Changes in porosity, permeability and surface area during rock dissolution: Effects of mineralogical heterogeneity

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Ting Min [a], Yimin Gao [a], Li Chen [b,c,*], Qinjun Kang [c], Wen-Quan Tao [b]

[a] State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, PR China
[b] Key Laboratory of Thermo-Fluid Science and Engineering of MOE, School of Energy and Power Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi 710049, PR China
[c] Computational Earth Science, Earth and Environmental Sciences Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

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ABSTRACT

Effects of heterogeneity of mineral distribution and reaction rate on the rock dissolution process are investigated using a pore-scale reactive transport model based on the lattice Boltzmann method. Coupled fluid flow, species transport, chemical reaction and solid structure alternation due to dissolution are simulated. Effects of mineral distributions and chemical heterogeneity on the dissolution behaviors and evolutions of hydrologic properties are studied under different reactive transport conditions. Simulation results show that the coupling between advection, diffusion and reaction as well as the mineralogical heterogeneity leads to complex reactive transport behaviors and complicated temporal evolutions of hydrologic properties including porosity, permeability and reactive surface. Diverse relationships between surface area and volume are predicted, which cannot be described by simple models such as the spherical-grain model. Porosity-permeability relationships also differ under different mineral distributions and reactive transport conditions. Simulation results indicate that it is extremely challenging to propose general relationships for hydrologic properties for dissolution of rocks with mineralogical heterogeneity, due to the complicated interactions between reactive transport and mineralogical heterogeneity.

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1. Introduction

Reactive mass transport in heterogeneous porous media with solid phase dissolution is ubiquitous in geological formations, scientific processes and industrial application [1–4]. Typical examples include karst formation [5], self-assembled patterns [6], spread of contaminants in fluid-saturated soils [7], nuclear waste remediation [8], geologic sequestration of carbon dioxide [9–12] and acid injection for enhanced petroleum recovery [13]. The heterogeneity of porous media in geological formations is embodied by the heterogeneous porous structures [14–22] as well as the mineralogical heterogeneity because of multiple components [23–27]. In such heterogeneous porous media, the observed reactive transport processes do not always behave according to the transport laws established for the homogeneous ones [14–27]. For continuum-scale reactive transport modeling applied at large scales, the

physicochemical heterogeneities are necessarily ignored at scales smaller than the size of the model discretization [4]. However, while under some scenarios the homogeneous assumption is reasonable, the pore-scale heterogeneities can result in significant "scaling effect" because of the spatial variations of concentrations and reaction rates, leading to the breakdown of the homogeneous assumption. Such "scaling effect" is one of the potential causes of the order-of-magnitude differences between lab measured reaction rates and those obtained from the field measurements [1,4]. Therefore, it is of significant importance to understand the effects of pore-scale heterogeneities on the reactive transport processes.

Theoretically, full resolutions of the spatial medium heterogeneity as well as the detailed mineral distributions down to the pore scale, with all the physicochemical processes considered, can help to understand the distinct reactive transport phenomena, to establish the reactive transport laws, and to reveal coupled mechanisms in heterogeneous porous media. The transport of a reactive fluid through a porous medium with dissolution is a very complex process encompassing multiple physicochemical sub-processes including fluid flow, species transport, chemical reactions, and alternations of solid and porous structures. These sub-processes occur simultaneously and are closely coupled with

* Corresponding author at: Key Laboratory of Thermo-Fluid Science and Engineering of MOE, School of Energy and Power Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi 710049, PR China.
E-mail addresses: min.ting@stu.xjtu.edu.cn (T. Min), ymgao@mail.xjtu.edu.cn (Y. Gao), lichennht08@mail.xjtu.edu.cn (L. Chen), qkang@lanl.gov (Q. Kang), wqtao@mail.xjtu.edu.cn (W.-Q. Tao).

each other. With the improvement of the computational resources, pore-scale modeling and simulations have been developed as a powerful tool for studying such reactive transport processes. A desirable pore-scale reactive transport model must be able to address the multiple physicochemical sub-processes. Various numerical methods have been adopted to model the fluid flow and species transport with chemical reactions. Conventional numerical methods based on the discretization of NS equations, such as finite volume, finite difference and finite elements methods, have been adopted to simulate reactive transport in porous media [14]. However, such finite-type methods are not efficient in treating the boundary conditions at the complex fluid–solid interface in porous media. Pore network models are flexible and computationally efficient, which are suitable for relatively large systems. However, in such models, porous media are abstracted into a network of pore volumes connected by channels or pore throats. Such idealization can lead to loss of geometrical and topological information. Besides, for the transport mechanism, the pore network models are not based on first-principle, but is rather based on mechanisms that are incorporated into the model in advance [27]. Smoothed particle hydrodynamics is a fully Lagrangian mesh-free particle-based method, which describes fluid flow and other porous media dynamics by solving discretized forms of partial differential equation and is a powerful solver for the pore-scale simulation involving moving interface and dynamic pore geometry. However, for the system with high heterogeneity, high density of discrete particles is need, which will dramatically increase computational resources [15]. Solid structure alternations resulting from dissolution-precipitation have also been addressed by different interface capturing or tracking models such as the phase field method [28], the cellular automaton method [29] and the level set method [30,31]. The lattice Boltzmann method (LBM) considers flow as a collective behavior of pseudo-particles at a mesoscopic level whose behavior is described by a discrete Boltzmann equation [32,33]. The LBM is particularly suitable for simulating non-equilibrium dynamics, such as reactive transport involving interfacial dynamics and complex boundaries [34–37]. Recently, a great progress has been made using the LBM to understand and explain the pore-scale reactive mass transport processes including solid dissolution/precipitation [3,8,12,19,21,24,38–42].

