

RESEARCH ARTICLE

10.1002/2014JB011812

Key Points:

- Coupled electrokinetic and reactive transport is a natural process
- Established a numerical framework to combine all effects
- We clarified when the coupling is necessary and when negligible

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Citation:

Zhang, L., and M. Wang (2015), Modeling of electrokinetic reactive transport in micropore using a coupled lattice Boltzmann method, *J. Geophys. Res. Solid Earth*, 120, 2877–2890, doi:10.1002/2014JB011812.

Received 4 DEC 2014

Accepted 10 APR 2015

Accepted article online 15 APR 2015

Published online 13 May 2015

Modeling of electrokinetic reactive transport in micropore using a coupled lattice Boltzmann method

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Abstract It is well known that a solid surface will be charged when it comes into contact with liquid, especially with electrolyte solutions. The surface charge influences ion distribution and transport and, therefore, affects the chemical reaction. Such an effect may become significant in micropores/nanopores when the electrical double layer thickness is comparable to the pore size, but this has never been well studied. This work investigates the coupled electrokinetic and reactive transport in micropores using mesoscopic modeling. We established a numerical framework by coupling multiple lattice Boltzmann models to combine all effects on ion transport from convection, diffusion and electrokinetics, and therefore, on heterogeneous reactions in micropore. After validations, the mechanism of surface charge effects on reactive transport is studied for an ion precipitation case and a solid dissolution case. The results show that two factors, transport and reaction, compete in such complicated processes based on their characteristic rates. When the transport rate, including diffusion and convection, is much lower than the reaction rate, i.e., the transport-dominated process, the surface charge significantly reduces the reaction. Otherwise for a reaction-dominated process, the surface charge effect may be negligible.

1. Introduction

Ionic transport in porous media coupled with chemical reactions is ubiquitous in various energy and environmental systems. Typical examples include corrosion [e.g., *Nordsveen et al.*, 2003], contaminant removal in soil [e.g., *Acar and Alshawabkeh*, 1993], nuclear waste management in geological disposal [e.g., *McCarthy et al.*, 1978], and CO₂ sequestration in saline aquifer [e.g., *Xu et al.*, 2003; *Wang et al.*, 2010]. A better understanding of these processes at pore scale provides valuable information for prediction and design in practice, especially for coupled transport in heterogeneous porous media [Li et al., 2008; Steefel et al., 2013]. In addition, knowledge in ionic transport helps to analyze and interpret the results of geophysical measurements like electrical methods [e.g., *Revil and Leroy*, 2004; *Revil et al.*, 2005]. Basically, the process usually includes convection, diffusion, and chemical reactions. Since the surface will get charged on account of surface adsorption or dissociation, the electrostatic interaction between ions and charged surface will generate the electrical double layer (EDL) [Hunter, 1989; Li, 2004], which modifies the ionic distribution in the EDL region considerably.

Though the study of EDL and the related electrokinetic phenomena in porous media has been a long-lasting topic in the field of microfluidics, colloidal, and membrane science [e.g., *Fair and Osterle*, 1971; *Hunter*, 1989; *Li*, 2004], little attention has been paid on the chemical reaction during electrokinetic transport. On the other hand, the effect of EDL has rarely been discussed in the study of reactive transport, mainly in the field of chemical engineering and geochemistry [e.g., *Rubin*, 1983; *Lichtner*, 1985; *Cederberg et al.*, 1985; *Yeh and Tripathi*, 1989; *Engesgaard and Kipp*, 1992]. Although it has been recognized for a long time that electrical interaction can play an important role in multicomponent transport in porous media through electromigration, the assumption of electroneutrality prevails in the previous research [e.g., *Ben-Yaakov*, 1972; *Ovaysi and Piri*, 2013]. In fact, the existence of surface charge will make the electroneutrality break down, especially at microscale and nanoscale. Up to now, only some efforts have been devoted to couple the reactive transport and electrokinetic transport on account of surface charge together [Hiorth et al., 2013].

It is known that for solution with high ionic strength, the Debye length, which characterizes the length of EDL, is much smaller than the characteristic length of the pore. In this thin double-layer limit, the solution is electroneutral everywhere except for an electrical potential on the surface. This is called the thin double-layer (TDL) model. Recently, Hiorth et al. [2013] presented a lattice Boltzmann model including ion exchange and surface complexation models using the TDL model as a result of the high ionic strength in their case.

However, when the ionic strength of a solution is low, the Debye length is comparable to the size of the pore. Under this circumstance, transport in the EDL, especially the diffuse layer, becomes important and thus surface charge can have an effect on the transport rate. Furthermore, the overlap of EDL may occur and modify the distribution of ions [Goncalves *et al.*, 2007; Wang and Kang, 2010]. To the author's knowledge, a fully coupled electrokinetic and reactive transport model for low ionic strength is still missing and no work has been done to investigate the effect of EDL on the reactive transport.

In this work, to account for the surface charge effect, the Nernst-Planck equation is employed for ion transport. Since the electrical potential is closely related to the distribution of ions, the Nernst-Planck equation and the Poisson equation for electrical potential have to be solved iteratively. This is the Poisson-Nernst-Planck (PNP) model. Meanwhile, the Navier-Stokes (NS) equation is solved for liquid velocity. In order to extend the present work for future research in porous media, lattice Boltzmann method (LBM) is employed to obtain the distribution of velocity, ion concentration, and electrical potential field. The lattice Boltzmann method has been proved to be a powerful tool to simulate transport process in porous media [e.g., Chen and Doolen, 1998; Aidun and Clausen, 2010] because of the simplicity for complex geometry and the intrinsic parallelism for coding. Originally proposed to solve the Navier-Stokes equation, LBM then extended to solve other partial differential equations [e.g., Zeiser *et al.*, 2001; Zhang and Ren, 2003; Yamamoto *et al.*, 2005; Sullivan *et al.*, 2005; Wang *et al.*, 2006; Wang and Kang, 2010; Yoshida and Nagaoka, 2010]. In order to implement reactions into the lattice Boltzmann model, researchers proposed several models to account for both homogeneous and heterogeneous reactions [e.g., Sullivan *et al.*, 2005; Kang *et al.*, 2006; Bresolin and Oliveira, 2012; Mishra and Ashoke, 2013; Hiorth *et al.*, 2013; Chen *et al.*, 2014]. Particularly for heterogeneous or surface reactions, different methods of boundary conditions have been used to incorporate the complicated surface chemical reaction kinetics [e.g., He *et al.*, 2000; Kang *et al.*, 2002; Verhaeghe *et al.*, 2005, 2006; Kang *et al.*, 2007; Arcidiacono *et al.*, 2008; Walsh and Saar, 2010; Zhang *et al.*, 2012; Chen *et al.*, 2013]. When precipitation or dissolution is involved, both discrete methods, like volume-of-fluid method [Kang, 2003; Kang *et al.*, 2006] and more accurate methods for interface dynamic evolution were developed [Verhaeghe *et al.*, 2005; Yu and Ladd, 2010] to capture the geometry change.

