

# **Measuring the diffusion coefficient for He and Ar in Callovo-Oxfordian Clay**

Final report

Elke Jacops and Norbert Maes

**ANDRA contract 059046**  
**SCK-CEN contract CO-90-13-3301-00**

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RDD



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## **1 Preface**

This final report describes the results obtained within Task 1 and Task 2 of the project under contract ANDRA ref. N° 059046; SCK-CEN ref. CO-90-13-3301-00 (internal project name: CoxGasDif). As the diffusion coefficients for He and Ar have been obtained for the two samples, Tasks 1 and 2 are considered to be completed.

## **2 Introduction**

Many countries prefer for their long-term management of high- and intermediate level radioactive waste and/or spent fuel the disposal of this waste in a geological repository. In Belgium, Switzerland and France, argillaceous formations are being explored as potential host formations for this purpose. In this context, knowledge of the diffusion coefficient of He is relevant within two research areas. First, diffusion coefficients are used in safety calculations to evaluate the balance between gas generation (mainly H<sub>2</sub>) and gas dissipation, but due to experimental difficulties with H<sub>2</sub>, the diffusion coefficient of He is often used as an approximation. Second, the diffusion coefficients of He and Ar are needed in the diffusion models of natural tracers. These models predict transport processes on a large temporal and spatial scale and provide important information to support safety assessments. Due to the lack of data on the diffusion coefficients of He and Ar for the different clay host formations, diffusion experiments with dissolved He and Ar have been performed on Boom Clay, Opalinus Clay and Callovo-Oxfordian Clay with the set-up developed by the Belgian Nuclear Research Centre. The results obtained on Callovo-Oxfordian Clay (1 sample oriented parallel and 1 sample oriented perpendicular to the bedding plane) are discussed in this report.

## **3 Materials and methods**

### **General methodology**

SCK•CEN has developed a versatile method to measure the diffusion coefficient of dissolved gases in low-permeability materials (Jacops *et al.*, 2013). The method is based on the through diffusion technique (Put and Henrion, 1988; Shackelford, 1991; Van Loon *et al.*, 2003) with two dissolved gases placed on opposite sides of a test core (Figure 1). In a classical through-diffusion test, the porous medium is placed between two vessels, one containing a known concentration (high concentration compartment) of the diffusant while the other compartment is free of the diffusant (low concentration compartment). From the evolution of the diffusant concentration in both compartments, the diffusion characteristics of the diffusant can be obtained.

