Diffusion coefficients of alkaline cations in Bure mudrock

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Abstract

In this work, the diffusivities of alkaline cations (Li^+, Na^+, K^+, Rb^+ and Cs^+) were measured in a mudrock sample from Bure (ANDRA site, Meuse/Haute-Marne, France). The material is a natural rock, mainly composed of interstratified illite/smectite, quartz and calcite. It was saturated with a Na-Cl-dominated synthetic solution with an ionic strength of 57 mM and a pH ~8.0. The effective diffusion coefficients (D_e) for the cations were determined from their steady-state flux through mudrock slices at 23 °C (through-diffusion technique). HTO diffusion coefficients were systematically measured as well. Measured D_e for the cations were found to be higher than values predicted from water diffusion alone. Moreover, this observation appeared to depend on the considered species: the ratio between measured and calculated effective diffusion coefficients ranged between two for lithium and nearly one order of magnitude for rubidium and cesium. An interpretation with different models dealing with sorption–diffusion processes is proposed and discussed.
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1. Introduction

Clayey materials exhibit a number of attractive features as barrier for radioactive waste such as low permeability, high retention capacity and long-term stability. The low permeability of such materials makes diffusion the principal mechanism for migration of radionuclides potentially released from waste canisters. Therefore, diffusion of dissolved species has been extensively investigated in clay-based porous media.

For a given clayey material, negatively charged species exhibit lower diffusion coefficients than neutral species (Henrion et al., 1991; Kozaki et al., 1998, 1999; Van Loon et al., 2003). The difference is attributed to electrostatic repulsion between clay surfaces and dissolved anions, that reduces the porosity accessible to the latter while increasing their diffusion path (Oscarson et al., 1992). It is the so-called anionic exclusion effect.

On the other hand, positively charged solutes exhibit "elevated" diffusion coefficients, compared to neutral species (Gast, 1962; Van Schaik et al., 1966; Neretnieks, 1982; Muurinen et al., 1987; Berry and Bond, 1992; Kim et al., 1993; Eriksen and Jansson, 1996; Lee et al., 1997; Melkior et al., 2005). Some authors attribute this observation to the migration of ions within the electrical double layer, next to mineral surfaces (see for example Muurinen et al., 1987; Berry and Bond, 1992; Kim et al., 1993; Eriksen and Jansson, 1996; Lee et al., 1997). This is the so-called surface diffusion mechanism.

The occurrence of a surface diffusion mechanism is still an open debate. Nevertheless, enhanced diffusion of cations in clayey materials has often been reported and seems to be widely accepted. This observation possibly highlights the inaccuracy of current models to properly represent diffusion processes. As a consequence, the clayey barrier performances for radioactive waste confinement could be overestimated for some positively charged radionuclides.

According to published data, the extent of enhanced diffusion seems to depend on the considered cation. Muurinen et al. (1987) used both sorption data and diffusion

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measurements under steady-state conditions to evaluate surface diffusion coefficients for Cs and Sr in compacted Na-bentonite. A higher surface diffusion coefficient was obtained for Sr than for Cs (9×10^{-12} m^2 s^{-1} and 3×10^{-12} m^2 s^{-1} respectively). Jensen and Radke (1988) performed Cs and Sr diffusion measurements through Na-montmorillonite at 90 °C. Again, the diffusion coefficient was found to be higher for Sr than for Cs. Molera and Eriksen (2002) studied the diffusion of Na, Cs, Sr and Co in compacted Na-bentonite. Both sorption and diffusion data enabled them to calculate a mobile fraction for sorbed ions. Na, and to a lesser extent Sr, were found to have significant mobile fractions, while the mobile fractions of Cs and Co appeared to be very weak (or zero).