This paper is organized as follows. Section 2 describes the mathematical and numerical models. Section 3 presents the validations of submodels. Results and discussion are given in section 4 with both precipitation and dissolution cases. Section 5 concludes the work and elucidates future work.

2. Mathematical and Numerical Models

This section presents the mathematical model and the corresponding numerical models. To be specific, the lattice Boltzmann method is employed to solve the governing equations for velocity, ion concentration, and electrical potential.

2.1. Fluid Flow

For the case we considered in microscale, flow is laminar and incompressible. The Navier-Stokes equation can be simplified to the form

$$\nabla \cdot \mathbf{u} = 0, \quad (1)$$

$$\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} = -\frac{\nabla p}{\rho} + \nu \nabla^2 \mathbf{u} + \frac{\mathbf{F}}{\rho}, \quad (2)$$

where $\mathbf{u}$ is the velocity vector, ν is the kinetic viscosity, p is the pressure, ρ is the density, and $\mathbf{F}$ can be any kind of effective body force. For example, to include electrical force for electro-osmotic flow, $\mathbf{F} = \mathbf{F}_e = \rho_e \cdot \mathbf{E}$, where ρ_e is the volumetric charge density and $\mathbf{E}$ is the external electrical field.

The evolution equation of lattice Boltzmann model recovering the governing equation for fluid flow [Chen and Doolen, 1998] has the following form

$$f_\alpha(\mathbf{r} + \mathbf{e}_\alpha \delta t_f, t + \delta t_f) - f_\alpha(\mathbf{r}, t) = -\frac{1}{\tau_f} [f_\alpha(\mathbf{r}, t) - f_\alpha^{eq}(\mathbf{r}, t)] + \omega_\alpha F_\alpha, \alpha = 1 - 9, \quad (3)$$

where $\mathbf{r}$ denotes the position vector, $\mathbf{e}_\alpha$ the unit discrete velocity vector, δt_f the time step, and τ_f the dimensionless relaxation time for flow, which is defined as $\tau_f = \frac{3\nu\delta t_f}{\delta x^2} + 0.5$. For two-dimensional, nine-speed (D2Q9) model we use, the discrete directions are

$$\mathbf{e}_\alpha = \begin{cases} (0, 0) & \alpha = 1 \\ (\cos \theta_\alpha, \sin \theta_\alpha), & \theta_\alpha = (\alpha - 2)\pi/2 \quad \alpha = 2 - 5. \\ \sqrt{2}(\cos \theta_\alpha, \sin \theta_\alpha), & \theta_\alpha = (\alpha - 6)\pi/2 + \pi/4 \quad \alpha = 6 - 9 \end{cases} \quad (4)$$

The density equilibrium distribution f_α^{eq} can thus be expressed as

$$f_\alpha^{\text{eq}} = \omega_\alpha \rho \left[1 + \frac{3\mathbf{e}_\alpha \cdot \mathbf{u}}{c_f} + \frac{9(\mathbf{e}_\alpha \cdot \mathbf{u})^2}{2c_f^2} - \frac{3\mathbf{u}^2}{2c_f^2} \right], \alpha = 1 - 9, \quad (5)$$

with the distribution coefficients

$$\omega_\alpha = \begin{cases} 4/9 & \alpha = 1 \\ 1/9 & \alpha = 2 - 5, \\ 1/36 & \alpha = 6 - 9 \end{cases} \quad (6)$$

and the lattice speed for flow $c_f = \frac{\delta x}{\delta t_f}$. F_α is the discrete form of external force [e.g., Guo et al., 2002].

After evolution, the macroscopic density and velocity can be calculated by

$$\rho = \sum_\alpha f_\alpha, \quad (7)$$

$$\rho \mathbf{u} = \sum_\alpha \mathbf{e}_\alpha f_\alpha. \quad (8)$$

2.2. Ion Transport

Here we neglect dispersion, radiation, and anisotropy for diffusivity and assume the activity coefficient to be unity since the concentration in this work is low enough. The famous Nernst-Planck equation for transport of the i th ion has the following form

$$\frac{\partial C_i}{\partial t} + \nabla \cdot \left[C_i \left(\mathbf{u} - \frac{e z_i D_i}{k_b T} \nabla \psi \right) \right] = D_i \nabla^2 C_i, \quad (9)$$

where C_i , z_i , and D_i denote the concentration, ion algebraic valence, and the diffusion coefficient for i th ion, respectively; and e , k_b , and T denote the charge of proton, the Boltzmann constant, and the absolute temperature, respectively. ψ is the electrical potential and the term, $\frac{e z_i D_i}{k_b T} \nabla \psi$, can be seen to act as a kind of velocity induced by electrical field. If we define $\mathbf{u}_i^e = -\frac{e z_i D_i}{k_b T} \nabla \psi$ [Lichtner, 1985; Warren, 1997], equation (9) can be written as

$$\frac{\partial C_i}{\partial t} + \nabla \cdot [C_i (\mathbf{u} + \mathbf{u}_i^e)] = D_i \nabla^2 C_i. \quad (10)$$

Similar to the process in solving NS equation, LBM is available for solving convection-diffusion type equation [Yoshida and Nagaoka, 2010]. In consideration of efficiency, the two-dimensional, five-speed (D2Q5) model is adopted [Sullivan et al., 2005; Kang et al., 2007] with the discrete directions defined as

$$\mathbf{e}_\alpha = \begin{cases} (0, 0) & \alpha = 1 \\ (\cos \theta_\alpha, \sin \theta_\alpha), & \theta_\alpha = (\alpha - 2)\pi/2 \quad \alpha = 2 - 5. \end{cases} \quad (11)$$

The evolution equation for Nernst-Planck equation can be written as

$$g_\alpha(\mathbf{r} + \mathbf{e}_\alpha \delta t_{D_i}, t + \delta t_{D_i}) - g_\alpha(\mathbf{r}, t) = -\frac{1}{\tau_{D_i}} [g_\alpha(\mathbf{r}, t) - g_\alpha^{\text{eq}}(\mathbf{r}, t)], \alpha = 1 - 5, \quad (12)$$

with

$$g_\alpha^{\text{eq}} = \omega_\alpha C_i \left[1 + 3 \frac{\mathbf{e}_\alpha \cdot (\mathbf{u} + \mathbf{u}_i^e)}{c_{D_i}} \right], \alpha = 1 - 5, \quad (13)$$

where $\omega_\alpha = \frac{1}{3}$, $\alpha = 1$; $\omega_\alpha = \frac{1}{6}$, $\alpha = 2 - 5$, and the dimensionless relaxation time $\tau_{D_i} = \frac{3D_i\delta t_{D_i}}{\delta x^2} + 0.5$. $c_{D_i} = \frac{\delta x}{\delta t_{D_i}}$ denotes the lattice velocity for i th ion transport. The macroscopic concentration is calculated by

$$C_i = \sum_{\alpha} g_{\alpha}. \quad (14)$$

Note that by employing equation (13), the electrochemical migration contributing to the ion flux is incorporated to the collision operator, and thus, the locality of the algorithm in LBM is preserved. *Yoshida et al.* [2014] recently proved that this scheme had a better efficiency and accuracy for simulating time-dependent process.

