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Cation diffusion in the interlayer space of swelling clay minerals – A combined macroscopic and microscopic study

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Abstract

This study investigates the diffusion process of calcium cations confined in the interlayer space of 5 mm disks of vermiculite swelling clay minerals during the Na-for-Ca exchange process. Diffusion experiments were performed at four NaCl salinities (3×10^{-3}, 5×10^{-2}, 0.1 and 1 M) of the exchanger solution. A macroscopic analysis of the diffusion process based on the aqueous calcium concentrations released in the solution and on Ca-profiles obtained in the solid was performed using a pore diffusion model that has been classically used in the literature. The results obtained at the macroscopic scale showed that the apparent diffusion coefficients describing both aqueous and profiles data for Ca depend on the diffusion time and salinity of the aqueous reservoir. Such variations suggested that interlayer diffusion was driven by (1) the gradient of the sorbed species in the interlayer, which depends on the diffusion time due to the ion exchange equilibrium; and (2) the discontinuity, due to Donnan equilibrium, existing at the limit between the "internal disk border" and the "external disk border" in contact with the aqueous reservoir. Then, a set of molecular and Brownian dynamics simulations was used to (1) assess such interpretations and (2) quantitatively predict aqueous and profile data obtained at the macroscopic scale. For an aqueous reservoir with high salinity (1 M NaCl), a good agreement was obtained between the macroscopic data and the predictions obtained from Brownian dynamics simulations, confirming the role played by the gradient of the interlayer species that is suggested at the macroscopic scale and which is at the basis of the "surface diffusion models" published in literature. In addition, for aqueous reservoirs with lower salinity (5×10^{-2} M), the results obtained by Brownian dynamics simulations and normalized to the exchange rate measured at infinite time showed that the diffusion properties of the species in the aqueous reservoir cannot be neglected to correctly interpret macroscopic data. This behavior confirms the role played by the ionic flux that exists at the "disk border", which can limit the global diffusion process in a low salinity reservoir, even if it is well stirred. Moreover, by assuming a tortuosity equal to 1 for monocrystals, the self-diffusion coefficient issued from molecular dynamics simulations is in good agreement with the apparent diffusion coefficient describing macroscopic data when the gradient of sorbed concentrations within the solid is null; this latter condition is obtained in our case at infinite time (20 days) when the initial Ca-saturated disks are fully exchanged with Na cations. Finally, the use of monocrystals allows us to have only interlayer porosity and then to obtain a self-diffusion coefficient for Ca from Molecular Dynamic simulations, which is in good agreement with Ca-surface mobility, which was defined by some authors to predict the "surface diffusion process" at the macroscopic scale.

1. INTRODUCTION

Swelling clay minerals are natural lamellar silicates that are composed of two tetrahedral sheets (silica) sandwiching an octahedral sheet (dioctahedral aluminum hydroxide or

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trioctahedral magnesium hydroxide) constituting the so-called TOT layer (Brigatti et al., 2006). As a result of isomorphic substitutions by lower charge cations in the tetrahedral or octahedral sheets, the TOT layer has a net negative charge. This charge is compensated by interlayer cations whose valence and hydration properties control the swelling of the crystal structure (Ferrage et al., 2010, and references therein). In addition, the interlayer cations can easily be exchanged with others from the surrounding environment (McBride, 1994). For these reasons, swelling clay minerals play a major role in controlling water and solute migration in natural soil/rock environments and in the design of disposal facilities for hazardous waste (including high level nuclear waste), where their main role is to inhibit the migration of contaminants from the waste into the surrounding environment (Madsen, 1998). In these systems, the low hydraulic conductivity due to the high degree of compaction of the material generally implies that diffusion is the main process of water and solute migration.

