Research paper

Modeling the transport of water and ionic tracers in a micrometric clay sample

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ABSTRACT

Brownian dynamics simulations were performed to examine the self-diffusion of cationic (Na^+), anionic (Cl^-), and water tracers in a saturated compacted clay at the micrometric scale. Clay minerals particles, representing stacks of montmorillonite layers, are modeled as cylindrical platelets with characteristics that depend on the dry bulk density of the porous medium, ρ_b. The tracers are allowed to diffuse between the platelets with their diffusion coefficient in bulk aqueous solution as well as inside the platelets with a diffusion coefficient that depends on the hydration level of the interlayer pores as determined from experiments or molecular dynamics simulations. The probability for a tracer to enter a platelet is related to its charge as predicted by the Poisson–Boltzmann equation. The apparent diffusion coefficients are calculated as a function of ρ_b for various salinities and compared with the values obtained from tracer diffusion experiments available in the literature. Despite the simplicity of the clay model, the simulations predict most features of the experimental data and keep the door open for further improvements.

1. Introduction

Clay minerals are highly abundant natural materials that play significant roles in many environmental and engineering applications because of their high cation exchange capacity and specific surface area, swelling behavior, water and solute retention properties, and low permeability. In particular, compacted swelling clay minerals (smectites) has been proposed as barrier materials for the long-term isolation of high-level radioactive waste in geologic formations (McCombie, 1997; H12 report, 2000; ANDRA report, 2001). Because of the very low hydraulic permeability of compacted clay, molecular diffusion is the predominant mass transfer process in these barriers. This has motivated numerous experimental and theoretical studies of diffusion in compacted, water-saturated smectite, as well as in smectite-rich materials commonly known as bentonite. A particularly large experimental database exists for the self-diffusion of cations (Cs^+, Sr^{2+}, Na^+) (Kozaki et al., 1996a, 1996b, 1998a; Liu et al., 2003a), anions (I^-, Cl^-, TcO_4^-) (Sato et al., 1992; Kozaki et al., 2001a) and water tracers such as HDO or HTO (Nakazawa et al., 1999; Nakashima, 2001; Sato and Suzuki, 2003; Suzuki et al., 2004) in clayey media at various degrees of compaction with dry bulk densities from $\rho_b = 0.02$ to 1.95 kg L^{-1}, where ρ_b is the ratio of the mass of solid to the volume of the sample, i.e., $\rho_b = m_{clay}/V_{TOT}$.

The transport of solutes in clays can be quantified by empirical parameters such as adsorption constants or effective diffusion coefficients, which are measured at the macroscopic scale but need to be related to microscopic mechanisms. One difficulty arises from the complex, multi-scale structure of clay materials. Clay mineral particles consist of stacks of parallel negatively-charged layers separated by interlayer nanopores. Consequently, compacted smectite contains two major classes of pores: interlayer nanopores (located inside the particles) and larger mesopores (located between the particles). The permanent negative charge of the clay mineral layers is compensated by counterions located both in the interlayer nanopores and on the external surfaces of particles. Both types of cations are mobile and contribute to the overall cation diffusive flux (Glaus et al., 2007; Melkior et al., 2009). In contrast, inert anions such as Cl^- can be viewed as non-adsorbing species that migrate in the 'free' pore water (far from the clay mineral surfaces) and, to some extent, in the electric double layer water on the external surfaces of particles. The partial exclusion of anions from the interlayer space due to the negative layer charge has been extensively studied by molecular dynamics simulations (Rotenberg et al., 2007; Hedström and Karnland, 2012) and experimental methods (Kozaki et al., 2001a; Van Loon et al., 2007) and modeled using mean-field theories such as the mean electrostatic model and the Poisson-Boltzmann equation (Birgersson and Karnland, 2009; Jardat et al., 2009).