2.3. Electrical Potential Distribution

To give the electrostatic potential in the Nernst-Planck equation, it is required to solve the Poisson's equation, which is self-consistent with the continuum charge density. We add a time-dependent term in the Poisson's equation to make it compatible with LBM [Wang et al., 2006; Wang and Kang, 2010],

$$\frac{\partial \psi}{\partial t} = \nabla^2 \psi + \frac{\rho_e}{\epsilon}, \quad (15)$$

where ρ_e denotes the volumetric charge density and ϵ the fluid dielectric permittivity. Together with the Nernst-Planck equation, they form the PNP equations.

Similar with the model for ion transport, the evolution equation for equation (15) is written as

$$h_{\alpha}(\mathbf{r} + \mathbf{e}_{\alpha}\delta t_{\psi}, t + \delta t_{\psi}) - h_{\alpha}(\mathbf{r}, t) = -\frac{1}{\tau_{\psi}} [h_{\alpha}(\mathbf{r}, t) - h_{\alpha}^{\text{eq}}(\mathbf{r}, t)] + \omega_{\alpha}\delta t_{\psi} \frac{\rho_e}{\epsilon}, \quad (16)$$

with

$$h_{\alpha}^{\text{eq}} = \omega_{\alpha}\psi, \quad (17)$$

for $\alpha = 1 - 5$ and the dimensionless relaxation time for electrical potential $\tau_{\psi} = \frac{3\delta t_{\psi}}{\delta x^2} + 0.5$. The distribution coefficient ω_{α} are the same with that for ion concentration. The macroscopic electrical potential is calculated by

$$\psi = \sum_{\alpha} h_{\alpha}. \quad (18)$$

In fact, in the calculation of ion transport, the quantity we need is not electrical potential but the gradient of electrical potential. Finite difference method is the most common approach to calculate the gradient when the macroscopic quantities are known. In the lattice Boltzmann framework, the gradient can be alternatively calculated by distribution functions [Noble, 1997; Yoshida and Nagaoka, 2010; Yoshida et al., 2014] as

$$\frac{\partial \psi}{\partial x_j} = -\frac{1}{\beta\tau_{\psi}} \sum_{\alpha} (\mathbf{e}_{\alpha} \cdot \mathbf{e}_j) h_{\alpha}, \quad (19)$$

where $\mathbf{e}_j$ is the unit vector in the x_j direction and β is a constant determined by lattice Boltzmann model, i.e., $\beta = \frac{1}{3}$ for D2Q5, D2Q9 and $\beta = \frac{1}{2}$ for D2Q4 [Yoshida and Nagaoka, 2010]. The distribution function approach has a better accuracy and needs no special treatment for boundary nodes [Yoshida et al., 2014].

2.4. Chemical Reactions

Basically, chemical reactions are divided into two groups: homogeneous reactions and heterogeneous reactions [Kang et al., 2006]. More detailed classification can refer to Rubin [1983]. Homogeneous reactions, which usually occur in the interior of the system can be incorporated as a source term and evaluated using an operator-splitting method [Dawson et al., 1993; Zeiser et al., 2001; Sullivan et al., 2005; Wang et al., 2012]. Recently, Bresolin and Oliveira [2012] reported an algorithm based on collision theory to account for the chemical reaction.

In terms of the heterogeneous reactions, approaches are roughly divided into two categories. The first one follows the idea of conventional continuum formulation and converts the reaction flux through the boundary into a volume-averaged source term of the near-wall node [Wells et al., 1991]. This method can be easily incorporated with other homogeneous reaction solver [Patel et al., 2013]. However, as pointed out by

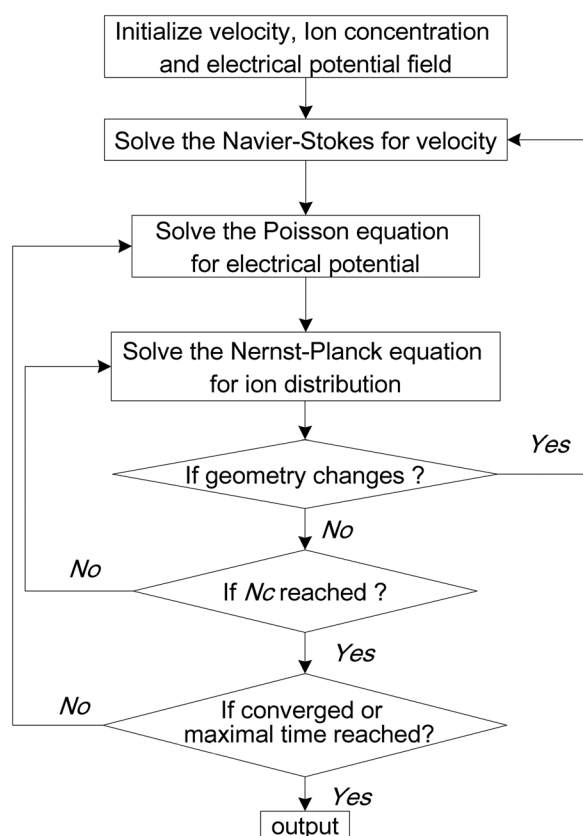


Figure 1. Flow chart of the numerical scheme for coupled electrokinetic and reactive transport.

Kang *et al.* [2006, 2007], there is no constraint mechanism for continuum formulation and therefore this method breaks down for fast reactions.

The other category includes all the approaches seeking to formulate equations for the unknown distribution functions in LBM and recovers the macroscopic boundary conditions. Most previous work fall into this category [He *et al.*, 2000; Kang *et al.*, 2002; Verhaeghe *et al.*, 2005, 2006; Kang *et al.*, 2007; Walsh and Saar, 2010; Zhang *et al.*, 2012; Chen *et al.*, 2013; Hiorth *et al.*, 2013]. According to mass conservation on the interface, the boundary condition for ionic concentration can be written as

$$J_{\text{trans}}^{\Gamma} = J_{\text{heter}}^{\Gamma} \quad (20)$$

where Γ denotes the interface, $J_{\text{trans}}^{\Gamma}$ represents the mass transfer rate from bulk to the interface because of diffusion, electrical interaction, or convection, and $J_{\text{heter}}^{\Gamma}$ represents the heterogeneous reaction rate which is a function of surface concentrations of reactants, temperature, charge density, and so on. When two or more reactions occur simultaneously, Kang *et al.* [2007] and Hiorth

et al. [2013] have shown an iterative method. However, Gillissen and Looije [2014] recently proposed an explicit method based on Taylor expansion to replace the iterative procedure and we use this method in our work.