In this context, determining the macroscopic values of the diffusion coefficients of the different species (water, anions and cations), especially the cations, is important for the prediction of contaminant migration. These macroscopic diffusion coefficients can be obtained from different types of experiments using tracers, such as “out” and “in” diffusion experiments or through-flow experiments. These latter experiments consist of a compacted swelling clay sample placed between two aqueous reservoirs, where the upstream reservoir contains the tracers of interest and the downstream reservoir does not. The diffusing species then migrates from the upstream reservoir toward the downstream reservoir, and the effective diffusion coefficient is obtained by modeling the stationary flux of the diffusing species measured in the downstream reservoir. Different models have been used to obtain the diffusion properties of the tracer, such as the simple “pore diffusion model” based on one type of porosity and the external chemical gradients between the upstream and downstream reservoirs (see references in Glaus et al., 2007) or more sophisticated models based on (a) the multi-porosity structure of clay materials (Ochs et al., 2001; Ochs et al., 2006; Appelo and Wersin, 2007; Bourg et al., 2007; Appelo et al., 2010, among others), (b) the surface diffusion concept (see references in Gimmi and Kosakowski, 2011) or (c) Donnan and ion exchange equilibria (Birgersson and Karnland, 2009). The effective diffusion coefficients obtained from the “pore diffusion model” for cations commonly increase when the salinities of both reservoirs decrease and when the degree of compaction decreases (Muurinen et al., 1985; Melkior et al., 2004; Glaus et al., 2007, 2010). Based on geometric assumptions about the porous material (tortuosity, constrictivity, porosity of the compacted swelling clay medium), these effective diffusion coefficients can be compared to those calculated from microscopic self-diffusion coefficients from molecular dynamics (MD) (Marry and Turcq, 2003). Furthermore, apparent macroscopic diffusion coefficients can also be used to predict the profile of tracer concentration within the solid sample (Bourg et al., 2008 and references therein). For cations, these apparent macroscopic diffusion coefficients are systematically lower than the self-diffusion coefficients derived from MD simulations due to geometrical factors such as the tortuosity of the porous material and contribution of sorption. However, as shown by Bourg et al. (2007) and Bourg and Sposito (2010), these macroscopic diffusion coefficients for cations can be interpreted in terms of (i) the interlayer self-diffusion coefficients derived from MD simulations, (ii) the contributions of macropores and interlayer spaces to the overall porosity and (iii) the geometric factors (i.e., tortuosity, pore size variability and pore connectivity) of the porous media (Dykhuizen and Casey, 1989). Because these geometric factors are empirical values, the validity of using microscopic self-diffusion coefficients to account for the interlayer diffusion coefficient during the macroscopic migration of a diffusing species remains to be fully confirmed, especially in the case of contrasting solution salinities.

This study focuses on the macroscopic measurement of interlayer Ca diffusion on a single monocrystal disk of a swelling clay mineral (vermiculite) immersed in aqueous NaCl reservoirs of different salinities. The diffusion of Ca in the interlayer of the vermiculite is driven by the Na-for-Ca ion exchange reaction. For this type of model system, the interlayer region is the only pore space that contributes to the overall diffusion process, and the geometric factors that are commonly considered for compacted powders of particles can be considered negligible (e.g., tortuosity factor is 1). Vermiculite was chosen as this swelling clay does not display osmotic swelling in water saturated conditions, compared to montmorillonite clays that are commonly used in macroscopic diffusion experiments (Muurinen et al., 1985; Kosaki et al., 1998; Glaus et al., 2007, 2010; Kosakowski et al., 2008). When immersed in a solution, vermiculite has a fixed interlayer thickness in the bi-hydrated state for both Ca- and Na-saturating cations (de la Calle et al., 1978 and de la Calle et al., 1985). This property is beneficial in constraining MD simulations to mimic the diffusion properties of interlayer cations in the sample. The out-diffusion of Ca from vermiculite monocrystals was determined by measuring the amount of Ca released in the solution as a function of time for solutions with four NaCl concentrations. For each salinity, the effective diffusion coefficients were determined using a formalism based on the chemical gradient existing between the “disk border” and the aqueous reservoir; this formalism is similar to the one commonly used to interpret macroscopic diffusion experiments in literature and is often called the “pore diffusion model”. The validity of associated apparent diffusion coefficients describing aqueous data was checked by comparing the predicted Ca-profiles in the solid with those measured by a Scanning Electron Microscope. Then, the different apparent diffusion coefficients describing both aqueous and solid data were compared with the self-diffusion coefficients derived from MD simulations. Finally, Brownian dynamics simulations were performed to reproduce the evolution of the Ca released into the solution as a function of time and the salinity of the solution. The combination of microscopic simulations and macroscopic analysis allowed a critical assessment of the formalism used to interpret macroscopic diffusion experiment data and the determination of the main parameters that control the