# Diffusion experiments in Callovo-Oxfordian clay from the Meuse/Haute-Marne URL, France. Experimental setup and data analyses

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## ARTICLE INFO

## ABSTRACT

Diffusion is the main transport mechanism in clay rocks. To study diffusion processes in these formations, that are adequate as host-rocks for high-level radioactive waste repositories, laboratory experiments with small samples are usually carried out. More complex, expensive in situ essays can be performed to complement these small-scale studies and to evaluate scale effects.

This work presents the results of conventional and large-scale diffusion experiments carried out in consolidated Callovo-Oxfordian clay (COx) from the underground research laboratory (URL) at Bure (France).

Conventional laboratory experiments, in-diffusion (ID) and through-diffusion (TD), were carried out with HTO, Cl, Na and Sr; large-scale laboratory diffusion experiments with HTO and Sr were carried out at a scale comparable to the one used in situ.

In the large-scale experiments, cylindrical blocks of consolidated clay (30 × 30 cm) were used and the radionuclide was introduced as a compacted "solid source", which was prepared by mixing the tracer with the clay and compacting to a density similar to the one of the consolidated clay. Compared to conventional in situ tests, this setup is more realistic because the contact between tracer and clay is improved. A 3D analysis of diffusion pathways can be carried out after a thorough sampling of the solid block at the end of the experiment. Graphical representations of experimental results along vertical and horizontal planes obtained according to the samples orientation demonstrated the 3D capacity of this methodology and its capability to evaluate anisotropy and heterogeneities.

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## 1. Introduction

Clay formations are being considered potential host-rocks for radioactive waste disposal in many countries. Because clays have a very low hydraulic conductivity ($<10^{-12}$ m/s), diffusion is the main transport mechanism for radionuclides released from the canisters. The understanding of diffusion processes and the determination of diffusion coefficients for critical radionuclides are crucial for the performance assessment of deep geological repositories.

The French National Radioactive Waste Management Agency (Andra) is performing research at the Meuse/Haute-Marne Underground Research Laboratory (URL) located at Bure (300 km east of Paris) to evaluate the use of the Callovo-Oxfordian (COx) argillite formation as a repository for high-level radioactive waste in France. The argillaceous COx formation is a 130 m thick clay lying at a depth between 420 and 560 m at the laboratory site.

The host formation contains 40–60% clay minerals, associated with 20–30% carbonates, 20–30% quartz, and a small percentage of subordinate minerals (Gaussen, 2002). The dry density is between 2.40 and 2.47 g/cm$^3$, the water content is around 5–8%, and the total porosity range from 13% to 17%.

The Andra investigations include in situ diffusion experiments with a design similar to that used in the underground laboratory of Nagra (National Cooperative for the Disposal of Radionuclide Waste) at Mont Terri (Switzerland).

The "classical" experimental setup of these in situ diffusion experiment includes the injection of a tracer diluted in water that is representative of indigenous ground water into a packed-off borehole section. The packed-off section contains a stainless steel sinter of high porosity. In general, between the sinter chamber and the wall of the borehole a void volume is always left, leading to a decrease in the clay density and an increase in porosity of the clay at the clay/chamber interface. As a consequence, the introduction of a chamber filled with water could modify the properties

of the saturated clay in the first few centimetres, near the clay/experimental chamber interface, just where radionuclide diffusion will take place.

A methodology for large-scale tests which overcomes the above mentioned problem was described by García-Gutiérrez et al. (2006) who used it for diffusion experiments in the Opalinus clay (Mont Terri). Basically, in this setup, a re-compacted clay/radionuclide mixed solid source is placed in the centre of a large clay block, allowing the tracer to diffuse into the closed system. At the end, a thorough sampling of the rock provides a 3D distribution of the tracer activity, evidencing the diffusion paths.

The objective of this study was to determine diffusion coefficients of several radionuclides in the Callovo-Oxfordian clay (COx) obtained from the underground research laboratory (URL) at Bure (France). Herein large-scale diffusion experiments performed in cylindrical samples of $30 \times 30$ cm (HTO, Sr) using the methodology reported by García-Gutiérrez et al. (2006) are presented as well as the results of small-scale laboratory diffusion experiments in samples of approximately 1 cm thick (HTO, Sr, Cl, Na).

The results of small-scale experiments and their modelling are described in this paper, as well as the experimental details and the first modelling approach of the large-scale laboratory experiment. A deeper modelling study of the large-scale tests is described by Samper et al. (this volume).

## 2. Materials and methods

The clay used in this study was provided by Andra from their URL site at Bure (Meuse/Haute-Marne, north-eastern France). The main gallery of the laboratory is located in Callovo-Oxfordian host rock at an approximate depth of 490 m.