In this work, zigzag boundary is used to replace the accurate curved boundary, which simplifies the implementation of boundary conditions in LBM and reduces the computational cost. For implementation of curved boundary in LBM, the readers can refer to some previous work either for NS equation [e.g., Mei *et al.*, 1999] or for advection-diffusion equation [e.g., Ginzburg, 2005; Li *et al.*, 2013; Geback and Heintz, 2013]. When heterogeneous reaction occurs on the solid-liquid surface, it leads to the geometry change. The volume-of-fluid method is adopted to capture the solid/liquid interface. A boundary node becomes a fluid node once the volume is below the critical volume and becomes a solid node once the volume reaches the critical volume. Unlike the critical value used by Kang *et al.* [2006], we use 0.5 as dimensionless critical volume, which is recommended in Verhaeghe *et al.* [2005] and Patel *et al.* [2013] for better accuracy.

2.5. Flow Chart

The Nernst-Planck equation for ion concentration and the Poisson equation for electrical potential are explicitly coupled together so that we have to solve them iteratively. Figure 1 shows the flow chart of the numerical scheme. After initialization, we first solve the Navier-Stokes equation for initial velocity field. In the iteration procedure, the evolution equation (16) for the Poisson equation is solved until steady state in which the net charge density is calculated by the ion distribution of the last iteration (or from the initial state for the first iteration). Next, the electrical potential gradient in the Nernst-Planck equation can be obtained by equation (19). Next, the ion distribution is calculated by the evolution equation (12) for N_c steps. N_c is selected to be 10 in this work, which has been carefully tested for convergence. In each step, if the geometry changes because of chemical reactions, i.e., fluid node becomes solid node or solid node becomes fluid node, the velocity field needs to be updated.

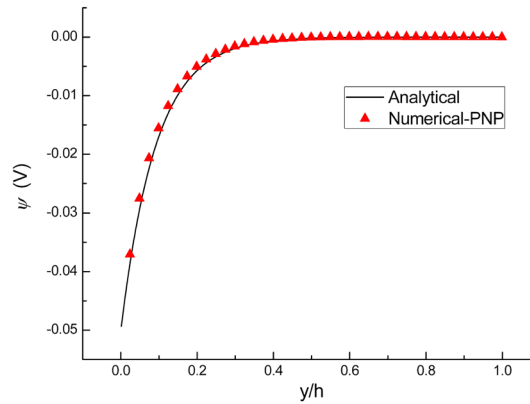


Figure 2. Analytical results and numerical results from PNP models for 1-D equilibrium electrical potential distribution. The black line is the analytical solution; the red symbols are results from the PNP model.

try change caused by reactions are not involved, such as results in Figure 6 in section 4.1, we seek the ionic distribution at steady state and thus a convergence criteria for ionic concentration similar to equations (21) and (22) can be defined as

$$\delta_{C_i} = \sqrt{\frac{1}{N_{\text{fluid}}} \sum_{\mathbf{r}} (C_i^n(\mathbf{r}) - C_i^{n-1}(\mathbf{r}))^2} < \epsilon_{\text{err}}, \quad (23)$$

where C_i is chosen to be the concentration of the counterion in this work.

On the other hand, if the geometry changes with time, the simulation stops when the reaction reaches some critical value. For the case of Figure 7 in section 4.1, the simulation goes on until the thickness of precipitant reaches $\frac{2}{5}h$, where h is the initial height of the system.

In this paper, we employ 2-D modeling for demonstration and extension to 3-D model can be done without much effort by changing the corresponding parameters of lattice Boltzmann method.

3. Validations

3.1. Equilibrium EDL

First, our algorithm is used to calculate the equilibrium distribution of the electrical potential of EDL. One side of the domain is the solid wall with a given surface potential, while the other side is defined as the bulk solution with zero electrical potential and bulk concentration. To ensure the validity of constant bulk concentration, the length of the domain is much larger than the Debye length (usually 10 or larger). Figure 2 shows that the numerical results from PNP model are consistent with the analytical solution for Poisson-Boltzmann equation, which has the form [Hunter, 1989]

$$\psi_{\text{exact}} = 4 \frac{k_b T}{e} \tanh^{-1} \left(\tanh \left(\frac{\psi_0 e}{4 k_b T} \exp \left(-\frac{y}{\lambda_D} \right) \right) \right), \quad (24)$$

where ψ_0 is the surface potential and $\lambda_D = \sqrt{\frac{\epsilon k_b T}{2 e^2 z_1^2 C_\infty}}$ is the Debye length. We take $\psi_0 = -50$ mV, $C_\infty = 10^{-5}$ mol/L.

3.2. Stefan Problem for Solid-Liquid Interface Movement

The Stefan problem has been used to test the algorithm for chemical reaction and geometry change [Verhaeghe et al., 2005; Patel et al., 2013]. Details of the mathematical description for the Stefan problem can refer to Aaron [1970]. Solid dissolves into unsaturated liquid and the interface moves toward the solid side. The position of the interface S has an analytical solution, (here we set initial interface position zero)

$$\begin{aligned} S &= \frac{\lambda}{2} (Dt)^{1/2}, \\ (\pi)^{1/2} \lambda e^{\lambda^2} \text{erfc}(-\lambda) &= k/2, \\ k &= 2(C_l - C_0) / (C_p - C_l), \end{aligned} \quad (25)$$

To judge if the simulation reaches steady state or not, we define the convergence criteria for electrical potential and velocity as

$$\delta_\psi = \sqrt{\frac{1}{N_{\text{fluid}}} \sum_{\mathbf{r}} (\psi^n(\mathbf{r}) - \psi^{n-1}(\mathbf{r}))^2} < \epsilon_{\text{err}}, \quad (21)$$

$$\delta_{\mathbf{u}} = \sqrt{\frac{1}{N_{\text{fluid}}} \sum_{\mathbf{r}} (\mathbf{u}^n(\mathbf{r}) - \mathbf{u}^{n-1}(\mathbf{r}))^2} < \epsilon_{\text{err}}, \quad (22)$$

where $\mathbf{r}$ denotes the location vector, and the superscript n represents the n th iteration. The summation applies to the fluid region and N_{fluid} denotes the total number of fluid nodes. Typically, we employ a value of 10^{-6} for ϵ_{err} .

