction terms in the fluid node next to solid node which can be expressed using equation (1), thus representing heterogeneous reaction as a volumetric reaction instead of flux boundary [8]. Hence, a fluid node next to solid consists of both homogenous and heterogonous reactions and change in concentration due these reactions is computed using *PHREEQC*. This approach thus ensures complete decoupling of LB calculations and reaction calculations allowing use of existing geochemical reaction modelling codes to execute reaction step.

To update pore geometry, static update rules in essence similar to the one proposed by Kang et al. [28] are implemented. Information of the amount of moles of dissolved or precipitated solid phase at each time step is obtained from *PHREEQC* based on which the volume occupied by a single mineral can be calculated as

$$V_m(t + \Delta t) = V_m(t) + \bar{V}_m[N_m(t + \Delta t) - N_m(t)] \tag{10}$$

where, V_m is the volume occupied by a solid mineral phase m [L^3], $\bar{V}_m$ is the molar volume for a solid mineral phase m [$N^{-1}L^3$], and N_m represents number of moles of solid mineral phase present at a node [N]. Hence, to allow the presence of multiple mineral phases at a given node, the total amount of volume occupied by the solid phase, V_{total}, is the sum of the volumes occupied by all mineral phases at that node given by

$$V_{total}(t + \Delta t) = \sum_m V_m(t + \Delta t) \tag{11}$$

When the ratio of V_{total} to the effective volume (effective volume can be defined as the

maximum volume that can be occupied by solid mineral phase at a given node, $V_{effective}$) reaches a threshold value the pore geometry is updated. For dissolution track of solid volume is kept at solid node and when $\emptyset = \mathrm{V_{total}}/\mathrm{V_{effective}} \leq 0.5$, the corresponding solid node is converted into a fluid node. For precipitation track of solid volume is kept at fluid node and when $\emptyset = \mathrm{V_{total}}/\mathrm{V_{effective}} \geq 0.5$ the corresponding fluid node is converted into a solid node.

4 BENCHMARK CASES AND EXAMPLES

In this section, the following benchmarks and example are presented: (i) cation exchange example for verification of the coupling between the LB and a generic geochemical solver with an alternative code, (ii) verification of solid boundary update of LB code with analytical solution by simulating diffusion controlled dissolution and (iii) a hypothetical example of portlandite dissolution with geometry update to demonstrate the applicability of develop code.

4.1 Example of cation exchange

The developed code is applied to model advective-diffusive transport in the presence of a cation exchanger to demonstrate coupling of the LB method with *PHREEQC*. This benchmark aims at verifying the formulation defined in section 3 for a porous media at the continuum scale, i.e. solving equation (1). The chemical composition of effluent from a column containing a cation exchanger is simulated and the result of LB method is compared with *COMSOL Mutliphysics* (this example is based on example 11 described in [1]). The model setup consists of an 8 cm long column containing initially 1mM of $NaNO_3$ solution and 0.2 mM of KNO_3 solution in equilibrium with 1.1 mM of cation exchanger. The column is then injected with a 0.6 mM of $CaCl_2$ solution. At each time step, the exchanger is in equilibrium with *Na*, *K* and *Ca*. The water flow velocity in domain is assumed to be 2.77 x 10^{-6} m/s and the diffusion coefficient is 5.54 x 10^{-9} m^2/s. At inlet Cauchy boundary equal to the product of fixed boundary concentration and velocity is applied using equation (7) and the outlet is an open boundary. This example was found to be sensitive to the type of boundary condition applied, due to the presence of exchange reaction and serves as a good benchmark example. It should be noted that the formulation of flux boundary condition in terms of particle's distribution function given by Verhaeghe et al. [34] represents only the diffusive part of flux [30] whereas, equation (7) represents both diffusive and advective components of flux and thus offers more generic formulation for application of Cauchy boundary condition. Figure 2 shows a comparison between the LB results and *COMSOL Mutliphysics* and indicates an excellent agreement.

