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Cesium sorption and diffusion in Bure mudrock samples

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Abstract

This work deals with cesium diffusion and sorption in rock samples from Bure (Meuse/Haute-Marne, France). Four different samples extracted from the Callovo–Oxfordian layer (between −423 m and −478 m) were investigated to quantify the Cs diffusion parameter range. HTO diffusion properties were also evaluated. The through-diffusion method was used in both cases. The steady-state was reached, allowing a direct access to the values of effective diffusion coefficients (D_e). Major attention was paid to experimental chemical conditions. Cs and HTO diffusion parameters were quite homogeneous for the different investigated rock samples. D_e(Cs) was found about one order of magnitude higher than D_e(HTO). Such observation was already reported in the literature mainly for compacted bentonite. Results presented here show this trend also exists in mudrocks. Batch tests were performed in order to characterize cesium sorption on ground Bure mudrock samples. The isotherms were fitted with a 2-site ion exchange model. This model was extrapolated to intact rock samples and coupled with diffusion equations, using the measured D_e(Cs) values. This coupled model was tested against experimental data measured in the transient part of Cs diffusion experiments. A fairly good agreement between model and experimental data was found.

Keywords: Cesium; Tritiated water; Diffusion; Reactive transport; Radioactive wastes; Cation exchange; Bure; Mudrock

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1. Introduction

Underground repository is a concept envisaged in France for highly radioactive and long-lived radioactive wastes. Argillaceous or clay media are presently considered as potential host rocks for repositories due to numerous properties favorable for confinement, e.g. low permeability, high radionuclide retention capacity, large chemical buffering, etc. Studies are carried out in order to evaluate the feasibility of such a concept and its safety over the

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time scale relevant to radioelement lives. Whether such a host rock may be efficient for radionuclide confinements will be assessed by data collected in the Underground Research Laboratory (URL) of Bure (Meuse/Haute-Marne, France). This site is being drilled in the clayey Callovo–Oxfordian layer by the French nuclear agency for waste management (ANDRA).

Bure mudrocks exhibit low permeability (between 10^{-13} and 10^{-11} m/s; ANDRA, 1999) and the migration of dissolved species in pore water is assumed to be governed solely by molecular diffusion. Furthermore, diffusion of positively charged solutes may be slowed down by sorption processes. Sorption and diffusion are strongly coupled in cation migration. This work firstly aimed at studying the cesium sorption and diffusion in Bure mudrock samples from the Callovo–Oxfordian layer. Cesium was chosen because it is one of the radionuclides occurring in radioactive wastes, its speciation in solution is simple and it exhibits a significant but not to high sorption onto this material. Recent developments showed that the mineralogical composition evolution of this material along the borehole could affect the sorption/diffusion parameters (Sammartino et al., 2003). Hence, four different samples extracted along the borehole were investigated in this study. HTO diffusion was also measured in the considered rock samples. Diffusion tests were performed by through-diffusion method. Measurements performed when stationary state is reached give directly the effective diffusion coefficient values. Sorption factors can be evaluated on the basis of the same test as well, using the transient stage of the curve.

The second objective of this work was to compare the sorption factors evaluated for solid Bure mudrock samples with retention data measured using batch experiments. Usually the sorption of a solute on a solid phase is evaluated with ground samples and then extrapolated to the compact material. The validity of such an extrapolation is questionable because the solid/liquid ratio notably differs between batch conditions and raw material (O'Connor and Connolly, 1980).

This problem has been rather poorly discussed in the context of diffusion experiments with reactive solutes. Muurinen et al. (1987) provided direct measurements of Cs and Sr distribution coefficients (K_d) in compacted Na-bentonite deduced from through-diffusion tests. Though, K_d values for compacted samples seemed to be somewhat higher than for dispersed bentonite, the values deduced from compacted bentonite were quite similar to those obtained in batch experiments. Tsai et al. (2001) performed similar tests in compacted bentonite saturated with distilled water. The retardation factors obtained from the diffusion experiments were about one order of magnitude lower than those derived from the batch tests. Oscarson et al. (1994) performed direct measurements of Cs sorption on compacted bentonite. They observed in compact samples a decrease of K_d by a factor of 2 to 3 compared to measurements involving loose samples. The difference was attributed to a reduced accessibility to sorption sites in the dense samples. In some published works, apparent diffusion coefficients of cations in clays were measured and sorption factors were then back-calculated with the transport equation. Sato et al. (1992) derived K_d values from apparent diffusion coefficients measured with Cs, Sr and Tc in compacted sodium bentonite samples with different densities. K_d decreased with increasing compaction density. The authors suggested that such an evolution may be due to an increase of the solution salinity with the density. Robin et al. (1987) observed differences between calculated and measured values of Sr apparent diffusion coefficients in clay-based materials. This was attributed to variations of K_d between ground and compacted materials. This shift was assumed to be caused by the evolution of the bulk composition between ground and compacted samples. These data highlight the necessity of properly controlling the fluid composition to get a correct extrapolation of the retention model. In this work, attention was paid to the fluid composition to ensure equivalent chemical conditions for both batch tests and diffusion experiments.

2. Theory and method

2.1. The pore diffusion model

The solute migration through a clayey material is modelled here with the conventional "pore diffusion model". It consists in a macroscopic representation of the transfer with