As a part of the scientific investigations three vertical down boreholes, DIR1001, DIR1002, and DIR1003, were drilled in 2005 in the shaft at −490 m. These boreholes were drilled perpendicular to the bedding planes. The first part of these boreholes has a diameter of 300 mm. The samples used for large-scale laboratory diffusion experiments, "blocks" came from two of these vertical down boreholes, DIR1002 between 3.05 and 3.30 m and DIR1003 between 2.90 and 3.09 m. The first one was used for the HTO experiment and the second one for the $^{85}$Sr experiment.

Small cylinders of diameter of approximately 2 cm from DIR1003 were used for classical laboratory diffusion experiments with $^{85}$Sr. Additional samples for small-scale laboratory experiments were obtained from borehole EST212 (core EST12449 from 514.86 to 515.01 m depth, one cell) and EST211 (core EST15095 from 578.60 to 578.75 m depth, three cells). Cylindrical cores of 76 mm were placed on a lathe to obtain smaller samples of 50 mm diameter to fit the diffusion cells. These cores were cut to a thickness of 11–12 mm to obtain several diffusion samples.

To hydrate the clay samples, in all cases, a synthetic Bure groundwater (Table 1) was used (Melkior et al., 2004). The water was prepared under atmospheric conditions.

**Table 1**
Chemical composition of the synthetic Bure pore water.

| Element | Bure (mol/L) |
|---|---|
| Na | $7.39 \times 10^{-3}$ |
| K | $2.56 \times 10^{-3}$ |
| Mg | $6.58 \times 10^{-3}$ |
| Ca | $8.73 \times 10^{-3}$ |
| Cl | $3.47 \times 10^{-2}$ |
| SO$_4$ | $1.77 \times 10^{-3}$ |
| CO$_3$/HCO$_3$ | $1.64 \times 10^{-3}$ |
| pH | 7.2 |

### 2.1. Theoretical description

In a porous medium, such as a clay formation, the diffusion process is different from diffusion in free water, because it is affected by the length of the diffusion path, tortuosity ($\tau$), and the form of the pores, constrictivity ($\delta$). Then, the pore diffusion coefficient, $D_p$, is related to the diffusion coefficient in free water, $D_w$, by

$$D_p = \frac{\delta}{\tau^2} D_w \tag{1}$$

In a diffusion experiment, only the pores that are connected and contribute to the transport of the dissolved species are important. Therefore, for each ion an "accessible porosity" has to be considered. The *effective* diffusion coefficient, $D_e$, defined by

$$D_e = \phi \cdot D_p \tag{2}$$

where $\phi$ is the diffusion-accessible porosity, which can be experimentally obtained when the steady state is reached. In the case of sorbing elements, reaching the steady state can be very time consuming, so an *apparent* diffusion coefficient, $D_a$, can be calculated from the diffusion profile into the sample. Thus, $D_a$ takes into account implicitly the retardation of the solute due to the interactions with the porous material, and is defined by

$$D_a = \frac{D_p}{R_f} \tag{3}$$

where $R_f$ is the retardation factor. If lineal sorption is considered, the sorption isotherm can be described by the simple relation $S = K_d \cdot C$, where $S$ is the tracer concentration on the solid phase; $C$, the tracer concentration in the liquid phase; and $K_d$, the distribution coefficient. In this case, $R_f$ is

$$R_f = 1 + \frac{\rho_d}{\phi} K_d \tag{4}$$

where $\rho_d$ is the dry density of the material.

### 2.2. Classical diffusion experiments

Two different types of classical laboratory diffusion experiments were performed: through-diffusion (TD) and in-diffusion (ID).

TD experiments were carried out with HTO (neutral), $^{36}$Cl$^-$ (anionic), and $^{22}$Na$^+$ (cationic). In this method, the sample is located between two reservoirs, "in" and "out" where the solution is continuously stirred.

After water saturation of the clay sample, the in-reservoir is spiked with the tracer. The concentrations in both reservoirs are kept constant such that steady-state diffusion across the sample is achieved. When the steady state is reached, the diffusive flux across the sample is constant. Different approximations can be used to maintain the constant concentration gradient: spiking additional tracer in the in-reservoir, as necessary, or using large volumes to minimise the concentration decrease; carrying out frequent sampling in the out-reservoir to maintain the concentration near zero or to use a small reservoir which is changed periodically. In the present study, the configuration used was a large (1 L) in-reservoir and a small (20 mL) out-reservoir that was changed periodically.

For a clay sample of thickness $L$, which is initially tracer free, and where the in-reservoir has a constant concentration $C_0$ and the out-reservoir is kept to "quasi" zero concentration, the expression for the cumulative mass of tracer, $Q$, that has passed to the out-reservoir, through a cross-sectional area $A$, as a function of the time, is (Crank, 1975; Bourke et al., 1993):

$$Q = A \cdot L \cdot C_0 \left[ \frac{D_e}{L^2} t - \frac{\alpha}{6} - \frac{2\alpha}{\pi^2} \sum_1^\infty \frac{(-1)^n}{n^2} \exp\left( \frac{-D_e n^2 \pi^2 t}{L^2 \alpha} \right) \right] \tag{5}$$