Modeling multicomponent ionic transport in groundwater with IPhreeqc coupling: Electrostatic interactions and geochemical reactions in homogeneous and heterogeneous domains

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ABSTRACT

The key role of small-scale processes like molecular diffusion and electrochemical migration has been increasingly recognized in multicomponent reactive transport in saturated porous media. In this study, we propose a two-dimensional multicomponent reactive transport model taking into account the electrostatic interactions during transport of charged ions in physically and chemically heterogeneous porous media. The modeling approach is based on the local charge balance and on the description of compound-specific and spatially variable diffusive/dispersive fluxes. The multicomponent ionic transport code is coupled with the geochemical code PHREEQC-3 by utilizing the IPhreeqc module, thus enabling to perform the geochemical calculations included in the PHREEQC's reaction package. The multicomponent reactive transport code is benchmarked with different 1-D and 2-D transport problems. Successively, conservative and reactive transport examples are presented to demonstrate the capability of the proposed model to simulate transport of charged species in heterogeneous porous media with spatially variable physical and chemical properties. The results reveal that the Coulombic cross-coupling between dispersive fluxes can significantly influence conservative as well as reactive transport of charged species both at the laboratory and at the field scale.

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1. Introduction

The importance of coupling subsurface solute transport models with geochemical codes, capable of simulating a wide variety of equilibrium and kinetic reactions, has been increasingly recognized and has led to major developments of reactive transport codes for subsurface environmental simulation (e.g., Steefel et al., 2015; Barry et al., 2002). The coupling of fluid flow, mass transport and geochemical reactions is instrumental for understanding and predicting the complex interplay between physical and bio-geochemical processes in sediments and groundwater systems, as well as for the quantitative interpretation of experimental observations both at the laboratory and field scales. Combining flow and transport codes with geochemical reaction packages has led to a first generation of now well-established reactive transport simulators for both groundwater (e.g., CrunchFlow (Steefel and Lasaga, 1994), Geochemist's Workbench (Bethke, 1997), PHT3D (Prommer et al., 2003), PHAST (Parkhurst et al., 2005)) and unsaturated/

multiphase flow (e.g., HYDROGEOCHEM (Yeh and Tripathi, 1990), TOUGHREACT (Xu and Pruess, 2001; Xu et al., 2006; Xu et al., 2011), MIN3P (Mayer et al., 2002)). Developments have continued over the last decade with increasing capabilities added to existing simulators as well as new couplings between different transport and geochemical codes (e.g., HP1/HPx (Šimunek et al., 2012), PHWAT (Mao et al., 2006), RICH-PHREEQC (Wissmeier and Barry, 2010)). Impetus to such advances was certainly provided by the release of modules such as IPhreeqc (Charlton and Parkhurst, 2011) and PhreeqcRM (Parkhurst and Wissmeier, 2015) devised to increase the flexibility in interfacing the widely used USGS's geochemical reaction package PHREEQC (Parkhurst and Appelo, 1999; Parkhurst and Appelo, 2013) with other codes. In particular, IPhreeqc is a C++ PHREEQC module designed for coupling PHREEQC's reaction capabilities (e.g., equilibrium reactions, ion exchange, surface complexation, solid solutions, mineral dissolution and precipitation, as well as kinetic reactions both abiotic and microbially mediated) to other software programs (for example, MATLAB®, Excel®, Visual Basic®) and/or programming and scripting languages (for instance, C, C++, FORTRAN, Python, R). IPhreeqc offers a wide range of extensive features to combine multidimensional transport simulators with comprehensive geochemistry

packages including thermodynamic databases (Wissmeier and Barry, 2011; Müller et al., 2011). Recent reactive transport simulators that benefited from the IPhreeqc capabilities include the couplings with COMSOL Multiphysics® (e.g., Wissmeier and Barry, 2011; Nardi et al., 2014; Nasir et al., 2014), OpenGeoSys (Kolditz et al., 2012; He et al., 2015) and UTCHEM (Korrani et al., 2015).