The criterion for terminating the calculation depends on the case we study. When the geome-

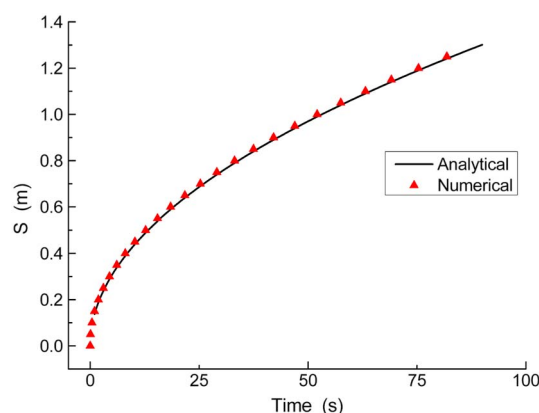


Figure 3. Interface position versus time for Stefan problem with analytical and numerical results. S indicates the interface position, which we assume to be zero initially. The black line is the analytical solution, the red symbols are results from modeling. The stepwise discontinuity of modeling result comes from discrete update criteria for geometry change. As the grid spacing decreases, the discontinuity decreases and the numerical result approaches a continuous line.

Helmholtz Plane) in Figure 4, which is the beginning of the diffuse layer. At P_{in} , the electrical potential is usually denoted as ψ_d [e.g., Leroy and Revil, 2004]. Strictly speaking, ψ_d is different from zeta potential ζ which is defined at the shear plane. However, this difference can be rather small and we assume $\psi_d = \zeta$ in this work [Leroy and Revil, 2004, 2009]. Furthermore, we always assume a constant zeta potential on the surface for simplicity. Otherwise, a boundary condition with given charge density can be implemented without any trouble [Wang et al., 2008] and the electrical triple-layer model [e.g., Leroy and Revil, 2004; Wang and Revil, 2010] will be modified to replace the constant zeta potential specified here in the future work.

At the solid/liquid interface, the solid species denoted by AB is negatively charged and in contact with an oversaturated solution containing counterion A^+ and coion B^- . Precipitation occurs as



Equation (26) can be considered as a representative form of several precipitation reactions in natural systems and experiments. For example, precipitation of calcite as $Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3$, which is a key step for mineral trapping in CO_2 sequestration [e.g., Steefel et al., 2013] and $Mg^{2+} + 2OH^- \leftrightarrow Mg(OH)_2$, which is important for weathering process [e.g., Pokrovsky and Schott, 2004].

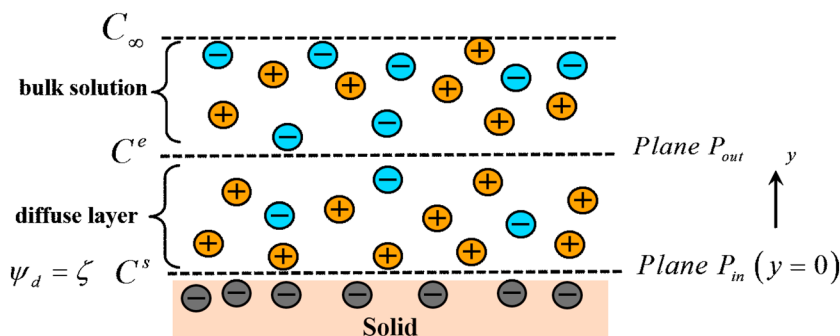


Figure 4. Schematic for 1-D precipitation problem with surface charge. Reaction, $A^+ + B^- \leftrightarrow AB(s)$, occurs on the interface with a given zeta potential. At the top of the system is the bulk electrolyte solution with $C_\infty = 10^{-5}$ mol/L. C^e and C^s denote the ion concentration located at plane, P_{out} , and plane, P_{in} , which are outside and inside of the EDL, respectively. In the thin double-layer model, P_{in} and P_{out} overlap.

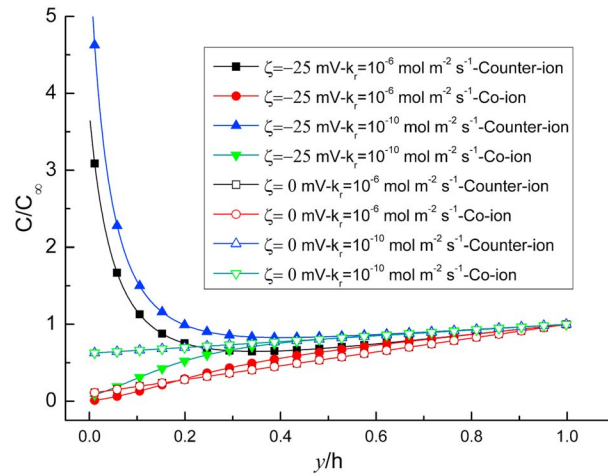


Figure 5. Profiles of nondimensional ion concentration with $\zeta = 0$ mV and -25 mV. The expression $y = 0$ represents the solid-liquid interface. The solid symbols indicate results with $\zeta = -25$ mV, while hollow symbols indicate those with $\zeta = 0$. The black squares and red circles represent counterion and coion concentrations for reaction rate constant $k_r = 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1}$ ($Da_{II} = 100$), while the blue triangles and green triangles represent those for $k_r = 10^{-10} \text{ mol m}^{-2} \text{ s}^{-1}$ ($Da_{II} = 0.01$).

The total height of the system is $h = 1 \mu\text{m}$, including one layer of solid grid and the upper boundary of the system keeps as the bulk solution with a constant concentration $C_\infty = 10^{-5} \text{ mol/L}$. The other physical parameters are the following: the dielectric constant $\epsilon = 6.95 \times 10^{-10} \text{ F/m}$, the temperature $T = 273\text{K}$, and the diffusion coefficients for both ions $D_1 = D_2 = 1 \times 10^{-9} \text{ m}^2/\text{s}$.

To describe the reaction kinetics, we follow Kang *et al.* [2006] in that the heterogeneous reaction is described by the transition state theory

$$I_{\text{heter}} = -k_r (1 - K_{\text{eq}} Q), \quad (27)$$

where k_r and K_{eq} are the reaction rate constant and equilibrium constant, respectively. Q is the ion activity product defined by

$$Q = \prod_i (\gamma_i C_i^s)^{\alpha_i}, \quad (28)$$

where γ_i is the activity coefficient, C_i^s the ionic concentration on the surface, and α_i the stoichiometric coefficients of reactions for the i th ion. Since the concentration we consider here is low (typically 10^{-5} mol/L), the ion activity coefficients are close to unity and thus we neglect them.

