

Simulation of chemical reaction localization using a multi-porosity reactive transport approach



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ABSTRACT

Results of reactive transport laboratory experiments often suggest that pore scale heterogeneity induces localization of reactions (the generation of local micro environments favoring reactions that would not occur in a well-mixed Representative Elementary Volume, REV). Multi-Rate Mass Transfer (MRMT), which has been employed to reproduce hydrodynamic heterogeneity, may also be used to simulate geochemical localization. We extended the Water Mixing Approach (WMA) designed for single porosity media, to simulate chemical reactions caused by the mixing of mobile and immobile zones. The method is termed Multi-Rate Water Mixing (MRWM). The MRWM approach was employed to simulate laboratory experiments of CO₂-rich brine transport through carbonate rich samples (Luquot et al., 2016). Chemical heterogeneity in space was reproduced by varying the mineral assemblages in immobile regions. This enabled us to reproduce the generally low pH environment while allowing for high pH local zones required for the localized precipitation of kaolinite, which has been observed in reality, but cannot be modeled with conventional reactive transport formulations. The resulting model is very rich, in that it can reproduce a broad range of pore scale processes in a Darcy scale model, and complex, in that the interaction between chemical kinetics and immobile zones physical parameters is non-trivial.

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1. Introduction

Reactive transport deals with geochemical processes that occur in porous media due to the physical transport of reacting chemical species. It plays a major role in many civil and/or environmental issues such as cleanup of contaminated aquifers, nuclear waste storage, mining and geological storage of CO₂. Reactive transport may be very complex and non-trivial. As a result, numerical models are an indispensable tool for understanding and predicting these processes. One problem encountered is the high level of heterogeneity, which can be both chemical and hydrodynamic. Reactive transport models typically assume local equilibrium with fast dissolution kinetic minerals. Even so, non-equilibrium is commonly observed and is attributed to this heterogeneity (Alcolea et al., 2008; Vogel et al., 2006). For instance, breakthrough curves

typically display tailing at late times (Valocchi, 1985; Carrera, 1993). This non-equilibrium may be due to diffusion into immobile regions, kinetic sorption or heterogeneity. This implies that reactive transport should be formulated as non-local in time which means that the concentration at a given point depends on its concentration history. A large number of formulations (Carrera et al., 1998; Dentz and Berkowitz, 2003; Haggerty and Gorelick, 1995; Silva et al., 2009; Sudicky, 1989), simulation approaches (Ray et al., 1997; Salamon et al., 2006; Suresh Kumar, 2008; Tsang, 1995; Willmann et al., 2008; Zhang et al., 2006, 2007) and analytical solutions (Toride et al., 1993) have been proposed to deal with non-local in time transport (see Dentz et al., 2011a, for a review).

In parallel with Darcy scale models, a number of researchers have overcome this non-locality by formulating transport at pore scale because chemical processes occur at pore scale (Steeffel et al., 2005). One such formulation is the Lattice Boltzmann equation, which replaces the velocities of individual particles by a distribution function of velocities in which the population of particles moves (Benzi et al., 1992; Chen and Doolen, 1998; Kang et al., 2006; Acharya et al., 2007; Willingham et al., 2008). Another formulation is Smoothed Particle Hydrodynamics, which is based on the idea

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that a continuous field can be represented by a superposition of smooth bell-shaped functions centered on a set of points whereas the gradient of the field is given by the same superposition of the gradients of the smoothing function (Liu and Liu, 2010; Tartakovsky et al., 2007, 2009, 2015). A third option consists of simulating the pore network to explicitly simulate the pore volumes and connecting necks (Blunt, 2001; Blunt et al., 2002; Li et al., 2006; Meile and Tuncay, 2006; Raouf et al., 2010; Raouf and Hassanizadeh, 2012; Varloteaux, 2013). These formulations are very accurate in reproducing local physics, but are computationally demanding for large scale models or when many chemical species and reactions are involved. Moreover, the upscaling of the results to field scale has not yet been resolved.

Other researchers prefer continuous models at larger than pore scales to gain in computational cost and model simplicity. The classic approach consists on representing heterogeneity by a dispersion tensor, but it fails to quantify solute mixing accurately (Ginn et al., 1995; Kitanidis, 1988; MacQuarrie and Sudicky, 1990; Molz and Widdowson, 1988; Dreuzy et al., 2012), which is critical for reactive transport as reaction rates are driven by mixing (De Simoni et al., 2007). There are a number of approaches to quantify mixing rates more accurately. The most widely used are the Multi-Rate Mass Transfer (MRMT) and Continuous Time Random Walk (CTRW). MRMT is a non-local in time continuous formulation that simulates mass transfer between a mobile and multiple immobile regions by diffusive or first-order mass transfer terms (Benson and Meerschaert, 2009; Carrera et al., 1998; Donado et al., 2009; Fernandez-Garcia and Sanchez-Vila, 2015; Geiger et al., 2013; Gouze et al., 2008; Haggerty and Gorelick, 1995; Haggerty et al., 2000; Roth and Jury, 1993; Wang et al., 2005; Willmann et al., 2010; Zhang et al., 2007). Models similar to MRMT exist for diffusion from a fracture into the matrix of the rock (Cvetkovic et al., 1999; Gerke and van Genuchten, 1996; Grisak and Pickens, 1980; Małoszewski and Zuber, 1985; Moreno and Neretnieks, 1993; Shapiro, 2001). CTRW is a class of Random Walk methods in which not only particle displacements, but also time steps are modeled as a stochastic process (Montroll and Weiss, 1965; Berkowitz and Scher, 1998; Metzler and Klafter, 2000; Barkai and Cheng, 2003; Cortis, 2004; Dentz et al., 2004; Berkowitz et al., 2006). Its validity has been proven using pore network models (Bijeljic and Blunt, 2006). CTRW has been applied to reactive transport using particles explicitly, which is computationally demanding. But, in practice, CTRW and MRMT are equivalent (Dentz and Berkowitz, 2003; Neuman and Tartakovsky, 2009; Silva et al., 2009).