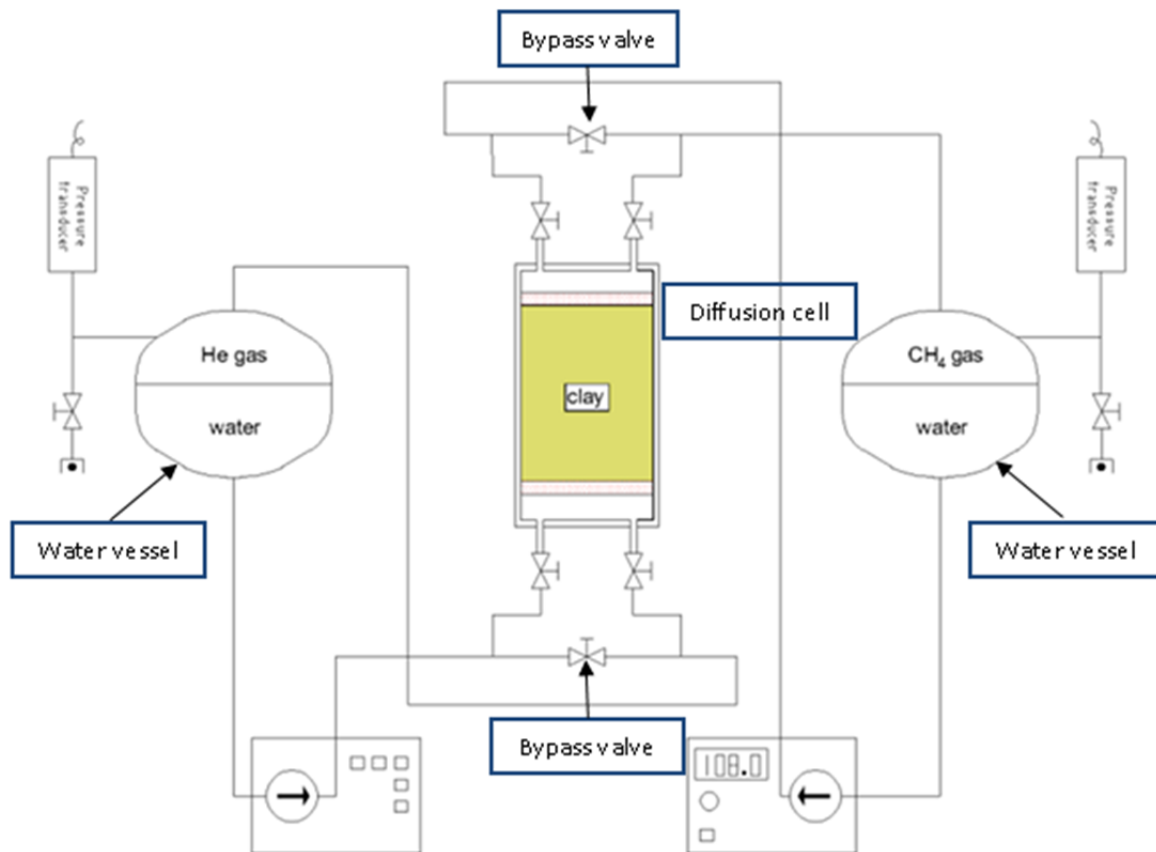


Figure 1: set-up to measure the diffusion coefficient of dissolved gas in low-permeability materials

The set-up consists of a diffusion cell, two water vessels with a volume of 1 liter, two pumps and two pressure transducers (Figure 1). A more detailed description can be found in (Jacops et al., 2013).

Prior to starting the diffusion experiment, the diffusion cell is loaded with the sample. This diffusion cell consists of a cylindrical stainless steel body with an internal diameter of 80 mm. As the plasticity/swelling capacity of the Callovo-Oxfordian clay is limited compared to Boom Clay, the Callovo-Oxfordian clay sample has to be embedded in a resin in order to seal the interface clay sample – cell. First, the Callovo-Oxfordian clay sample is processed on a lathe into a cylinder of 70 mm diameter and approximately 40 mm height. After the sample has been placed in the cell, the remaining void between the sample and the cell (thickness 5 mm) is filled with resin (Sikadur 52 Injection Normal). After one day, the resin has hardened and the cell is machined again on a lathe in order to remove the upper and lower part of the sample until a remaining height of 30 mm is obtained. The top- and bottom flanges (including a teflon filter of 2 mm thickness, diameter 70 mm) are welded to the diffusion cell. Both flanges are provided with a circulation loop to ensure good contact between the water containing the dissolved gas and the clay sample.

As a good sealing between the sample, the resin and the inner wall of the diffusion cell is essential for a correct interpretation of the data, this sealing is verified by performing a hydraulic conductivity ( $K_h$ ) measurement. The obtained value also gives a good indication on the status of



the sample: large cracks or other anomalies will influence  $K_h$ . A scheme of the used set-up is given in Figure 2 .