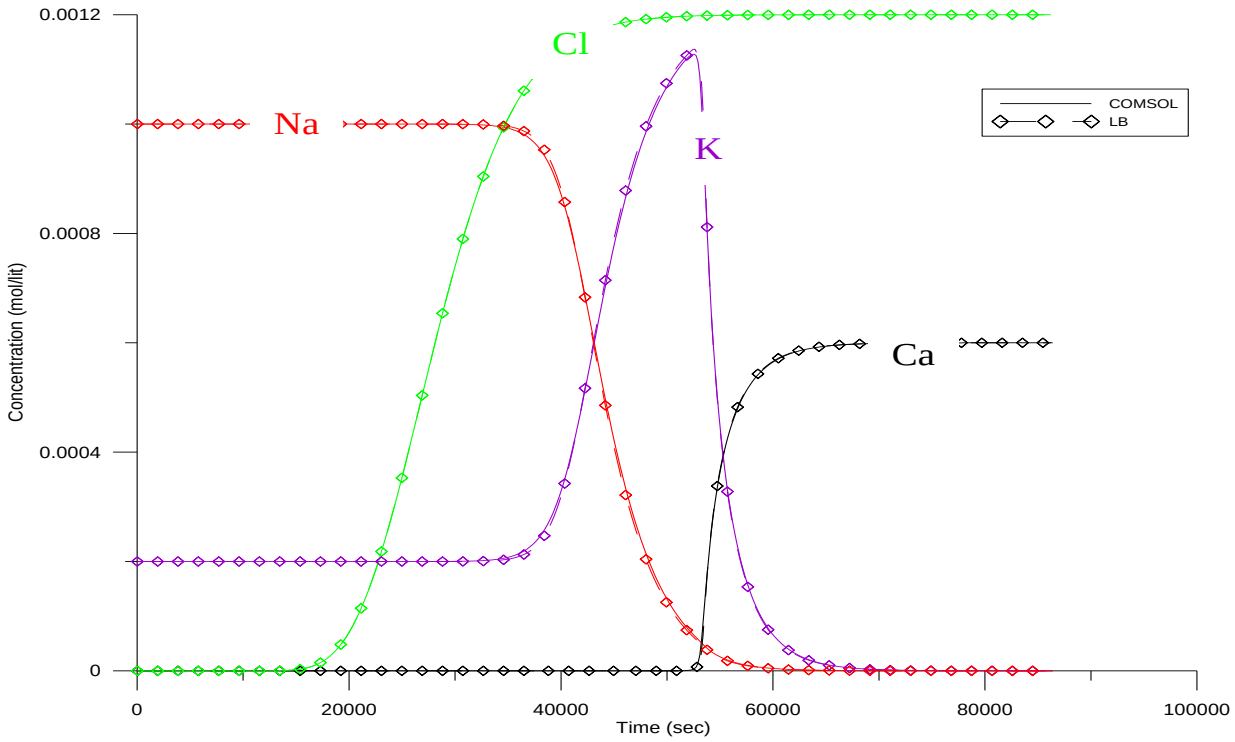
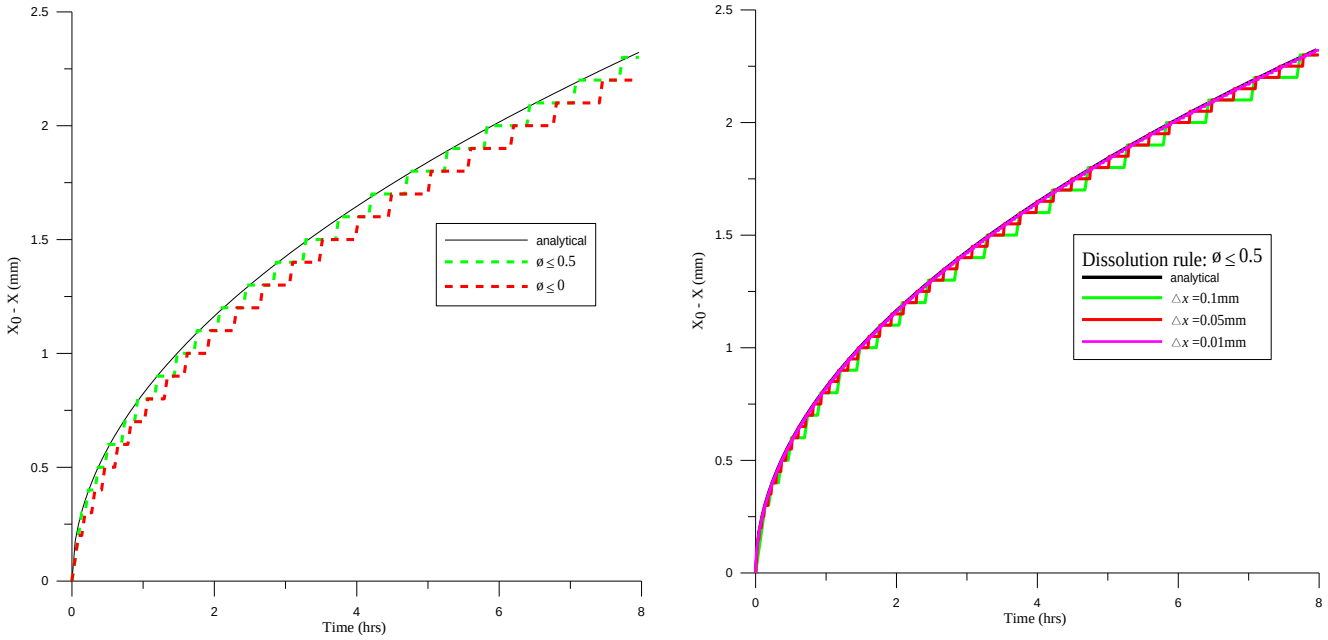


