Pore-scale study of diffusion–reaction processes involving dissolution and precipitation using the lattice Boltzmann method

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ABSTRACT

A pore-scale model combining the lattice Boltzmann method (LBM) and a fluid–solid interface tracking method is employed to simulate the diffusion–reaction processes involving dissolution and precipitation. Coupled sub-processes including mass transport, chemical reactions, and solid structure evolution are considered. Effects of the precipitation of the secondary solid phase on the dissolution of the primary solid phase are investigated under different dissolution–precipitation reaction kinetics, molar volumes of the primary and secondary solid phases, powder size, surface roughness, and nucleation and crystal growth mechanisms. Different morphologies of the precipitates are predicted by the pore-scale simulations. It is found that the precipitation has opposite effects on the underlying dissolution processes. The favorable effect is that the precipitation reaction consumes the product of the dissolution reaction, thus facilitating the dissolution; while the adverse effect is that the generated precipitates cover the surface of the primary solid phase, thus separating the reactive surface from the reactive components. Based on the extent to which the precipitates affect the dissolution, four types of coupled dissolution–precipitation processes are identified and discussed.

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1. Introduction

Reactive transport processes involving dissolution–precipitation are pervasive in a variety of scientific, industrial and engineering processes. Typical examples include self-assembled patterns such as Liesegang rings or bands [1], formation of mineral deposits in boilers and heat exchangers, biofilm growth in aqueous environment [2], environmental contaminant transport [3,4], recovery of oil and geologic sequestration of carbon dioxide (CO_2) in the subsurface [5–7]. Among these reactive processes, it is commonly encountered that a second solid phase precipitates when a primary solid phase dissolves, and the precipitation and dissolution reactions are closely coupled with each other [8,9]. For example, during mineral trapping of CO_2, primary silicate mineral dissolves due to decrease of pH caused by the dissolved CO_2; meanwhile the dissolved CO_2 can react with cations released by the dissolution reaction to form a secondary precipitate of carbonate mineral [6]. Another typical example is the uptake of Cd^{2+} by carbonate minerals from polluted water. As the $CaCO_3$ dissolves, it releases carbonate leading to the aqueous solution to be supersaturated with respect to otavite which then precipitates [4]. These non-linear non-equilibrium transport processes with dynamic evolutions of solid structures pose great challenges to the numerical simulations. The numerical models and methods proposed should be capable of simulating the fluid flow, predicting mass transfer, incorporating homogeneous and heterogeneous reactions, updating the solid structures, and taking into account the interactions between different sub-processes.

Usually, for simulating such complex reactive transport processes with the solid structure evolution, a solver for transport processes, such as the finite volume method (FVM), is coupled with a model for tracking the fluid–solid interface, such as the phase-field method (PF). Conventionally, the prediction of transport processes is based on solving the macroscopic density, momentum, energy, and concentration conservation equations using a FV, finite difference (FD), or finite element (FE) method. As these methods are continuum based, it is not easy to properly handle the discontinuity of variables at the complex fluid–solid interfaces, limiting their applications for transport processes in domains with complicated structures such as porous media. Pore-scale methods have been developed which have the capacity of taking into account the complex porous structures, such as pore network model [10], smoothed particle hydrodynamics [11,12] and the lattice Boltzmann method (LBM) [13–17]. Evolutions of fluid–solid interfaces

are ubiquitous in processes including melting–solidification and dissolution–precipitation. For tracking the fluid–solid interfaces, the PF method [18] and the cellular automaton (CA) methods [19] are widely used. Other methods such as Volume of Fluid (VOF) and Level Set (LS) method, which are commonly used for multiphase flow, are also adopted for this purpose [20].

There have been several pore-scale studies in the literature to study the reactive transport processes involving dissolution and precipitation by coupling different transport process solvers and fluid–solid interface tracing methods since the work of Ref. [21]. Single-phase fluid flow and reactive transport with dissolution–precipitation was studied by Kang et al. [22,23] in which the LBM was used to simulate flow, mass transport and reaction, and the volume of pixel (VOP) was adopted to track the moving fluid–solid interfaces caused by dissolution–precipitation. They predicted the relationship between permeability and porosity under different Pe (Peclet number, representing the relative strength of convection to diffusion) and Da (Damköhler number, representing the relative strength of reaction to diffusion) numbers. Li et al. [20] studied a similar problem using LS to track the fluid–solid interfaces. In addition, Luo et al. [24] implemented a model using a diffuse interface method to track the fluid–solid interface, in which they also considered the natural convection caused by concentration gradients. Smoothed particle hydrodynamics was also adopted for investigating dissolution–precipitation processes in fractures and porous media [11,12]. Later, Kang et al. extended their model to multi-component systems [14] and used the model to study reactive transport processes associated with geological CO_2 sequestration [15]. Yoon et al. [16] adopted LBM for fluid flow and FVM for mass transport in mixing – induced calcium carbonate dissolution and precipitation processes. Huber et al. [17] combined LBM and PF method for dissolution–precipitation processes involving single or multiple species. All the above studies are for systems of a single phase fluid with one or multiple chemical species dissolved in it. The numerical studies of multiphase fluid flow coupled with reactive transport with moving fluid–solid interfaces are scarce in the literature [25,26]. Recently, Parmigiani et al. [25] used the LBM to study the process of injection of a non-wetting fluid into a wetting fluid coupled with dynamic evolution of the solid geometries. Very recently, Chen et al. [26] constructed a pore-scale model based on the LBM and the VOP to simulate multiphase reactive transport with phase transition and dissolution–precipitation processes [26]. Their pore-scale model can capture coupled non-linear multiple physicochemical processes including multiphase flow with phase separation, mass transport, chemical reaction, dissolution–precipitation, and dynamic evolution of the pore geometries.