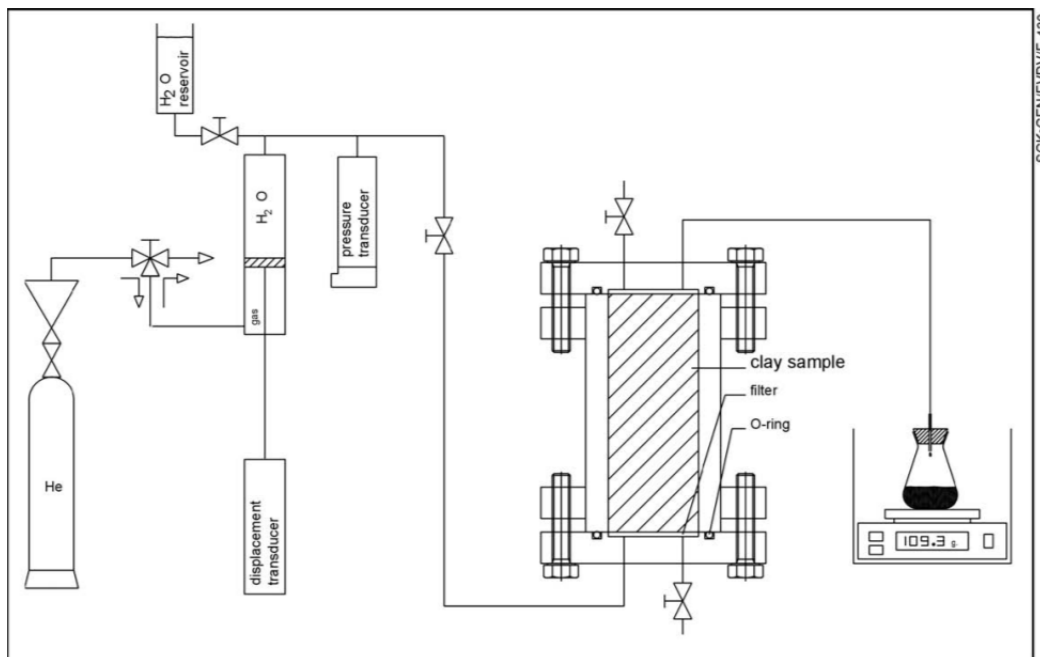


Figure 2: Scheme of the set-up to measure hydraulic conductivity.

The design of the experimental set-up and the methodology have been developed within an internal R&D project of SCK•CEN. A detailed description can be found in (Wemaere et al., 2008). After the sample is embedded in the diffusion cell, it is installed in the experimental set-up (Figure 2). Water is injected under constant pressure at the bottom of the sample with a piston that is connected to a displacement transducer. The applied pressure is controlled by a pressure regulator (connected to a He gas bottle) and is measured by means of a pressure transducer (relative pressure). The water flowing out of the cell is collected in a flask (at atmospheric pressure) that is placed on a precision balance. During the experiment, the water inflow (displacement transducer), water outflow (balance) and applied pressure are registered. The hydraulic conductivity  $K_h$  (m/s) is determined by applying Darcy's law:

$$K_h = (Q \cdot dl) / (S \cdot dh)$$

where  $Q$ : in-flow rate ( $m^3/s$ ),  $S$ : surface area perpendicular to the flow rate ( $m^2$ ),  $dh$ : pressure gradient (m water column) and  $dl$ : length of the sample (m).

In the described experiment, the water used to measure the hydraulic conductivity was synthetic Callovo-Oxfordian pore water (composition in Table 1). For sample 1, a pressure gradient of 0.53 MPa was used and the measurement lasted 129 days. For sample 2, a pressure gradient of 0.57 MPa was used and the measurement lasted 85 days.

**Table 1: composition of synthetic Callovo-Oxfordian pore water based on (Savoie et al., 2012; Savoie et al., 2010)**

	mg/l
NaCl	1059
Na <sub>2</sub> SO <sub>4</sub>	2216
CaCl <sub>2</sub> .2H <sub>2</sub> O	947
MgCl <sub>2</sub> .6H <sub>2</sub> O	911
KCl	78
NaHCO <sub>3</sub>	216

Once the hydraulic conductivity has been measured and the sample is considered to be ready for the gas diffusion experiment, the diffusion cell is mounted in the gas diffusion set-up. The pumps are calibrated at a flow rate of 10 ml/min. Air is removed by performing at least five cycles of evacuation and refilling with the diffusing gases (respectively He and Ar on each side of the set-up). After the last flushing cycle, the set-up is evacuated and ready to be filled with 500 ml Callovo-Oxfordian clay pore water.