This system can be described by the Poisson-Nernst-Planck model coupled with surface reaction, and distribution of velocity, concentration, and electrical potential can be obtained by solving the governing equations. Different from the full PNP model, the thickness of the EDL is seen as infinitesimally small in the thin double-layer (TDL) model. The concentration outside the EDL is related to the surface concentration by the Boltzmann factor, $\exp\left(-\frac{z_i e \zeta}{k_b T}\right)$. In case of the reaction as equation (26),

$$\begin{aligned} Q &= C^s(A^+) \times C^s(B^-) = C^e(A^+) \exp\left(\frac{-e\zeta}{k_b T}\right) \times C^e(B^-) \exp\left(\frac{e\zeta}{k_b T}\right) \\ &= C^e(A^+) \times C^e(B^-), \end{aligned} \quad (29)$$

where C^e denotes the concentration just outside the EDL. Equation (29) shows that the activity product in TDL model is the same with the model without EDL or $\zeta = 0$ mV. That is to say, zeta potential in TDL actually has no effect on reaction and previous work without EDL can be seen as a model using the thin double-layer assumption. However, if the surface complexation model is introduced, this will be different because concentrations of surface complexes have to be included and are coupled with zeta potential [Hiorth *et al.*, 2013].

Figure 5 illustrates the concentration profile with $\zeta = 0$ and -25 mV when $k_r = 10^{-10}$ and $10^{-6} \text{ mol m}^{-2} \text{ s}^{-1}$. When $\zeta = -25$ mV, the concentration of counterion is much larger than that of coion near the surface, while there is no difference between concentrations of counterion and coion with $\zeta = 0$ mV. In fact, for cases without zeta potential, the governing equation for ion concentration reduces to diffusion equation, which has a simple linear solution.

Figure 6 shows the reaction flux on the surface per unit area at steady state for different Da_{II} with $\zeta = 0, -20$, and -50 mV. Da_{II} denotes the second Damköhler number which is defined as $Da_{II} = \frac{k_r h}{C_\infty D}$ [Probstein, 2005; Kang *et al.*, 2006; Steefel *et al.*, 2013]. The dimensionless Da_{II} represents the ratio of reaction rate over diffusive mass transfer rate. According to Figure 6, when Da_{II} is small (below 10^{-2}), zeta potential has little effect on the reaction flux. However, when Da_{II} gets larger, the reaction flux decreases with the increase of $|\zeta|$, which indicates a slower precipitation rate with higher zeta potential. Note that in this paper, higher zeta potential

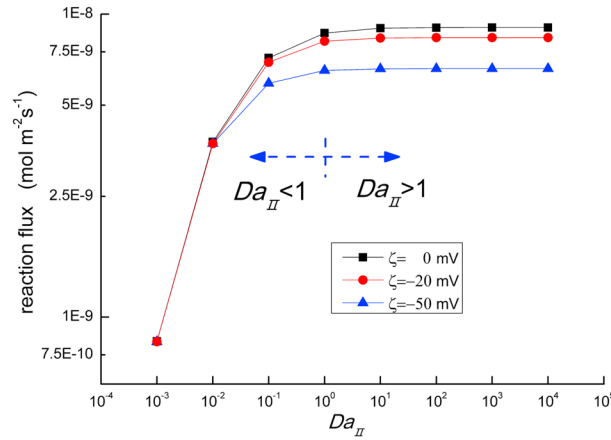


Figure 6. Reaction flux at steady state on the surface for different Da_{II} . The black squares, red circles, and blue triangles represent results with $\zeta = 0$ mV, -20 mV, and -50 mV, respectively.

$$Q = C^s(A^+) \times C^s(B^-) = C_\infty \exp\left(-\frac{e\zeta_A}{k_b T}\right) \times C_\infty \exp\left(-\frac{e\zeta_B}{k_b T}\right) = C_\infty^2. \quad (30)$$

This means that the activity product is a constant, thus, the reaction flux is not affected by zeta potential.

When Da_{II} is large, the reaction rate is rather fast compared to the mass transfer rate. In another word, the process is transport dominated. In this case, qualitative identification can be made through analysis for extreme case. First, we assume initially that there is no reaction and the electrical double layer is in equilibrium. So the concentrations of A^+ and B^- on the surface are $C_\infty \exp(-\frac{e\zeta}{k_b T})$ and $C_\infty \exp(\frac{e\zeta}{k_b T})$, respectively. Then, by assuming that the solution is oversaturated, reaction starts. Because of the large Da_{II} , the surface region can be seen as a closed batch reactor. This means that there is no mass transfer into the region and concentrations of A^+ and B^- are only consumed by precipitation. We assume that the consumption of ions by reaction in a very short time is ΔC . Accordingly, the activity product becomes

$$\begin{aligned} Q &= (C_\infty \exp(-\frac{e\zeta}{k_b T}) - \Delta C)(C_\infty \exp(\frac{e\zeta}{k_b T}) - \Delta C) \\ &= C_\infty^2 + (\Delta C)^2 - (\exp(-\frac{e\zeta}{k_b T}) + \exp(\frac{e\zeta}{k_b T}))C_\infty \Delta C. \end{aligned} \quad (31)$$

From simple algebraic analysis, it is shown that Q decreases with increase of $|\zeta|$. A smaller activity product will lead to a slower precipitation, which is consistent with the numerical results. In addition, this

effect enhances with higher ζ . Therefore, we can expect a large deviation of previous results without EDL for transport-dominated process with high zeta potential.

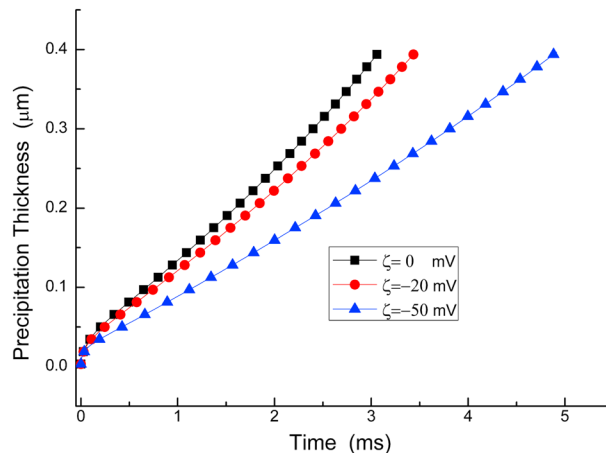
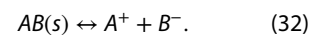


Figure 7. Increase of precipitation thickness over time for $Da_{II} = 100$. The black squares, red circles, and blue triangles represent results with $\zeta = 0$ mV, -20 mV, and -50 mV, respectively.