Along with experiments, conceptual models have been developed to describe the transport of water and solutes in water-saturated bentonite Bourg et al. (2006); Bourg and Sposito (2010) and simulations from

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the atomic scale (Delville, 1992; Leote de Carvalho and Skipper, 2001; Skipper et al., 2006) to larger scales (Churakov and Gimmi, 2011; Churakov et al., 2014) have been performed. In particular, an emerging concept consists in explicitly accounting for nanopores (nanometer-scale interlayer pores) and mesopores (all other pores) as two distinct compartments of the bentonite pore space (Hueckel et al., 2002; Bourg et al., 2006).

In this paper, the diffusion of water, Na^+ and Cl^- in compacted, water-saturated bentonite was studied at the micrometric scale using Brownian dynamics (BD) simulations. The clay mineral particles are modeled as cylindrical platelets, the dimensions and the distribution of which depend on ρ_b. The description of the platelets based on experimental data is made in Section 2.1. The principles of the procedure for generating clay samples are described in Section 2.2. Brownian dynamics simulations are, then, carried out according to the method described in Section 3.1. Briefly, tracers are modeled as moving through the sample with different diffusion coefficients depending on whether they are located inside or outside a platelet. Diffusion in the interparticle pores (i.e., outside the platelets) occurs with the same diffusion coefficient as in bulk solution, whereas diffusion inside the platelet is slowed down by confinement. In addition, tracer mass fluxes across particle edge boundaries are influenced by salinity and the valence of the tracer. Micrometer-scale diffusion coefficients in the modeled clay sample are calculated from the tracer trajectories obtained from BD simulations. Both the concentrations and the diffusion coefficients in the interlayer and interparticle pores are necessary input parameters for the BD simulations. Section 3.2 describes the evaluation of these parameters based on experimental data and molecular dynamics (MD) simulations. The existing experimental database on centimeter-scale apparent diffusion coefficients in compacted, water-saturated clay is described in Section 4. The features of the samples are discussed in the first part of Section 5, while the accuracy of the interlayer/interparticle pore model is evaluated by comparing predicted diffusion coefficients with the experimental database in the second part of Section 5. Finally, the last section contains a conclusive discussion.

2. Model of clay microstructure

In this model, the sample is composed of a set of clay mineral particles represented as cylindrical platelets overlapping each other. As explained below, the dimensions of the platelets and the volume fraction they occupy in the simulation box are calculated for each dry density ρ_b. These quantities are then used to generate a porous medium at each ρ_b, as represented on Fig. 1.
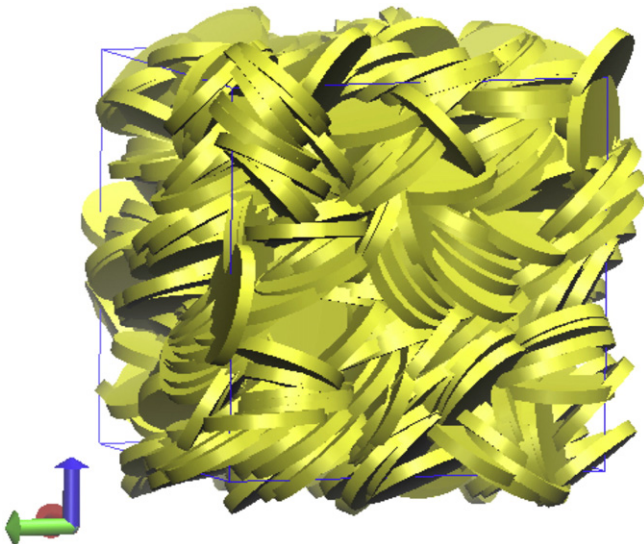

Fig. 1. A Gay–Berne configuration of 1000 platelets in a cubic box of length 19,186 Å corresponding to $\rho_b = 0.7$ kg L^{-1} (parameters: $R = 2500$ Å, $h = 688.3$ Å).