The water (MilliQ) used to prepare synthetic Callovo-Oxfordian clay pore water is degassed to remove all atmospheric oxygen and stored in a glove box with N<sub>2</sub> atmosphere. After preparation of the Callovo-Oxfordian clay pore water, 500 ml is transferred into a clean, previously evacuated vessel, called "the transfer vessel". As this water is still in equilibrium with N<sub>2</sub>, the transfer vessels are flushed with He and Ar, respectively, in order to remove as much dissolved N<sub>2</sub> as possible.

Each transfer vessel is now connected to the corresponding (same gas) water vessel of the set-up, and the water is transferred from the transfer vessel into the water vessel of the set-up by applying a gas pressure gradient. For the pressure gradient, the same gas as the gas used in the transfer vessel is used. The amount of transferred water is determined by weighing the transfer vessels before and after filling the set-up.

In order to verify that no contamination of the gas phases occurred, a gas chromatography analysis is performed prior to the start of the diffusion test. As no He is found in the vessel with Ar and vice versa, the experiment is ready to be started. The pressure is set at 10 bar for both sides of the set-up, the bypass valves are closed, the valves of the diffusion cell are opened and the pumps are started.

The gas phases are sampled (sample volume approximately 6 ml) approximately every 2 weeks and samples are analyzed with a Compact GC (Interscience), equipped with a Molsieve 5A column and a TCD detector.

## **Samples**

Both samples originate from the Bure Underground Research Lab.

For sample 1, the ID is EST49109 – Drilling OHZ6560 (start 9.37m – end 9.67m) with coördinates (X: 823024.64 – Y: 1091669.04 – Z:-112.32). The sample was cored at a depth of 478.52m. The sample axis is perpendicular to the bedding plane.

For sample 2, the ID is EST51008. The sample was cored at a depth of 490m (level of the URL). Distance: 10.85 – 11.15 m. The sample axis is parallel to the bedding plane.

## Modelling

The tests are interpreted with a simple diffusive transport model. This model represents the transport equation in a 1D geometry. The model is based on the first and second Fick's laws for diffusive transport in porous media.



Figure 3: Geometry used in the diffusive transport model. Blue cells indicate where the evolution of the dissolved gas concentrations is recorded.

In the numerical implementation of this model, the clay core is represented by 30 elements (see Figure 3). At one end, a gas concentration was imposed as boundary condition, corresponding to the dissolved fraction at the prevalent pressure in the vessel following Henry's law. At the other end, the concentration of the considered gas is assumed to be 0. The diffusion-accessible porosity is set at 0.18. As output, fluxes at both faces are calculated with Fick's first law, as well as concentration profiles at regular time intervals and concentration in selected elements (shown in blue in Figure 3). The modelling accounts for reduction in pressure in both vessels because of sampling. All calculations are performed with COMSOL multiphysics version 3.5a, Earth science module. The diffusion coefficients are obtained by using a least squares fitting procedure to the experimental data with the MATLAB Optimization Toolbox. In fact, the model is able to calculate the best fit for 2 factors:  $D_{\text{pore}} \times \eta$  and  $R \times \eta$ . However, in our procedure  $\eta$  is set to 0.18 and  $R$  is set to 1 (no retardation). Therefore, the value for  $D_{\text{pore}}$  is directly fit and obtained.

Diffusion coefficients were calculated with an updated version of the diffusive model, which uses the experimentally measured water and gas volumes instead of standard volumes of 500 ml each.

## 4 Results

### 4.1 Hydraulic conductivity

The measured hydraulic conductivity is given in Table 2

Table 2: measured hydraulic conductivity

	reference	Orientation w.r.t. bedding plane	Kh (m/s)	Stdev on Kh (m/s)
Sample 1	EST49109	Perpendicular	$3.4 \times 10^{-13}$	$0.1 \times 10^{-13}$
Sample 2	EST51008	Parallel	$1.3 \times 10^{-13}$	$0.1 \times 10^{-13}$

## 4.2 Measured diffusion coefficients

### 4.2.1 Sample 1 (EST49109, oriented perpendicular to bedding plane)

All gas samples are analyzed with a compact GC (Interscience, The Netherlands).