There are two major objectives for pore-scale reactive transport modeling. One is to understand the underlying reactive transport phenomena and to reveal the coupled mechanisms between different processes. Pore-scale simulations have revealed a complex coupling between convection, diffusion and dissolution reaction under the effects of structural heterogeneity [16]. Different dissolution patterns have been found including uniform dissolution, face dissolution and wormhole dissolution under different reactive transport conditions. The other purpose is to determine the hydrologic properties of the porous medium such as porosity, permeability and reactive surface area, which are prerequisite in continuum-scale models [43]. Taking porosity-permeability relationship as an example, under the influence of heterogeneity, the complex interactions between dissolution and reactive transport will generate different dissolution patterns, and thus lead to quite different porosity-permeability curves [9,22].

Although some progresses have been made in the understanding of the coupling of dissolution reaction and fluid flow in porous rocks, there are still some fundamental problems remaining to be solved. First, while there have been some pore-scale studies regarding the evolutions of porosity and permeability during the dissolution [3,15,19,22,31,44], the work about the evolutions of the reactive surface area is scarce. In continuum-scale reactive transport models, the reactive surface area, which is not easy to measure during experiments, is an important prerequisite for calculating the dissolution rate [45,46]. Second, subsurface porous

media consist of multiple mineral components such as calcite, clay, quartz, dolomite and pyrite [24–26,46]. Such mineralogical heterogeneity also plays an important role on the dissolution process [24–26], which, however, was usually ignored in the open literature about pore-scale simulations of reactive transport with dissolution. In our previous study [24], we found that the undissolved mineral causes heterogeneous local dissolution behaviors, and leads to porosity-permeability curves which significantly differ from that in a mono-mineral system [24]. Wormhole formation also could be suppressed by the undissolved mineral [24]. Further studies are required to investigate the effects of spatial and chemical heterogeneities in multiple mineral porous systems.

In the present study, reaction transport with dissolution in binary-mineral rocks is simulated. Effects of mineral distributions and orientations on dissolution processes are explored. Temporal evolutions of important hydrologic parameters including porosity, permeability and reactive surface area are monitored and discussed. The relationship between reactive surface area and solid volume, and that between porosity and permeability are presented and discussed. An LB based pore-scale reactive transport model is adopted for the present study, which has been well developed for single-phase reactive transport with dissolution-precipitation [3,38–40] and has been extended for multiphase reactive transport very recently [8,12]. As a first step study to reveal the complexity of effects of mineral distributions and reactive transport conditions on dissolution process as well as evolutions of hydrologic properties, some idealized structures with relatively simple mineral distributions are studied. As will be shown in the results, even for such simple idealized structures, the evolutions of the hydrologic properties are very complicated and it is challenging to obtain a general relationship. The remainder of present paper is organized as following. In Section 2, physicochemical model is established and the LB reactive transport pore-scale model is introduced. The results about dissolution in the idealized structures as well as that in a system with relatively complex mineral distribution are presented and discussed in Section 3. Finally, some conclusions are drawn in Section 4.

2. Physicochemical models and numerical methods

2.1. Physicochemical models

It is ubiquitous that porous rock systems consist of multiple minerals, which have distinct chemical properties and spatial distributions [25,46]. During reactive mass transport these minerals existing in porous rock may or may not be dissolved by chemical fluid surrounding them [25]. To emphasis the effects of the chemical heterogeneity of rocks, it is assumed that there are two minerals in rocks: one soluble mineral, α, and the other insoluble mineral, β [24]. Without loss of generality, a simplified dissolution reaction of α is considered in the present study [3]

$$R_{(aq)} + \alpha_{(s)} \Longleftrightarrow P_{(aq)} \tag{1}$$

with $R_{(aq)}$ the reactant in aqueous phase, $\alpha_{(s)}$ the reactant in solid form and $P_{(aq)}$ the product in aqueous phase. An example of this kind of system is the limestone in acid fluid, which consists of calcite and clay, and calcite can react with acid solution and clay cannot [25]. It is assumed that the dissolution reaction is the first-order chemical reaction, and the dissolution rate can be calculated by [3]

$$r = k_r(C_{R_{(aq)}} - C_{P_{(aq)}}/k_{eq}) \tag{2}$$

with r [mol m^{-2} s^{-1}] the dissolution rate, k_r [m s^{-1}] the dissolution reaction rate constant, C_R [mol m^{-3}] the reactant concentration, C_P [mol m^{-3}] the product concentration and k_{eq} [mol m^{-3}] the reaction equilibrium constant.