In this study we also take advantage of the IPhreeqc capabilities to explore the coupling between a two-dimensional multicomponent ionic formulation of charged species advective-dispersive transport and reactive processes. Many studies have demonstrated the importance of electrostatic effects due to charge interactions and leading to multicomponent diffusion of ions in aqueous solutions. Experimental observations have shown the effects of Coulombic interactions on the diffusive mobility of major ions, heavy metals and radioactive tracers both at the laboratory (Vinograd and McBain, 1941; Liu et al., 2011) and at the field scale (Giambalvo et al., 2002; Appelo and Wersin, 2007; Appelo et al., 2008; Appelo et al., 2010). The description of such interactions in multicomponent diffusion models is usually treated by including an electromigration term in addition to the classical Fickian diffusion term (e.g., Ben-Yaakov, 1972; Lasaga, 1979; Felmy and Weare, 1991; Boudreau et al., 2004; Cussler, 2009). In a series of recent laboratory flow-through experiments we have shown that the role of Coulombic effects is critical not only in diffusion-dominated systems but also in advection-dominated flow regimes (Rolle et al., 2013b; Muniruzzaman et al., 2014; Muniruzzaman and Rolle, 2015). In fact, the results of such experiments demonstrated that the displacement of ions in porous media is coupled and the electromigration effects do not vanish at high flow velocities. These experimental findings represent a challenge as well as an opportunity for further development of reactive transport codes. Only recently a dataset of multicomponent conservative ionic transport obtained under flow-through conditions in a homogeneous porous medium has been used to benchmark the multicomponent transport capabilities of the CrunchFlow and MIN3P codes (Rasouli et al., 2015). However, to the best of our knowledge, the behavior and effects of Coulombic interactions for multidimensional conservative and reactive transport in physically and chemically heterogeneous porous media have not been investigated, yet. The purpose of this contribution is to present a reactive transport tool helping to address these issues in particular on the light of the increased recognition of the key role of molecular diffusion for solute transport from the pore to the field scale. Small scale diffusive processes have been shown to impact solute transport in flow-through systems not only at the laboratory (e.g., Bauer et al., 2009; Rolle et al., 2010; Chiogna et al., 2010; Haberer et al., 2012; Hochstetler et al., 2013; Ye et al., 2015b) but also at the larger field scale (e.g., Fiori et al., 2011; Hadley and Newell, 2014; LaBolle and Fogg, 2001; Liu and Ball, 2002; Chiogna et al., 2011; Rasa et al., 2011; Rolle et al., 2013a; Van Breukelen and Rolle, 2012). The impact of diffusion, which is the only true mixing process in groundwater (Kitanidis, 1994), on solute transport indeed does not vanish at larger scales but propagates through scales also under flow-through conditions (Rolle et al., 2013a). Models aiming at capturing these effects in heterogeneous flow fields need to implement improved and more realistic descriptions of local dispersion, linking the mechanical dispersion term to spatially-variable hydraulic conductivity values and avoiding using constant dispersivities that inevitably mask (or underestimate) the role of aqueous diffusion in porous media.

This work presents a two-dimensional reactive transport model that explicitly accounts for the Coulombic interactions coupled with geochemical reactions during multicomponent ionic transport in both homogeneous and heterogeneous flow-fields under transient transport conditions. The modeling approach is based on a charge-balanced multicomponent formulation and on the spatially variable description of local hydrodynamic dispersion that is of key importance for the coupling of the fluxes of the different ionic species in solution. Additionally, we couple the two-dimensional multicomponent ionic transport model with the widely used geochemical code PHREEQC (version 3, Parkhurst and Appelo, 2013) by using the reaction module IPhreeqc (Charlton and Parkhurst, 2011). Thus, the proposed numerical reactive-transport model provides a comprehensive framework that is based on the novel combination of three specific features: (i) detailed description of spatially variable local hydrodynamic dispersion; (ii) multicomponent ionic formulation; and (iii) extensive reaction capabilities through the coupling with PHREEQC. These features represent distinctive and unique characteristics for a reactive transport simulator and are particularly advantageous for performing transport simulations in physically and chemically heterogeneous domains. The 2-D multicomponent model is systematically benchmarked with the analytical solution of a 2-D transport problem, with experimental data, and with 1-D reactive transport scenarios solved in PHREEQC. Successively, application examples, with different levels of complexity, are presented to illustrate transient multicomponent ionic transport and the influence of charge interactions in both conservative and reactive systems in homogeneous and heterogeneous porous media.

2. Multicomponent ionic transport

The most distinguishing feature of aqueous diffusion of charged species compared to non-charged solutes is the electrostatic interactions between the dissolved charged species and/or with charged interfaces. Multicomponent ionic diffusion models are generally used to account for these inter-species interactions during diffusive movement of charged species at different scales (e.g., Liu et al., 2011; Giambalvo et al., 2002; Appelo and Wersin, 2007; Ben-Yaakov, 1972; Lasaga, 1979; Boudreau et al., 2004; Van Cappellen and Gaillard, 1996; Liu et al., 2004; Alizadeh et al., 2014; Zhang and Wang, 2015). These models, based on Nernst-Planck formulations, are typically derived from the chemical potential expressions by following a pragmatic extension of Fick's law (e.g., Boudreau et al., 2004; Cussler, 2009; Bard and Faulkner, 2001). Therefore, the multicomponent diffusive movement of a charged species in electrolyte systems can be expressed as (Appelo and Wersin, 2007; Cussler, 2009):

$$J_i = -D_i \nabla C_i - D_i C_i \nabla ln\gamma_i - D_i \frac{z_i F}{RT} C_i \nabla \Phi, \quad i = 1, 2, 3, ..., N \quad (1)$$

where D_i is the self-diffusion coefficient, C_i is the concentration of charged species i, γ_i is the activity coefficient, z_i is the charge number, F is the Faraday's constant, R is the ideal gas constant, T is the temperature, Φ is the electrostatic potential, and N is the number of species.

In dilute solutions and in the absence of strong ionic strength gradients, the gradient of the activity coefficients (second term of Eq. (1)) can be neglected (Lasaga, 1979). Thus, the above expression describing the multicomponent ionic diffusive fluxes reduces to:

$$J_i = -D_i \nabla C_i - D_i \frac{z_i F}{RT} C_i \nabla \Phi \quad (2)$$

This equation includes fluxes due to self-diffusion as well as electromigration, which is basically induced from the electrostatic interactions, for a particular mobile species. Following two physical constraints based on electroneutrality (i.e., (i) conservation of local charge balance, $\sum_{i=1}^{N} z_i C_i = 0$ and/or (ii) zero influx of electrical current, $\sum_{i=1}^{N} z_i J_i = 0$), the gradient of Φ can be expressed as:

$$\nabla \Phi = \frac{-\sum_{i=1}^{N} (z_i D_i \nabla C_i)}{\sum_{i=1}^{N} (z_i^2 F D_i C_i)/RT} \quad (3)$$