Based on the obtained results and the diffusive model (Figure 4), the calculated pore diffusion coefficient ( $D_{\text{pore}}$ ) for He is  $4.5 \times 10^{-10} \text{ m}^2/\text{s}$  with the 95% confidence interval between  $4.4 \times 10^{-10}$  and  $4.6 \times 10^{-10} \text{ m}^2/\text{s}$

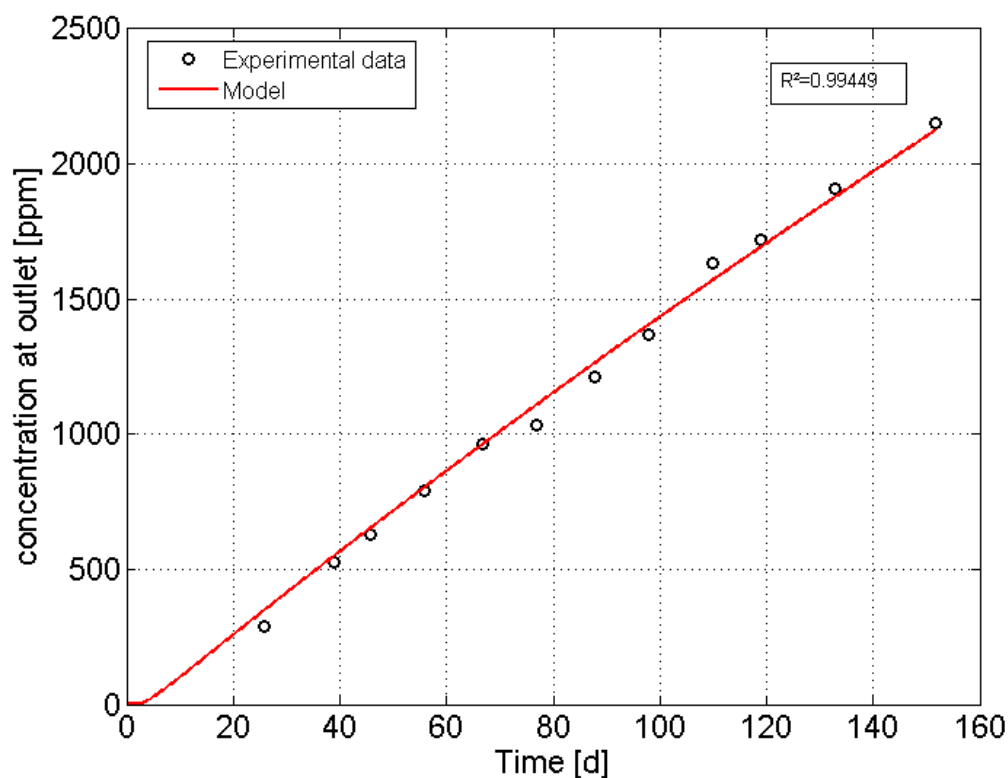


Figure 4: fit for diffusion coefficient of He on sample 1 (EST49109)

Based on the obtained results and the diffusive model, the calculated pore diffusion coefficient (Figure 5) ( $D_{\text{pore}}$ ) for Ar is  $4.1 \times 10^{-11} \text{ m}^2/\text{s}$  with the 95% confidence interval between  $4.0 \times 10^{-11}$  and  $4.2 \times 10^{-11} \text{ m}^2/\text{s}$ .

An overview of the obtained  $D_{\text{pore}}$  and  $D_{\text{eff}}$  is given in Table 3.

