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Incorporating electrical double layers into reactive-transport simulations of processes in clays by using the Nernst-Planck equation: A benchmark revisited

Peter Alt-Epping*, Thomas Gimmi, Paul Wersin, Andreas Jenni

University of Bern, Institute of Geological Sciences, Rock-Water Interaction Group, Baltzerstrasse 3, 3012 Bern, Switzerland

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ABSTRACT

Owing to their low permeability clay formations are considered as potential host rocks for nuclear waste or as seals capping permeable reservoirs for storing unconventional gases. Clay materials such as bentonite are considered as backfill or buffer material in nuclear waste repositories forming barriers to fluid flow owing to their hydraulic and swelling properties. The low permeability of clays implies that solute transport in the pore water is dominated by diffusion. Another important characteristic of clays is the negative surface charge of clay minerals which affects transport and the distribution of ions in the pore space: cations are attracted to while anions are repelled from clay mineral surfaces. Models of reactive transport need to consider these electrostatic effects to be able to accurately simulate the transport of ions through clay. Here we use a new approach which is entirely based on the solution of the Nernst-Planck equation to incorporate the effect of diffuse layers (DLs) into reactive transport simulations. A simulation benchmark is used to validate this new approach. In variants of this benchmark problem the impact of different activity models on the pore water composition, Donnan equilibrium versus a kinetic exchange between the DL and free pore water and the effect of diffusive transport in the DL are explored.

1. Introduction

Clay formations such as the Opalinus Clay (Switzerland), the Boom Clay (Belgium) or the Callovo-Oxfordian (France) are currently assessed for their suitability as host rocks for nuclear waste repositories. Clay materials such as bentonite are considered as backfill/buffer material for underground repositories as, for instance, in the KBS3 design proposed by POSIVA (Finland) and SKB (Sweden). When in contact with water, bentonite begins to swell, thus filling voids in the backfilled underground facility and, owing to its low permeability, it forms an effective barrier to advective groundwater flow. Solute transport is thus dominated by diffusion. Therefore, assessing the integrity of clay buffers requires a thorough understanding of solute diffusion in the pore water.

Bentonite clay is composed almost entirely of montmorillonite with few accessory minerals such as gypsum, calcite, quartz, feldspars and Fe-oxy/hydroxides. One important characteristic of montmorillonite crystals is their negative surface or layer charge. As a consequence, the effective diffusion coefficient of an ion in bentonite (and in other clay-rich materials) depends on the charge of that ion as well as on the electrostatic properties of the dominant clay minerals. Other factors influencing solute diffusion are the pore structure of the bentonite which is among others a function of the degree of compactness (commonly expressed in terms of the bulk dry density) and the ionic strength of the solution (e.g. Tournassat and Appelo, 2011). Rigorous modelling of solute diffusion in a bentonite and other clay materials requires specific diffusion coefficients of all species in pure water, a description of the pore structure (i.e. porosity and tortuosity) as well as an electrostatic model describing the attractive and repulsive forces between individual ions and between ions and mineral surfaces while local charge balance is maintained. In addition, the pore water composition in the clay is dependent on chemical reactions involving mineral dissolution/precipitation, sorption, complexation reactions, biogeochemical transformations and others (e.g. Bourg and Tournassat, 2015).

Given the stringent safety requirements for nuclear waste repositories, predictive numerical simulations have to be accurate and reliable and therefore require input data constrained by experimental and/or field observations as well as appropriate mathematical descriptions of the governing reaction and transport processes and the couplings between them. Numerous reactive transport codes exist

* Corresponding author.
E-mail address: alt-epping@geo.unibe.ch (P. Alt-Epping).

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which couple transport and chemical reactions (e.g. Steefel et al., 2015), many of which have been used to assess the evolution of waste repositories (e.g. Spycher et al., 2003; Savage et al., 2010; Kosakowski and Berner, 2013; Berner et al., 2013). In a recent benchmark proposal for reactive transport codes Alt-Epping et al. (2015) used data from a flow through experiment on a bentonite core as input constraints and calibration target for the model. The simulation results from four different reactive transport codes were compared and their ability to reproduce the main observations from the experiment was assessed.

The code benchmark showed that transport by advection and Fickian diffusion combined with conventional ion exchange and mineral reactions can at least semi-quantitatively reproduce the observed breakthrough curves of the major cations and SO_4^{2-}. This indicates the strong influence of chemical and sorption reactions of major cations on the effluent composition. However, simulations involving conventional ion exchange could not accurately reproduce the breakthrough of non-reactive species such as Cl^- and the charge neutral deuterium. Only simulations that accounted for a diffuse layer (DL) on clay sheet surfaces were able to reproduce the breakthrough behavior of these two species. At the time of the benchmark only two codes, PHREEQC (Parkhurst and Appelo, 2013) and CrunchFlowMC (Steefel et al., 2015), had the capability to explicitly consider the effect of DLs.