2.1. Dimensions of the platelets

Clay mineral particles consist of tens of negatively-charged stacked aluminosilicate layers, with lateral dimensions of hundreds of nanometers (Arnott, 1965). In the present model, the particles are modeled as cylindrical platelets with a diameter of 500 nm, each consisting of 20 stacked clay mineral layers (see Fig. 2). The parameter ΔL is defined as the distance between the mid-planes of two consecutive clay mineral layers; the height of each platelet is, then, $h = 20 \times \Delta L$. The distance ΔL depends on the dry density of the sample, because smectite interlayer nanopores (and, hence, the clay mineral particles contain a variable amount of water. Two swelling regimes are observed. At first, the process occurs in discrete steps (crystalline swelling) through the formation of crystallographically ordered layers of water molecules between the silicate layers. Beyond three layers of water molecules, the swelling is better described as a continuous phenomenon until isolated aggregates are formed and a colloidal dispersion is obtained. During the transition from the crystalline to osmotic swelling, the value of ΔL jumps from ~18.5 Å to ~40 Å (Norrish, 1954).

Here we consider the case of a montmorillonite (the predominant type of smectite clay mineral) with Na^+ counterions (designated as Na^+ Mt). On the basis of X-ray diffraction (XRD) data reported for Na^+ Mt (Norrish and Quirk, 1954; Calvet, 1973; Fu et al., 1990; Cases et al., 1992; Kozaki et al., 2001a; Ferrage et al., 2005b), the clay is modeled as having stable states at $\Delta L_{dry} = 9.5$ Å (dry clay), $\Delta L_{1W} \sim 12.5$ Å (one layer hydrate, 1W), $\Delta L_{2W} \sim 15.5$ Å (two layer hydrate, 2W) and $\Delta L_{3W} \sim 18.5$ Å (three layer hydrate, 3W) (Bourg and Sposito, 2010; Holmboe et al., 2012). The 3 Å increase in the ΔL between stable swelling states is consistent with the expected thickness of a monolayer of water molecules. Based on the XRD data of Holmboe et al. (2012), the interlayer spaces are viewed as a mixture of 1W and 2W states if $\rho_b \geq 1.7$ kg L^{-1} and as a mixture of 2W and 3W states if ρ_b ranges from 1.35 to 1.7 kg L^{-1}. The average interlayer distance ΔL is then calculated for $\rho_b > 1.35$ kg L^{-1} with the relation:

$$\Delta L_{nW+mW} = x_{nW}\Delta L_{nW} + (1-x_{nW})\Delta L_{mW}. \tag{1}$$

where x_{nW} is the fraction of nW state in the mixture $nW - mW$. In view of the evolution of x_{nW} with ρ_b given in Holmboe et al. (2012), the fraction x_{nW} of nW state in the mixture $nW - mW$ is considered to vary almost linearly between the boundaries of this domain: for instance, x_{3W} varies linearly from 0 to 1 as ρ_b varies from 1.7 to 1.35 kg L^{-1}. On the basis of this assumption and Eq. (1), $\Delta L_{nW + mW}$ can be evaluated for every $\rho_b > 1.35$ kg L^{-1}. The values are given in Table I of the Supporting information.

Once ΔL is calculated as described above, the fraction of fluid in the interlayer pores f_{il}, defined as the ratio between the volume of interlayer pores, V_{il}, and the volume of all pores, V_p, can be calculated using the following relation (where V_{TOT} is the total volume of the sample, V_{pl} is the volume occupied by the platelets in the sample)

$$f_{il} = \frac{V_{il}}{V_p} = \frac{V_{il}}{V_{il} + V_{TOT} - V_{pl}} = \frac{x_{il}}{x_{il} + 1/\varphi - 1}. \tag{2}$$

On the right side of Eq. (2), x_{il} is the volume fraction of pore space in each platelet and $\varphi = \frac{V_{pl}}{V_{TOT}}$ is the volume fraction of platelets in the entire sample. The value of x_{il} is a simple function of ΔL

$$x_{il} = \frac{\Delta L - \Delta L_{dry}}{\Delta L}. \tag{3}$$

Moreover, the evolution of φ with ρ_b can be determined using

$$\varphi = \frac{V_{pl}}{V_{TOT}} = \frac{\rho_b}{\rho_{pl}}, \tag{4}$$