Figure 2: Cation Exchange

4.2 Diffusion controlled dissolution

A Stefan problem for diffusion controlled dissolution [35] is used to validate the geometry update during dissolution. Comparison of LB model is made with analytical given by Aaron et al. [35]. The model setup consists of a 20 mm long domain with species concentration of 0.1 mol/m^3 with last 3 mm domain containing solid with initial mass of 1 mol/m^3. Hence, the fluid-solid interface, x_0 is initially located at 17 mm from the inlet. An equilibrium concentration of 0.4 mol/m^3 is maintained at the fluid-solid interface. The diffusion coefficient is taken as 1 x 10^{-9} m^2/s. Figure 3(a) shows a comparison of the LB results with analytical solution for the following two dissolution rules: (i) when a solid node contains less than 50% solid ($\emptyset \leq 0.5$), it is converted to fluid node and (ii) when a solid node contains no solid ($\emptyset = 0$), it is converted to fluid node. It can be seen that the rate of movement of boundary is slower for $\emptyset = 0$ and $\emptyset \leq 0.5$ better represents the movement of fluid solid interface. In Figure (3), the movement of interface is in discrete steps as update of boundary is carried out in a static way and as shown in Figure 3(b) that for $\emptyset \leq 0.5$, with higher number of nodes more continuous movement of fluid solid interface. However, the movement of fluid solid interface is fairly independent of number of nodes and good agreement with analytical solution is observed for all discretization.



