



Research paper

Perturbation induced by a nitrate plume on diffusion of solutes in a large-scale clay rock sample



R.V.H. Dagnelie^{a,*}, P. Arnoux^a, J. Eaux^a, J. Radwan^a, P. Nerfie^a, J. Page^a, D. Coelho^b, J.-C. Robinet^b

^a DEN-Service d'Etude du Comportement des Radionucléides (SECR), CEA, Université Paris-Saclay, F-91191 Gif-sur-Yvette, France

^b ANDRA, DRD/TR, Parc de la Croix Blanche, 92298 Châtenay-Malabry Cedex, France

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ABSTRACT

Mudstones are widely studied in the context of waste landfill leachates or as geological barriers for waste management. Some of the technological wastes undergo biogeochemical degradation, releasing sulfate or nitrate plumes. The concomitant increase of salts concentration and ionic strength may perturb the geological media and affect transport properties. The study investigated the effect of a nitrate plume on the diffusion of ions. The confinement of ionic solutes was quantified in Callovian-Oxfordian mudstone. A 0.5 mol L⁻¹ NaNO₃ solution was injected in a large-scale sample with a low water/rock ($\ll 1.0$ L kg⁻¹) close to environmental conditions. The in-diffusion of HTO, ³⁶Cl, NO₃⁻, ²²Na, ¹³⁷Cs was monitored during the perturbation. A minor impact was observed on poral water chemistry and on ions diffusion. The anion exclusion was only reduced by 19% for chloride and effective diffusion of cations reduced by 20 to 30%. Diffusion data of NO₃⁻ was quantified and anion exclusion found to be intermediate between that of halogen anions and that of water. Values of diffusion anisotropies were adjusted to $\alpha(^{36}\text{Cl}) = 1.9$ and $\alpha(^{22}\text{Na}) = 2.5$, close to data in sound sample. All these results confirmed a limited perturbation by 0.5 mol L⁻¹ nitrate plume on the confinement properties of the clay rock. Additional data is provided on major ions released from the rock and diffusing towards the injection solution. It may be useful for further chemistry-transport modeling including co-diffusion of ions, surface diffusion, anion exclusion and effect of ionic strength.

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1. Introduction

Clay-rich geological formations are currently considered in several countries for hosting a radioactive waste repository. The long-term safety of the repository concept depends on the rock capacity to limit the release of radionuclides from the waste canisters towards the biosphere. Several Intermediate-Level and Low-level radioactive wastes contain a high quantity of nitrate salts. The progressive dissolution of nitrate salts over time increases sodium nitrates concentration in the rock near the repository. Such modification of the porewater composition can alter the transfer properties of radionuclides in the surrounding clay-rich host rock.

The transport of solutes in mudstones is dominated by diffusion, mainly due to the nanometer size of the pore network (Andra, 2005). The diffusive behavior of anions and cations is also ruled by electrostatic interactions related to the presence of negative charges on the clay mineral surfaces. Anions are repelled from the clay surfaces and consequently diffuse in a reduced volume of the pore network. This leads to a lower accessible porosity and a lower effective diffusion coefficient

than neutral species (Descostes et al., 2008; Van Loon and Mibus, 2015). This phenomenon is named *anion exclusion*. The role of anion exclusion phenomenon in clay-rich media is particularly important in the framework of radioactive waste repository since anions are not or weakly adsorbed on clay minerals. On contrary, cations are characterized by a strong affinity with the clay surfaces. Retention processes strongly contribute to reduce the apparent mobility of cations in clay-rich media. Due to electrostatic phenomena, cations are concentrated in the vicinity of the clay mineral surface (e.g. the double diffusive layer) leading to preferential diffusion. This phenomenon is known as *cation enhanced diffusion* (Melkior et al., 2007; Oscarson, 1994; Savoye et al., 2012b). The porewater chemistry is also known to strongly influence the electrostatic interactions on clay surface. In particular, an increase of ionic strength due to sodium nitrate may reduce anion exclusion and alter the retention properties of cations (mainly for alkali and alkaline-earth metals). Moreover, increasing the salinity of the solution induces coupled transport phenomena, including co-diffusion and osmotic phenomena, which can enhance or inhibit the macroscopic transport (Glaus et al., 2013; Martens et al., 2011).

The Callovian-Oxfordian mudstone (COX) is a clay-rich sedimentary rock from the eastern part of the Parisian Basin in France (Gaucher et al., 2004). It has been extensively studied in the context of the

* Corresponding author.

E-mail address: romain.dagnelie@cea.fr (R.V.H. Dagnelie).

Underground Retrievable Nuclear Waste Repository project (Cigéo, Andra, 2005). Diffusion experiments on centimetric samples provide reliable transport data. They evidence the presence of anion exclusion (Dagnelie et al., 2014; Descostes et al., 2008; Savoye et al., 2012a) and cation enhanced surface diffusion (Melkior et al., 2007; Savoye et al., 2012b, 2015). Such phenomena are particularly developed in the Callovian-Oxfordian mudstone due to the small size of pores, in the same range than the size of the electrostatic field occurring at their surface. In this context, the study focused on the effect of high concentrations of sodium nitrate on solutes transport, including anion exclusion and surface diffusion. We tried to characterize the diffusion properties of the rock as close as possible to operational conditions: i.e. radionuclides and sodium nitrate released simultaneously in the rock. To this aim, some dedicated diffusion experiments were developed on large-scale samples such as described in Dagnelie et al. (2015). Large-scale experiments display low water/rock ratios ($\ll 1 \text{ L kg}^{-1}$) which are representative of in situ conditions. They help investigating a large volume of rock. This experimental setup was adapted for such specific context of interest as diffusion under perturbation.