4.2. Solid Dissolution With Water Flooding

To further investigate how the EDL affects the reactive transport at pore scale, a two-dimensional dissolution problem in straight microchannel is solved in this section for demonstration. Figure 8 illustrates the schematic diagram in which pure water is driven by pressure into a charged channel and leads to dissolution of solid phase following



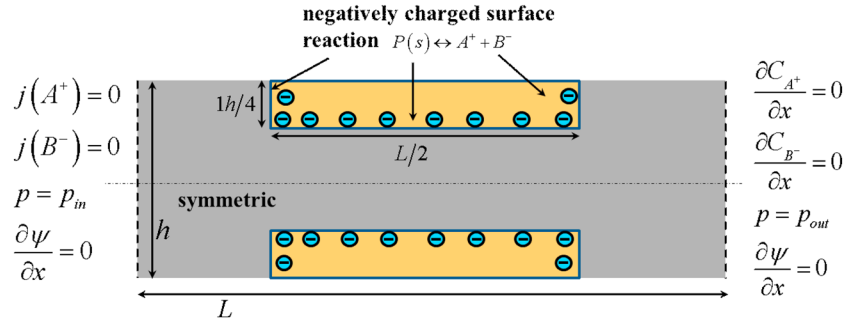


Figure 8. Schematic for 2-D dissolution. Pressure-driven pure water flows into a charged, dissolvable channel. The channel is connected to two large pore space with constant pressure and zero electrical field intensity at inlet and outlet. No ions flow in from the inlet and fully developed boundary is assigned at the outlet. Since the system is symmetric, simulation is conducted in half of the domain.

If the flow is driven by external electric field, electro-osmotic flow arises and it leads to a fully coupled electro-osmotic reactive transport [Wang and Kang, 2010]. Since we focus on the surface charge effects on reactive transport, this process is too complicated to be covered in this first-step paper. However, based on present model, it can be achieved by modifying the governing equations and numerical scheme.

The height of the system is $h = 2 \mu\text{m}$ and the length of the system, L , is around $16 \mu\text{m}$. Thanks to the symmetry of the system, only half of the domain is simulated. A mesh of 800×52 grids is used and the mesh independence has been tested. Initially, the electrical potential is given by solving the Poisson-Boltzmann equation and the corresponding concentration distribution is obtained by assumption of Boltzmann distribution with a bulk concentration $C_0 = 10^{-5} \text{ mol/L}$. The equilibrium constant for dissolution is chosen to ensure an initial equilibrium. As the pure water floods into the channel by pressure, the solid, AB , dissolves into ion A^+ and ion B^- . Since dissolution is the reverse process of precipitation, we follow the formulation of reaction rate of 1-D precipitation case in section 4.1, i.e., equation (27),

$$I_{\text{heter}} = k_r (1 - K_{\text{eq}} Q), \quad (33)$$

with a difference in the negative sign. Therefore, positive reaction flux here means dissolution, which is opposite to the case in precipitation.

To describe the process more generally, two dimensionless quantities, i.e., the Peclet number Pe and the Second Damköhler number Da_{II} are introduced. Pe is defined as $Pe = \frac{u_c h_c}{D} = \frac{\Delta p h_c^2}{6 \mu L} \frac{h_c}{D}$ where Δp is the pressure difference between inlet and outlet. We

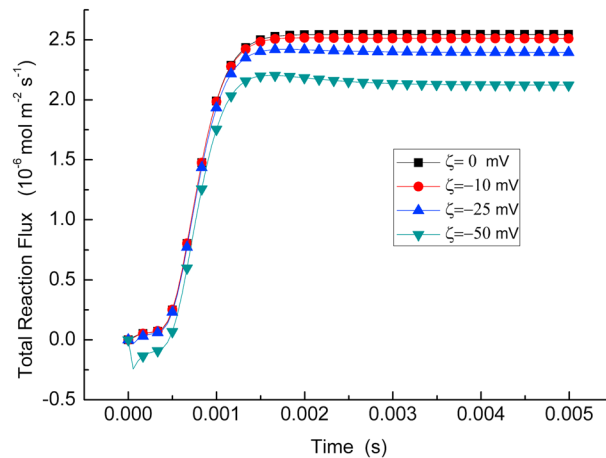


Figure 9. Total reaction flux for different zeta potentials with $Pe = 10$, $Da_{II} = 100$. Squares, circles, upright triangles, and inverted triangles represent results with $\zeta = 0 \text{ mV}$, -10 mV , -20 mV , and -50 mV , respectively.

use the average velocity of Poiseuille flow between infinite plates to estimate the characteristic velocity, u_c . Da_{II} follows the same definition in section 4.1 with h_c in place of h . Here we take the channel width as the characteristic length, i.e., $h_c = h/2$.

First, we ignore the geometry change due to dissolution and investigate the influence of zeta potential on reaction rate. As elucidated in section 4.1, because of the counter effects of zeta potential on counterion and coion in the thin double-layer model, the thin double-layer model actually has the same results with the model which neglects the surface charge. In Figure 9, for $Pe = 10$, $Da_{II} = 100$, total reaction flux on the surface decreases with the increase of zeta potential, and therefore,

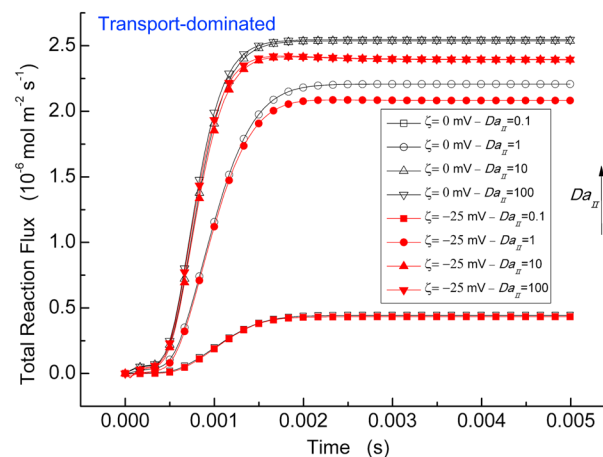


Figure 10. Change of total reaction flux with time for different Da_{II} with $Pe = 10$. Red symbols denote results with $\zeta = -25$ mV while black symbols denote results with $\zeta = 0$ mV. When Da_{II} is rather small, reaction dominates and the influence of zeta potential diminishes. When Da_{II} get larger, dissolution becomes transport dominated and zeta potential plays an important role.

dissolution gets slower with higher zeta potential. This follows the same trend with precipitation in section 4.1. The reason is that, in dissolution, the activity product, $Q = C^s(A^+) \times C^s(B^-)$, increases with the zeta potential because of the difference between the concentrations of counterion and coion. Consequently, the dissolution is depressed by the high activity product. In addition, it may lead to some negative reaction flux, e.g., precipitation, at the first stage for large ζ because of the initial Boltzmann distribution.