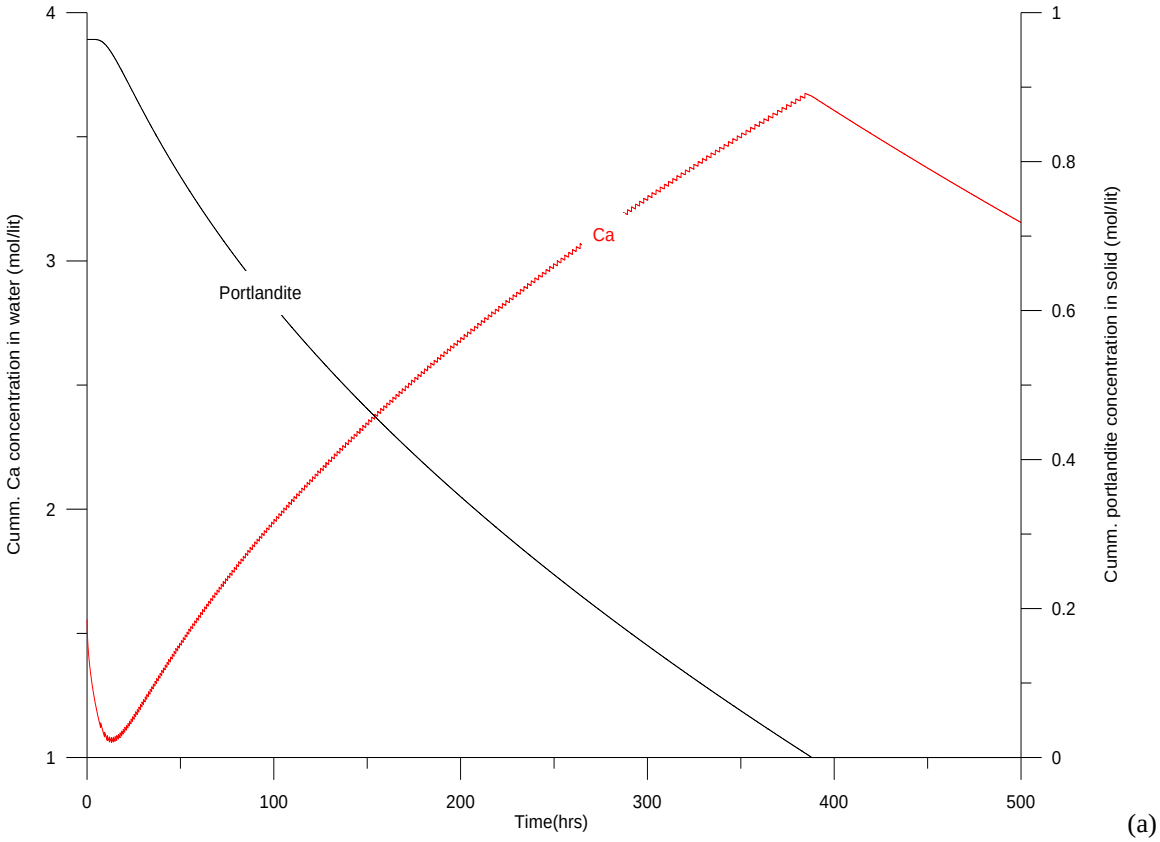
(a) (b)