The above pore-scale studies provide a detailed insight into the coupled mechanisms between the transport processes and the dissolution–precipitation processes. To the best of our knowledge, however, there are few studies taking the coexistence of dissolution and precipitation processes into account [14,15,26], and there are no studies especially devoted to investigating the coupled dissolution–precipitation processes where the precipitates may cover the surface of the solid phase undergoing dissolution. Existing experiments have shown that the way by which the precipitates affect the dissolution of primary solid phase is very complex and cannot be generalized. Instead, it is affected by several factors including the dissolution and precipitation reaction kinetics, concentrations of reactive components, and the nucleation and crystal mechanisms of the precipitates [3,4,6,7].

The objective of the present study is to numerically investigate the effects of the precipitation of the secondary solid phase on the dissolution of the primary solid phase by performing comprehensive studies including dissolution and precipitation reaction kinetics, molar volume ratio, powder size, surface roughness, and

nucleation and crystal growth mechanism. The LBM is adopted for solving the diffusion–reaction processes and the VOP is employed for updating the solid structures. With more than 20 year's development, the LBM has emerged as a powerful tool for the numerical simulations and investigations of a broad class of complex flows, including porous flow, thermal flow, reactive transport, turbulence flow, and multiphase flow. Since it is based on the discrete kinetic theory, the LBM is a promising tool in dealing with complicated non-linear characteristics as well as complex structures. The VOP developed by Kang et al. [13] is a CA method. The VOP has many advantages such as a clear physical concept, simple and stable arithmetic, easy implementation of various kinds of surface reactions, and flexible coupling with different nucleation and crystal growth mechanisms. For this reason, the method has been used successfully to predict many moving solid–fluid interface phenomena, such as crystal growth [13], rock dissolution due to acid injection [22,23], Liesegang bands or rings [1] and dissolution and precipitation involved in CO_2 sequestration[15,16].

The rest of the paper is arranged as follows. In Section 2 the physicochemical model is presented. In Section 3 the numerical method is introduced. In Section 4 two-dimensional (2D) simulation results are presented and discussed. Finally, in Section 5 some conclusions are drawn.

2. Physicochemical model

2.1. Chemical reaction

A simplified chemical model is constructed that can be readily used for studying transport and reaction kinetic parameters and for identifying dominant processes and mechanisms. It can be described by the following two principal dissolution and precipitation steps with three aqueous species and two solid phases

$$A_{(aq)} + D_{(s)} \leftrightarrows B_{(aq)} \qquad (1)$$
$$B_{(aq)} + C_{(aq)} \leftrightarrows P(s) \qquad (2)$$

where aq in the parenthesis stands for aqueous species and s denotes solid phase. Eq. (1) is the dissolution reaction in which aqueous $A_{(aq)}$ reacts with solid $D_{(s)}$ generating aqueous $B_{(aq)}$. The generated $B_{(aq)}$ reacts with another aqueous $C_{(aq)}$ according to precipitation reaction Eq. (2), producing the secondary precipitate $P_{(s)}$. Note that elements comprising the secondary precipitate may either be initially present in the aqueous solution or result from the dissolution of the primary phase. In the present study, the element $B_{(aq)}$ required for precipitation reaction is released from the dissolution, resulting in close coupling between the precipitation and dissolution reactions. Eqs. (1) and (2) can be considered as a simplified form of some realistic reactions in experiments [4,6]. For example for carbonation of silicates, $A_{(aq)}$ can be considered as H^+, $D_{(s)}$ as the silicate, $B_{(aq)}$ as the cation, $C_{(aq)}$ as the carbonate or bicarbonate and $P_{(s)}$ as the calcite. For uptake of Cd^{2+} by carbonate minerals, $A_{(aq)}$ can be considered as H^+, $D_{(s)}$ as carbonate mineral, $B_{(aq)}$ as the carbonate, $C_{(aq)}$ as the toxic cation and $P_{(s)}$ as the otavite. Although Eqs. (1) and (2) are not the same as the reactions in [4,6], they retain the basic principles of these realistic reactions.

2.2. Governing equation

In the present study, fluid flow is not considered for the purpose to focus on the coupled mechanisms between diffusion and dissolution–precipitation reactions. The general processes can be described as follows. Initially, primary solid phase $D_{(s)}$ in equilibrium with $A_{(aq)}$ and $B_{(aq)}$ is placed in the computational domain, and there is no secondary solid phase $P_{(s)}$ (see Fig. 1). Initial concentration of $C_{(aq)}$ is zero and thus the initial condition is not