The latter methods have been used to study the effect of hydrodynamic heterogeneity on reactive transport. Most of these studies used simple chemical systems of one or more chemical reactions (e.g., Donado et al., 2009; Willmann et al., 2010). Other studies have focused on more complex chemical systems (Ayora et al., 1998; Steefel and Lichtner, 1998). Research has been carried out on specific surface area heterogeneity (Cvetkovic and Gotovac, 2014) and on network fracture heterogeneities (Cheng et al., 2003; Frampton and Cvetkovic, 2007; Painter et al., 2008). The effect of chemical heterogeneity was addressed by Dentz et al. (2011b), but on an abstract system that did not allow acknowledging explicitly that porous media consist of multiple mineral phases, which create their own local conditions and precipitation/dissolution reactions. We use the term geochemical localization to describe the creation of local micro environments favoring reactions that would not occur in media that are fully mixed at the Representative Elementary Volume (REV) scale. We argue that geochemical localization is driven by mineral heterogeneity at the pore scale and may cause reaction heterogeneity at such scale. Geochemical localization has been observed by Luquot et al. (2016), who performed percolation experiments under in situ temperature, pressure and salinity conditions to predict the different chemical reactions which can occur

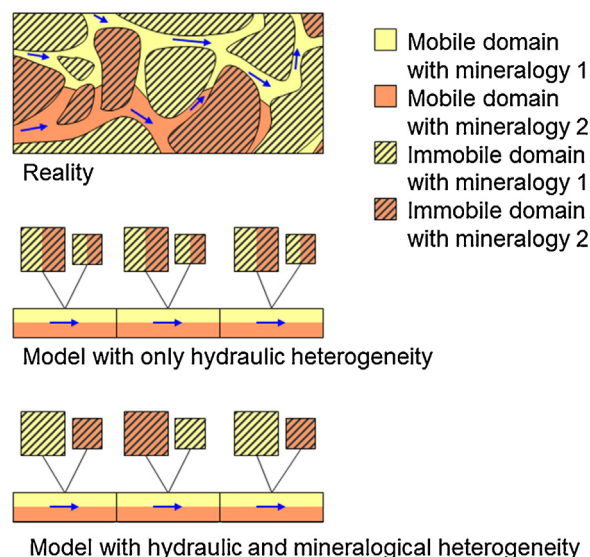


Fig. 1. Schematic spatial mineralogy distribution. The top image displays the 'real' distribution. The central image shows a classical MRMT distribution without considering mineralogical localization. The bottom image shows the distribution of the mineral phases in several immobile zones connected to a mobile node.

during the migration of CO₂-rich brine at the Heletz site (Niemi et al., 2012, 2016). These authors verified their experimental results using the CrunchFlow code (Steefel, 2009) that regards dispersion as the only mixing process. They obtained good matches between the experimental and numerical results for the main dissolved and precipitated minerals with fast reaction kinetics (carbonates and gypsum). Nevertheless, secondary mineral reactions were not predicted accurately (e.g., K-feldspar dissolution and clay precipitation). They concluded that these secondary reactions, which may play an important role in the change of hydrodynamic properties, occur at scales smaller than the REV and cannot be taken into account in conventional reactive transport models that are based on the Advection-Dispersion Equation (ADE).

We conjecture that geochemical localization can be reproduced using multi-porosity formulations, such as MRMT, provided that geochemical heterogeneity is included in the model. The objective of this work is to test such conjecture and to gain further insight into the effect of mineralogical and hydrodynamic heterogeneity. To this end, the MRMT based method was used, varying the mineral composition of mobile and immobile zones (see Fig. 1). A simplified chemical system based on Luquot et al. (2016), was employed. The mathematical formulation of reactive transport used in the MRMT approach is described in Section 2. In Section 3, we discuss the numerical solution of these equations, which basically consists of extending the Water Mixing Approach (WMA) of Soler-Sagarra et al. (2016, for publication) to MRMT, obtaining the proposed Multi-Rate Water Mixing (MRWM). Models definitions and their results are presented in Section 4. Finally, Section 5 is dedicated to discussion and conclusions.

2. Governing equations

The standard formulation for reactive transport is based on applying the ADE to all chemical species with sink/source terms to represent reactions (i.e., sinks for reactants and sources for reaction products). This leads to a complex set of N_s ADE (N_s is the number of species), which uses the vector concentrations c [M/L^3] as state variable, and N_r constraints (mass action laws for equilibrium reactions and rate laws for kinetic reactions) for the chemical reactions. The system may be simplified by the use of components.

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