Diffuse layers form adjacent to clay sheet surfaces and originate from the electrical potential induced by the negative surface charge of individual TOT layers. Charged surfaces can be divided into internal surfaces within and external surfaces on the outside of clay mineral grains. Thus the surface charge affects the composition of the pore water in the interlayers and of the pore water between mineral grains by attracting cations towards and repelling anions from the charged surface. A diffuse layer with excess cations evolves at surfaces, balancing the negative charge. In addition, cations may sorb directly onto the mineral surface forming what is commonly referred to as Stern layer. The sum of cations in the DL (on mineral surfaces and in interlayers) and in the Stern layer represent what in conventional ion exchange models is referred to as exchangeable cations. A common view is that owing to the small pore volume between individual TOT layers, DLs in the interlayer porosity overlap. That is, within a clay mineral grain the entire pore water is affected by the surface potential. In contrast, in the intergranular porosity between individual clay mineral grains typically only a fraction of the pore space is affected by the electrical potential while the other unaffected fraction remains internally charged balanced. While there is an excess of cations in the DL balancing the negative surface charge, anions are less abundant implying that the pore space accessible to anions is smaller than the total porosity. Consequently, transport of anions through clay is controlled by the fraction of the total porosity that is accessible to them leading to an effect that has been referred to as anion exclusion (e.g. Van Loon et al., 2007).

For modelling purposes we assume that the interlayer space and the DL fraction of the intergranular porosity can be combined into single porosity. In Alt-Epping et al. (2015) this combined porosity was referred to as micro-porosity while the remaining porosity containing the pore water not affected by the surface charge was named macro-porosity. Here we use a different terminology to be consistent with more recent publications (e.g. Gimmi and Alt-Epping, 2017; Jenni et al., 2017) and to emphasize that a Donnan model is used to describe the effects of charged surfaces on the pore water composition. We use the term Donnan porosity to refer to the pore space comprising the DL and the term free porosity to refer to the remaining pore space containing internally charge balanced pore water. Accordingly the pore waters situated in the former and the latter are referred to as Donnan water and free water, respectively.

2. Modelling approach

A model for the composition of the water in the DL can be derived from a combination of several equations, including the Poisson equation describing the distribution of electrical potential in water and the Boltzmann equation describing the distribution of species as a function of the electrical potential. A simpler approach is based on assuming Donnan equilibrium between the Donnan water and the free water. This approach implies a uniform electrical potential φ^D throughout the Donnan porosity and the same chemical potential in the Donnan and the free water.

If the chemical potential μ_j of a species j is the same in the Donnan and free porosity then

$$\mu_j^D = \mu_j^{FW} \tag{1}$$

Based on this assumption the following relationship between the species concentrations in the two porosity domains can be derived:

$$C_j^D = C_j^{FW} \exp\left(\frac{-z_j e \varphi^D}{k_B T}\right), \tag{2}$$

where C_j^D and C_j^{FW} are the concentration of species j in the Donnan and the free water, respectively, e is the elementary charge, z_j is the valence of species j, k_B is the Boltzmann constant, T is the absolute temperature and φ^D is the mean electrical potential in the Donnan porosity. The mean electrical potential in the Donnan porosity can be calculated from charge balance constraints involving the surface charge and the total charge of ions in the Donnan porosity. Note that Equation (2) is a relationship between species concentrations in the two porosity domains rather than between species activities. It is thus based on the assumption that activity coefficients of individual species in the two domains are identical. This explicit formulation of Donnan equilibrium (Equation (2)) has been implemented into the reactive transport codes CrunchFlowMC and PHREEQC and was used in the simulation benchmarks in Alt-Epping et al. (2015).

The diffusive flux of species j can be described by Fick's first law as:

$$J_j = -D_j \nabla C_j, \tag{3}$$

where J_j is the diffusive flux, D_j is the effective diffusion coefficient and C_j the concentration of species j. The effective diffusion coefficient D_j, the pore diffusion coefficient D_j^* and the diffusion coefficient in water D_j^0 are related via the porosity ϕ and the tortuosity factor τ (also sometimes referred to as geometric factor (e.g. Tinnacher et al., 2016) by

$$D_j = \phi D_j^* = \phi \tau D_j^0 \tag{4}$$

Fick's law does not account for the electrostatic interaction between charged species and is strictly valid only for uncharged species. The flux of an ionic species as a combination of multi-species diffusion, electromigration and advection can be described by the Nernst-Planck equation (e.g. Steefel et al., 2015; Tournassat and Steefel, 2015):

$$J_j = -D_j \nabla C_j - \frac{D_j C_j}{RT} z_j F \nabla \varphi + v C_j, \tag{5}$$

where z_j is the charge of species j, F and R are the Faraday and gas constants, respectively, T is the temperature in Kelvin, φ is the electrical potential and v is the average advective velocity of the solvent flow.

In the absence of advection, Steefel and Maher (2009) derived an expression for the total flux combining Fickian diffusion and electromigration as follows:

$$J_j = -D_j \nabla C_j + \frac{t_j}{z_j} \sum_i z_i D_i \nabla C_i \tag{6}$$

where t_j is the transference number describing the fraction of the current carried by species j defined as

$$t_j = \frac{z_j^2 u_j C_j}{\sum_i z_i^2 u_i C_i} \tag{7}$$

with u_j being the mobility of an ion which is related to the diffusion