Figure 3: Diffusion controlled dissolution

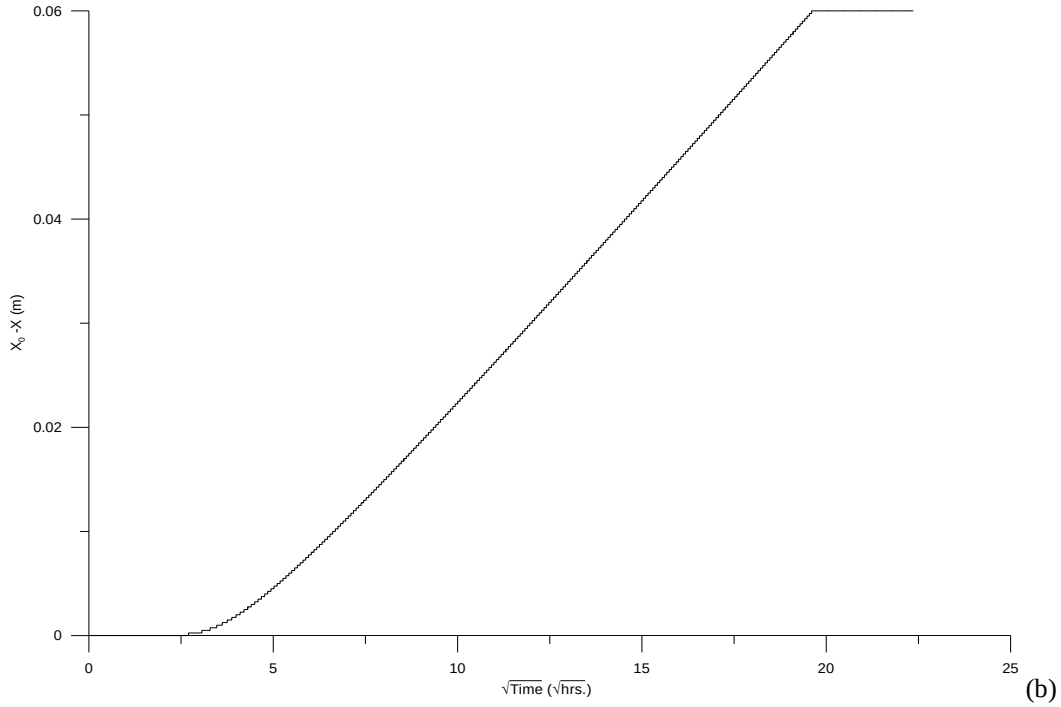
4.3 Dissolution of portlandite

Portlandite is an important mineral phase in hardened cement paste and dissolution of portlandite due to calcium leaching has adverse effects on transport and mechanical properties of cement paste [36]. In this example, applicability of the developed code for handling geochemical reactions along with geometry update to mimic the dissolution of portlandite is demonstrated. The model setup consist of 8 cm long domain with the first 2 cm of domain consisting of water in equilibrium with portlandite ($Ca \approx 20$ mM, pH ≈ 12.5) and the last 6 cm representing solid portlandite with initial mass of 4 mM. An aggressive water solution with pH 3 (obtained by adjusting *Cl* ion concentration to maintain charge balance) is present at the inlet boundary. At the fluid-solid interface, portlandite keeps the water in equilibrium by dissolving excess portlandite at a given time step. Diffusion coefficient for all species is assumed to be 1 x 10^{-9} m^2/s. Fixed concentration boundary is applied at the inlet and no flux boundary is imposed at outlet boundary on complete dissolution of solid.

Results of simulation are shown in figure 4. Figure 4(a) shows that when water with low pH is introduced from inlet boundary *Ca* ions gets flushed out from the water in the domain, causing decrease in *Ca* ion concentration in water. Once, the cumulative concentration of *Ca* in water drops to around 1.08 mM, dissolution of portlandite begins causing increase of *Ca* ion concentration in water till all portlandite is dissolved from the system. After complete dissolution of portlandite, a gradual drop in the *Ca* concentration in the water is observed due to the outward diffusion of *Ca*. Figure 4(b) shows the movement of interface with $\sqrt{t}$ which is linear as would be expected for diffusion controlled dissolution.



(a)



(b)

Figure 4: Dissolution of portlandite

5. CONCLUSIONS

In this paper we outlined the development of a LB–BGK model for pore scale reactive transport problems involving complex chemical systems by coupling LB method with *PHREEQC*. The LB mass transport step and reaction step were separated using a RD operator splitting approach and *PHREEQC* was used to solve both homogenous and heterogeneous reactions. The developed code was tested with a series of benchmarks to test the coupling of LB with *PHREEQC* and accuracy of geometry update. Finally, the ability of the code to handle geochemical reactions along with geometry update to mimic dissolution of portlandite was demonstrated. All the cases were restricted to 1-D but the examples and benchmarks show the ability of the developed approach to handle complex geochemical reactions and effective updating of pore geometry caused by dissolution and precipitation reactions.

In future, the developed code will be applied to 2D and 3D problems and further coupled with LB –BGK Navier stokes solver to handle coupled flow and reactive transport problems. Finally, the coupled model will be applied to study the evolution of cement microstructure due to cement degradation mechanisms such as carbonation and leaching.

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