The purpose of this work is to investigate the diffusion of alkaline cations (Li$^+$, Na$^+$, K$^+$, Rb$^+$ and Cs$^+$) in a natural rock. The material is a mudrock sample from the Bure site (Meuse/Haute-Marne, France). The first objective is to evaluate if accelerated diffusion is observed and, if so, to what extent this effect may vary between the considered cations. Diffusion coefficients are measured under steady-state conditions, using the through-diffusion technique. Different models, proposed to account for coupled sorption–diffusion processes in clay media, are used to deal with our results. For that purpose, side-experiments were performed to evaluate the sorption behaviors of the different cations involved in this study.

2. Theory and method

2.1. Diffusion of cations in clays

Diffusion is considered to occur in a single direction (1-D transfer), through an homogeneous medium. It is classically described by Fick's laws. When diffusing in clayey materials, positively charged solutes undergo interactions with the negatively charged surfaces of clay minerals. The diffusion, coupled to sorption processes, is represented by the partial derivative equation

$$\varepsilon \frac{\partial C_{(x,t)}}{\partial t} + (1-\varepsilon)\rho_S \frac{\partial \overline{C}_{(x,t)}}{\partial t} = \frac{\partial F_{(x,t)}}{\partial x} \tag{1}$$

where

C is the solute concentration in the liquid phase (in mol L^{-1})
$\overline{C}_{(x,t)}$ is the sorbed concentration (in mol (kg of solid)$^{-1}$)
ε is the porosity
ρ_S is the solid dry density (=mass of solid/volume of solid, in kg L^{-1})
$F(x,t)$ is the flux crossing a surface unit of porous medium (in mol dm^{-2} s^{-1})

The sorption is assumed to be instantaneous.
Different models are proposed in literature, resulting in various expressions of the flux $F(x,t)$. The differences between them arise from the potential contribution of cat-ions in the "sorbed-state" to diffusive transfer. A brief overview is given in what follows.

2.1.1. The pore diffusion model
The pore diffusion model is a macroscopic representation of the transfer with a minimum number of measurable transport parameters. In the pores, the fluid composition is assumed to be the same at any position, i.e. the charge effects occurring at the clay/liquid interface are not considered here. The species of interest is either sorbed on the solid and thus immobilized, or present as a solute in the liquid and thus mobile (see Fig. 1a).

The flux is written as (Fick's first law)

$$F(x,t) = -D_e \frac{\partial C_{(x,t)}}{\partial x} \tag{2}$$

where D_e is the effective diffusion coefficient. The latter is generally written as the product of a formation factor multiplied by the diffusion coefficient of the considered species in water ($D_0(Cs)$). Usually, this formation factor depends on the porosity and must also account for the tortuosity of the porous medium. Various expressions of the formation factor are proposed in the literature (see for example Van Brakel and Heertjes, 1974). One of the most used is

$$\Phi = \frac{\varepsilon \cdot \delta}{\tau^2} \tag{3}$$

where δ is the constrictivity and τ the tortuosity. The formation factor is assumed to be a feature of both the porous network structure and the physical properties of the considered species (Van Brakel and Heertjes, 1974; Ochs et al., 1998, 2001). The pore diffusion model is the simplest representation of diffusive transfer: it requires a minimum number of parameters.

2.1.2. Surface diffusion model
A possible explanation for enhanced diffusion would arise from the occurrence of a larger quantity of cation available for diffusion than expected. The excess is attributed here to the whole sorbed fraction, that also contributes to the global transfer (Fig. 1b). A surface diffusion coefficient, denoted here D_S, is introduced for the sorbed fraction. The flux crossing a surface unit of porous medium is obtained from

$$F(x,t) = -D_e \frac{\partial C_{(x,t)}}{\partial x} - (1-\varepsilon)\rho_S D_S \frac{\partial \overline{C}_{(x,t)}}{\partial x} \tag{4}$$

Using a K_d as sorption model leads to

$$F(x,t) = -D_e' \frac{\partial C_{(x,t)}}{\partial x} \tag{5}$$

with

$$D_e' = D_e + (1-\varepsilon)\rho_S K_d D_S \tag{6}$$

This model has been widely used to describe the diffusion of cations in clayey materials (in particular compacted bentonite). The surface diffusion coefficient is given for each