International Journal of Heat and Mass Transfer 120 (2018) 194–201

Contents lists available at ScienceDirect

International Journal of Heat and Mass Transfer

journal homepage: www.elsevier.com/locate/ijhmt

Numerical simulation of fluid-fluid-solid reactions in porous media

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ARTICLE INFO

Article history:
Received 18 August 2017
Received in revised form 20 November 2017
Accepted 28 November 2017

Keywords:
Reactive transport
Heterogeneous reaction
Pore-scale modelling
Rock properties

ABSTRACT

We present a numerical model to simulate reactive transport involving homogeneous (fluid-fluid) and heterogeneous reactions (fluid-solid) in porous media. The model includes mass transport, homogeneous reaction, heterogeneous reaction and solid modification. The model is validated by comparing reactive flow in simple geometries with analytical solutions and previously published experimental results. Fluid flow, solute transport, and chemical reactions are simulated directly on 3D images of carbonates. The concentration profiles are analysed for comparison of homogeneous and homogeneous-heterogeneous reactions. A large discrepancy is observed between the concentration profiles of reactants due to the mineral dissolution. The simulation results are also compared with the predictions of reactive transport model with only heterogeneous reactions. In such regimes, mineral dissolution occurs near the inlet. However, with addition of homogeneous reaction, more uniform dissolution is observed in the carbonate. Rock mechanical properties including Young's modulus and Poisson's ratio are also compared between the two reaction conditions. The results show that the homogeneous-heterogeneous reaction leads to pore geometries with higher mechanical strength. This work investigates the complex process of chemical reactions in carbonates and improves the understanding of reactive transport in porous media.

1. Introduction

Transport of reactive fluids is of importance for many applications including geological storage of carbon dioxide, contaminant transport, nuclear waste disposal and acid stimulation of petroleum reservoirs. Complex processes of reactions are usually involved in these problems, such as the transport of reactants and products, interactions between different fluids and chemical reactions at solid surfaces [1,2]. A typical example is the transport of contaminants in groundwater. Multiple reactions including dissolution and precipitation between contaminants, soils, groundwater and other semimetal materials commonly occur in subsurface. The contaminant-soil interactions are essential for predicting the fate and transport of the contaminant in the groundwater [3].

The reaction processes occur at the pore scale. Pore scale studies are necessary to quantitatively understand and describe the complex processes of reaction [4–9]. Numerical modelling, as a common method to characterise reactions at the pore scale, has been applied to study reactive transport in the past two decades. Reactive transport modelling in subsurface involves reactions between homogeneous (fluid-fluid) and heterogeneous (fluid-solid) reaction. For fluid-fluid reactive transport, the process includes fluid flow and reactions between different types of fluids [10–13]. Willingham et al. used a pore scale model to study transverse fluid mixing-limited reactions based on lattice Boltzmann and finite volume methods. They compared their results with micromodel experiments and investigated the effect of porous structure on reactive transport. The findings also showed that the pore structures have significant impact on fluid mixing and reaction in porous media [10]. Alhashmi et al. [15] applied a streamline-based particle tracking method to simulate homogeneous reactions in homogeneous geometries. The numerical model was validated against the analytical solutions for homogeneous reaction in a free fluid. They also simulated reactions in a glass beadpack and compared their predictions with experimental observations by Gramling et al. [14]. The results showed that their pore scale model was able to capture the changes of concentration and reaction rate in reactive transport [15]. Alhashmi et al. [16] extended the work on homogeneous reaction to explore the effect of pore structure heterogeneity on reaction rate. They simulated reactive flow on images of three different porous media: beadpack, Bentheimer sandstone and Doddington sandstone. They showed how the pore structure heterogeneity affects the effective reaction rate by controlling the amount of mixing and spreading reactants. The results also demonstrated the effect depends on the flow rates characterised by Péclet number [16].

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https://doi.org/10.1016/j.ijheatmasstransfer.2017.11.141

At the fluid-solid interface, heterogeneous reactions often lead to mineral dissolution into the solution [17–22]. Kang et al. used the lattice Boltzmann method for simulating mineral dissolution in a two-dimensional porous medium. They performed simulations for a series of acid injection rates and presented the variations of permeability and pore geometry due to dissolution. The results suggested an optimal injection rate for wormhole pattern generation [23]. Varloteaux et al. simulated heterogeneous reactions in two synthetic geometries by applying a pore network model and compared their results with direct simulation predictions based on the finite difference method. They showed that the pore network models can be used to characterise reactive transport with large velocities and irregular pore structures [24]. Mostaghimi et al. used a pore scale model based on lattice Boltzmann and finite volume methods to study the effect of pore structure heterogeneity on reactive transport. They simulated the dissolution at pore-mineral interface in different rocks and illustrated the significance of geometrical heterogeneity in reactive flow [25].