Table 3: Obtained diffusion coefficients for samples EST49109 and EST 51008

	$D_{\text{pore}}$ (m <sup>2</sup> /s)	95% confidence interval for $D_{\text{app}}$ (m <sup>2</sup> /s)	$D_{\text{eff}}$ (m <sup>2</sup> /s) *	95% confidence interval for $D_{\text{eff}}$ (m <sup>2</sup> /s)
Sample EST49109 (⊥)				
He	$4.5 \times 10^{-10}$	$4.4 \times 10^{-10}$ – $4.6 \times 10^{-10}$	$8.1 \times 10^{-11}$	$8.0 \times 10^{-11}$ – $8.3 \times 10^{-11}$
Ar	$4.1 \times 10^{-11}$	$4.0 \times 10^{-11}$ – $4.2 \times 10^{-11}$	$7.3 \times 10^{-12}$	$7.1 \times 10^{-12}$ – $7.5 \times 10^{-12}$
Sample EST51008 (//)				
He	$5.5 \times 10^{-10}$	$5.4 \times 10^{-10}$ – $5.7 \times 10^{-10}$	$1.0 \times 10^{-10}$	$0.97 \times 10^{-10}$ – $1.02 \times 10^{-10}$
Ar	$7.1 \times 10^{-11}$	$6.9 \times 10^{-11}$ – $7.2 \times 10^{-11}$	$1.3 \times 10^{-11}$	$1.2 \times 10^{-11}$ – $1.3 \times 10^{-11}$

\*  $D_{\text{eff}} = D_{\text{pore}} * \eta$  ( $\eta$  is set at 18%)