The influence of zeta potential also relies on the transport rate and reaction rate. Figure 10 shows the change of total reaction flux with time for different Da_{II} . The reaction rate goes up at the first stage and reaches a steady state quickly. Pe determines the time for the system to reach steady state, e.g., in Figure 10, it is about 0.0015 s. When Da_{II} is small, which indicates that reaction rate is

much smaller than the transport rate, the electrolyte solution is close to equilibrium state and the zeta potential has a minor effect. However, when Da_{II} gets larger, dissolution becomes transport dominated and zeta potential plays an important role. In this case with $Pe = 10$, total reaction flux almost stops to increase with $Da_{II} = 10$, which indicates that it is in the transport-dominated regime.

Figure 11 shows the geometry and concentration distribution at $t = 1.67 \times 10^{-3}$ and 3.33×10^{-3} s with $\zeta = 0$ and -25 mV. Even though a high-concentration region exists at the exit of the channel thanks to the EDL when $\zeta = -25$ mV, the process of water flooding and dissolution is similar. It is worth noting that the EDL gets weaker, with the intrusion of the pure water. This is because a constant zeta potential is employed as boundary condition for electrical potential, and with a lower concentration, less counterions will be attracted into the EDL region even though the Debye length will extend. In Figure 12, the dissolved volume corresponding to the cases $\zeta = 0$ mV and $\zeta = -25$ mV are shown. For models neglecting EDL, the dissolved volume will be overestimated by 5% after only 3×10^{-3} s. More difference is expected to emerge based on the present dissolving rate.

Finally, we estimate the typical values of Da_{II} for two important reactions: dissolution of calcite and brucite. The reaction rate for dissolution of calcite and brucite are approximately 10^{-5} mol m^{-2} s^{-1} and 10^{-8} mol m^{-2} s^{-1} for pH = 5, respectively [Chou et al., 1989; Pokrovsky and Schott, 2004]. This leads to corresponding Da_{II} of

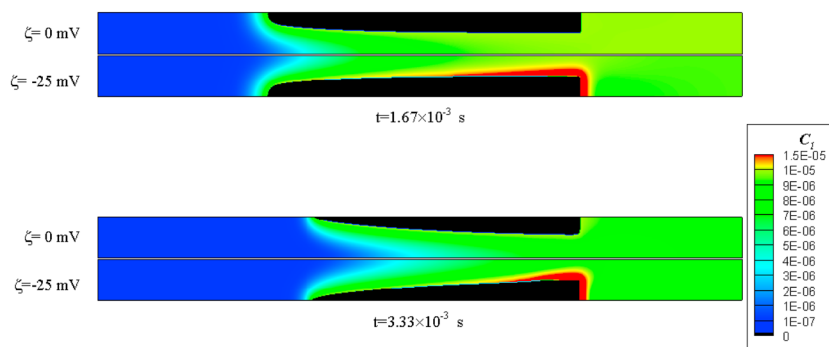


Figure 11. For $Pe = 10$, $Da_{II} = 100$, distribution of counterion concentration, C_1 , at $t = 1.67 \times 10^{-3}$ s, 3.33×10^{-3} s with (top) $\zeta = 0$ mV, (bottom) -25 mV. Black part represents the solid and decreases with time because of dissolution. For the cases with $\zeta = -25$ mV, the red part adjacent to the interface represents the EDL region with a high counterion concentration. As the pure water flows in, the EDL gets weaker.

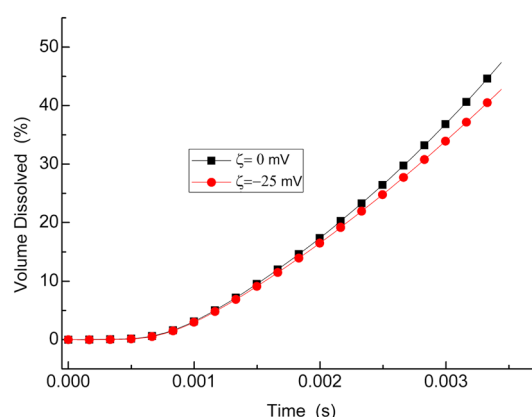


Figure 12. For $Pe = 10$, $Da_{II} = 100$, change of dissolved volume over time for 2-D dissolution. Black square symbols denote the case with $\zeta = 0$ mV, while the red circles denote the case with $\zeta = -25$ mV. It shows that a higher $|\zeta|$ reduces the dissolution rate, which is consistent with the results in Figure 9. For models neglecting EDL, the dissolved volume will be overestimated.

and nanopore. Numerical results show that transport of counterions and coions in EDL region may greatly influence the heterogeneous reaction rate on the surface. In both precipitation and dissolution, surface charge will reduce reaction rate as the process is in the transport-dominated regime, while the effect of surface charge is negligible for reaction-dominated regime.

Some geological processes are expected to be in the transport-dominated regime (e.g., dissolution of calcite for low pH in section 4.2). Consequently, results in this work may have twofold implications. First one is that reduction of reaction rate because of surface charge effect may be a reason for previously reported discrepancy between laboratory-measured and field-observed dissolution rates [Li *et al.*, 2008]. In fact, laboratory measurement usually employs well-mixed batch which accelerates reaction rate to eliminate effect of transport, while field rates are the results of combination of reaction and transport. Second, compared with present model, previous model without surface charge will overestimate the reaction rate and lead to an incorrect geometry. The alteration of the geometry is likely to further influence the motion of fluid. Therefore, neglect of surface charge would indirectly result in inaccurate prediction for seemingly irrelevant phenomena.

In the future, we will extend the reactive models to other reactions like ion-exchange reaction and surface complexation reactions [Hiorth *et al.*, 2013] and introduce the electrokinetic coupling like electro-osmosis, which are closely related to the process in geophysical measurements.

Acknowledgments

The data for this paper are available from M. Wang for free. This work is financially supported by the NSF grant of China (51176089 and 51321002) and Specialized Research Fund for the Doctoral Program of Higher Education of China (20130002110077). We gratefully thank J. Huang, P. Ravi, Y. Chen, Q. Kang, and W. Pfingsten for useful discussions. We are grateful to the anonymous reviewers for their helpful suggestions and comments.

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1 and 10^{-3} . Therefore, the effect of surface charge is expected to be nonnegligible for dissolution of calcite, which is important for mineral trapping of CO_2 sequestration. Meanwhile, since the reaction rates of calcite and brucite decrease with pH, the effect of surface charge may need to be considered for low pH.

5. Conclusions

We presented a lattice Boltzmann framework for coupled electrokinetic and reactive transport and aimed to correlate the relatively independent research for either electrokinetic or reactive transport. As a first-step work, the effect of surface charge on reactive transport is numerically investigated. Contrary to the conventional assumption of thin double-layer, ionic transport in EDL region is fully resolved in this work, which is necessary for dilute electrolyte in micropore

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