This paper details an in-diffusion experiment of a nitrate plume in a pluridimensional COx sample. Two similar experiments were designed with simultaneous injection of tracers and sodium nitrate (0.5 mol L^{-1}). The first experiment quantified the diffusion of neutral and anionic species (tritiated water HTO, ^{36}Cl). The second experiment quantified the diffusion of adsorbing cations (^{22}Na , ^{137}Cs). The diffusion parameters with the nitrate plume were compared to those obtained in sound clay rock. The interpretation of data focuses on the anisotropic diffusion of the plume and its effect on cations confinement/anion exclusion. The evolution of chemistry in solution and major ions transport is also reported and discussed. This large dataset on various species may be addressed elsewhere for further multi-species reactive-transport modeling.

2. Material and methods

Two experiments are described in this section. The first experiment (Exp. 1, Fig. 1) is dedicated to the diffusion of non sorbing species, with the following β -radiotracers: tritiated water (HTO) and chloride (^{36}Cl). The second experiment (Exp. 2) is dedicated to the diffusion of sorbing cations, using the γ -radiotracers (^{22}Na) and (^{137}Cs). Both experiments evaluate tracer's diffusion injected within nitrate solution at a concentration, $[\text{NaNO}_3] = 0.5 \text{ mol L}^{-1}$. Ionic strength of injected solution was I.S. $\sim 0.65 \text{ eq L}^{-1}$, compared to I.S. $\sim 0.1 \text{ eq L}^{-1}$ in the natural Callovian-Oxfordian porewater (Vinsot et al., 2008).

2.1. Mudstone sample

Experiments were carried out on a large diameter sample ($\varnothing = 290 \text{ mm}$), cored from the Callovian-Oxfordian rock formation (EST16517, in Meuse/Haute-Marne France). This core was extracted from the EST207 borehole, drilled between -501.8 and -502.0 m in depth from the surface. In order to prevent any oxidation, core samples were protected from O_2 after drilling. Mudstone samples were directly placed in anoxic containers under N_2 . These samples come from the clayey unit (UA) characterized as the most clayey levels of the formation (Pellenard et al., 2014). The mineralogy of the Callovian-Oxfordian mudstone was characterized by Andra (performed by ERM, Poitiers, France) on similar samples using the method described by Gaucher et al. (2004) and Cosenza et al. (2014). The contents of different minerals are the following: clay minerals (illite, interlayered R = 1 illite-smectite, kaolinite and chlorite) 50–55%, tectosilicates (quartz, feldspars) 18–20%, carbonates (calcite, dolomite) 22–27%, other minerals (pyrite, metal oxides...) <4%, organic matter (<1%). The oxidizing effect of NaNO_3 was assumed to be negligible in our experimental setup. Such pure chemical process was found to be slow in sediments containing pyrite and organic carbon under abiotic conditions (Mariën et al.,

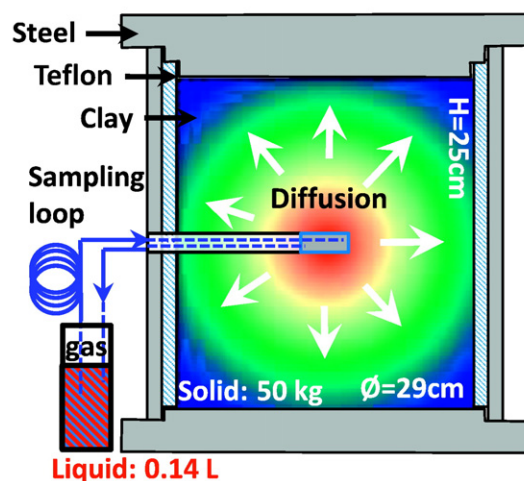


Fig. 1. (Top) Picture of experiment 1 (HTO, ^{36}Cl) (middle) scheme of experimental setup.

2011). An oxidizing perturbation of dissolved organic matter can be induced by nitrite and nitrate plumes under biotic conditions. Such effect recently studied by Bleyen et al. (2016), is outside the focus of the present study.

A synthetic solution was used for the rehydration of rocks, which were partially desaturated by drilling and during transport. The composition of the synthetic rehydration solution corresponded to porewater composition of the mudstone at the depth of the in-situ underground laboratory (Beaucaire et al., 2012; Vinsot et al., 2008). This ensured a chemical equilibrium and avoided minerals dissolution/precipitation. The concentrations of major ions are given in Table 1. The composition

Table 1

Composition of solutions used in this study: synthetic porewater used during rehydration and injection solutions for both experiments. Concentrations for Exp. 1 and Exp. 2 are experimental results measured before injection ($\pm 2\%$) and unity is ($10^{-3} \text{ mol L}^{-1}$). Composition of the last sample of Exp. 2 after 117 days is also given. n.a. (not available).

Species	Na^+	K^+	Ca^+	Mg^+	Sr^+	Cl^-	SO_4^{2-}	Alc^-	NO_3^-	pH
Synthetic water	49.5	1.0	4.92	3.35	0.40	49.3	7.5	2.7	0	7.0
Injection water, Exp. 1	571	1.0	7.0	6.9	0.31	63.5	10.6	n.a.	520	7.2
Injection water, Exp. 2	585	1.1	6.1	7.9	0.26	64.8	9.5	n.a.	529	7.2
Composition after Exp. 2	350	3.0	31	27	1.0	57	11.4	n.a.	380	7.1

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