In natural porous systems, the reactive transport is a complex process involving fluid flow, solute transport, homogeneous reactions, and heterogeneous reactions. For instance, acidic water is usually generated due to fluid mixing between ground water and landfill contaminants [26]. This acidic water will cause dissolution of rocks in subsurface [27]. Reactions between different fluids and solid in single and multiple phase fluid have been investigated in several studies [1,5,18,28]. Chen et al. applied the lattice Boltzmann method to simulate both favourable and unfavourable impact of fluid-fluid reaction on mineral precipitation in pore geometries [1]. Kang et al. employed a multi-component reactive transport model based on the lattice Boltzmann method to simulate CO_2 injection into brine in 2D porous media at different temperatures. They considered fluid-fluid reactions in a single phase and compared their pore-scale numerical results with a continuum scale model to illustrate its discrepancy in the reaction front [29]. However, these studies are only focused on 2D and simplified geometries of porous media. Consideration of homogeneous and heterogeneous reactions in 3D heterogeneous porous media can help improve the understanding of the complex reactive transport process. Herein, we present a pore scale model involving homogeneous and heterogeneous reactions to investigate reactive transport in porous media.

2. Physiochemical model

2.1. Chemical reactions

Homogeneous and heterogeneous reactions are included in this model. We establish a simplified chemical model to identify the physiochemical processes and mechanisms. It can be described by the following two reaction steps with three aqueous chemical species and one solid phase.

$$A_{(aq)} + B_{(aq)} \rightarrow C_{(aq)} \tag{1}$$

$$C_{(aq)} + M_{(s)} \rightarrow P_{(aq)} \tag{2}$$

where *aq* refers to aqueous species and *s* stands for solid phase. Eq. (1) is the homogeneous reaction of aqueous phase $A_{(aq)}$ and aqueous $B_{(aq)}$. The product $C_{(aq)}$ dissolves solid minerals $M_{(s)}$ generating aqueous $P_{(aq)}$ based on reaction Eq. (2).

2.2. Governing equations

The incompressible creeping fluid flow is considered in porous media. The continuity and Stokes equations are then expressed as [30],

$$\nabla \cdot \underline{v} = 0, \tag{3}$$

$$\nabla \mathrm{p} = \mu \nabla^2 \underline{v}, \tag{4}$$

where $\underline{v}$ is the velocity vector, p is pressure and μ is dynamic viscosity.

The transport of aqueous chemical species in porous media is governed by the advection-diffusion equation (Sahimi [30]),

$$\frac{\partial c}{\partial t} + (\underline{v} \cdot \nabla)c = \nabla \cdot (D\nabla c), \tag{5}$$

where c is the solute concentration t is time and D is the molecular diffusion coefficient of chemical species.

For homogeneous reaction, the irreversible reaction A + B → C is simulated. The reaction rate r is given by [31],

$$r = \frac{dc_C}{dt} = -\frac{dc_A}{dt} = -\frac{dc_B}{dt} = \kappa c_A c_B \tag{6}$$

where the subscripts A, B and C refer to the chemical species A, B and C, respectively. κ is the homogeneous reaction rate constant.

At fluid-solid interface, a first order reaction kinetics is considered such that,

$$D\frac{\partial c_C}{\partial \underline{n}} = k_r(c_C - c_S), \tag{7}$$

where $\underline{n}$ is the unit normal vector towards the fluid, k_r is the heterogeneous reaction rate constant and c_s is the saturated concentration.

Dissolution of minerals results in elimination of solid phase. The update of solid phase is governed by [32]:

$$\frac{\partial \beta}{\partial t} = -V_m S k_r (c_C - c_S), \tag{8}$$

where β is the volume fraction of minerals, V_m is the molar volume, and S is the specific surface area of the minerals.

Mechanical properties including Young's modulus and Poisson's ratio are calculated by assigning stresses on the boundaries of the pore structure. The isotropic linear elasticity is considered in this study. The balance law of stationary elasticity and Hooke's law are given by [33],

$$\nabla \cdot \boldsymbol{\sigma} = \vec{f} \tag{9}$$

$$\boldsymbol{\sigma} = \boldsymbol{w}\boldsymbol{\epsilon} \tag{10}$$

where $\boldsymbol{\sigma}$ is the stress tensor, $\vec{f}$ is the acting body force in the domain, $\boldsymbol{w}$ is the stiffness tensor and $\boldsymbol{\epsilon}$ is the strain tensor.

In this paper, the Stokes equations for fluid flow are solved by the Explicit Jump (EJ) solver [34] through the GeoDict package. The advantage of EJ method over standard finite difference approximations is to avoid grid generation by correcting the finite differences at the interface [34]. A no-slip boundary condition is applied on the solid surfaces. Periodic boundary conditions are applied on an equidistant Cartesian grid. The equations of solute transport and chemical reaction are discretised by a finite volume scheme. For details of our finite volume discretisation of chemical reactions, we refer to [25]. A Dirichlet boundary condition is considered at the inlet. To solve the equations for mechanical properties, a finite difference numerical framework through the GeoDict numerical package [33,35] is applied. More details about this framework can be found in [33].

3. Validation

The model is developed based on our previous heterogeneous reaction model [36]. The validation of heterogeneous reaction part