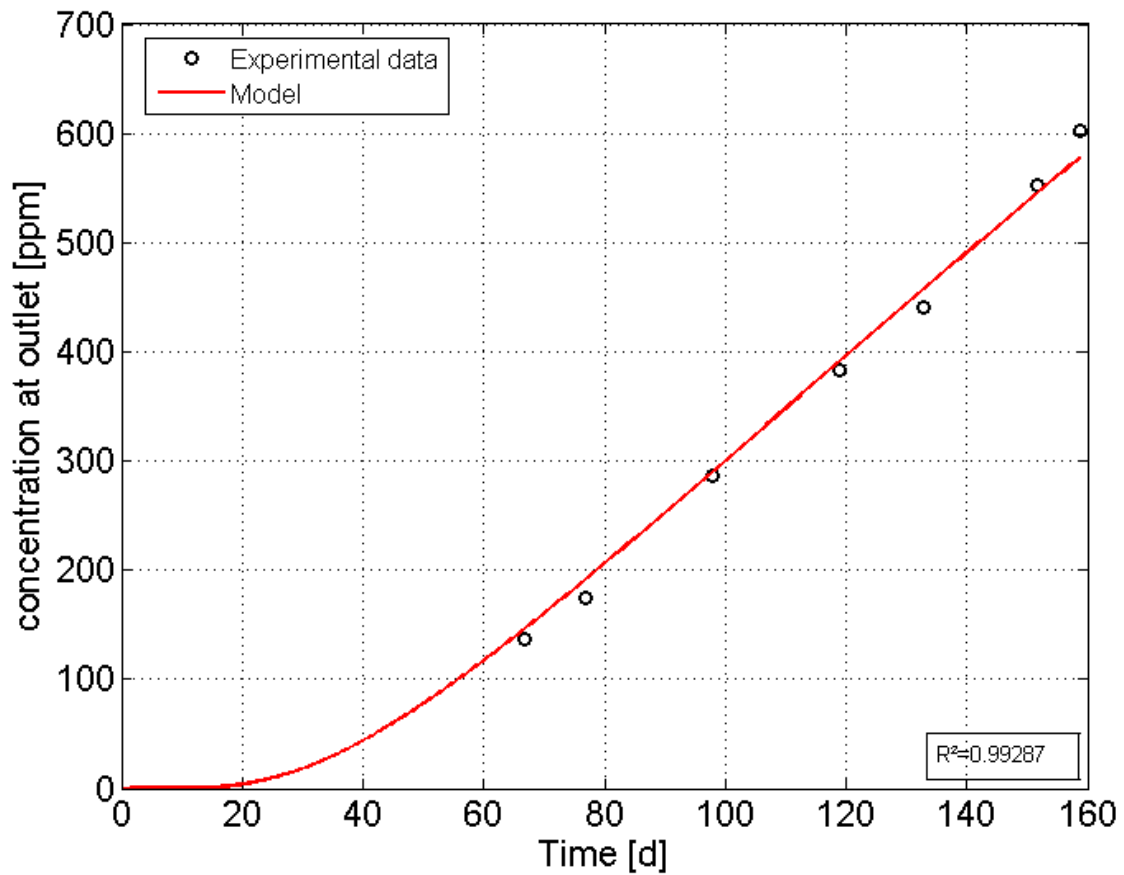


Figure 5: Fit for diffusion coefficient of Ar on sample 1 (EST49109)

#### 4.2.2 Sample 2 (EST51008, oriented parallel to bedding plane)

Based on the obtained results and the diffusive model (Figure 6), the calculated pore diffusion coefficient ( $D_{\text{pore}}$ ) for He is  $5.5 \times 10^{-10} \text{ m}^2/\text{s}$  with the 95% confidence interval between  $4.5 \times 10^{-10}$  and  $5.7 \times 10^{-10} \text{ m}^2/\text{s}$ .

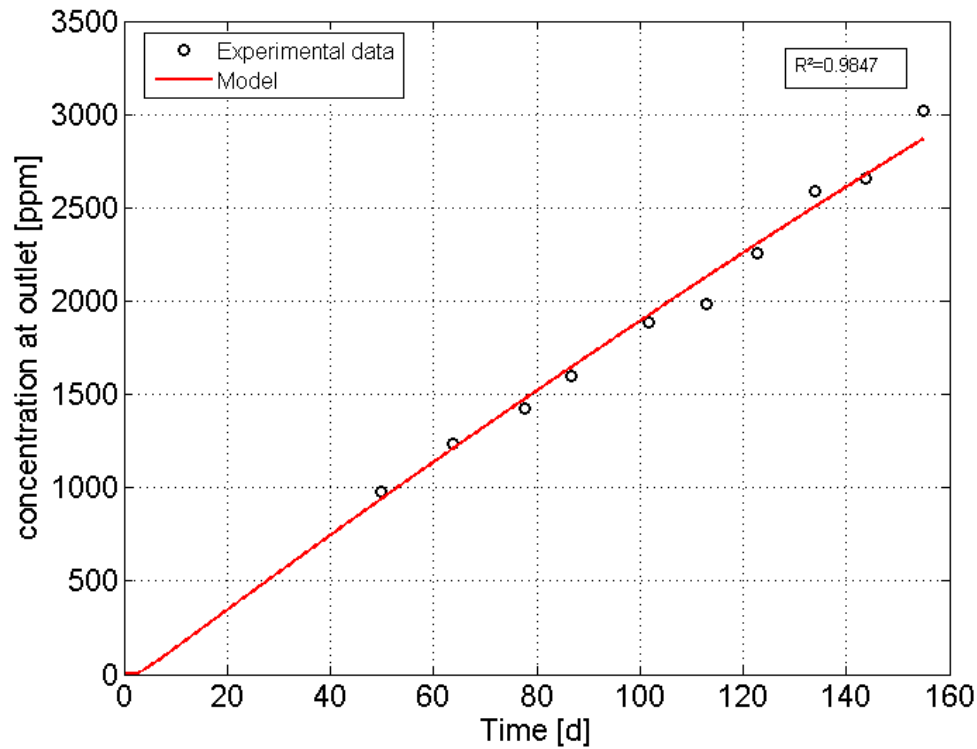


Figure 6: Fit for diffusion coefficient of He on sample 2 (EST51008)

Based on the obtained results and the diffusive model, the calculated pore diffusion coefficient (Figure 7) ( $D_{\text{pore}}$ ) for Ar is  $7.1 \times 10^{-11} \text{ m}^2/\text{s}$  with the 95% confidence interval between  $6.9 \times 10^{-11}$  and  $7.2 \times 10^{-11} \text{ m}^2/\text{s}$ .

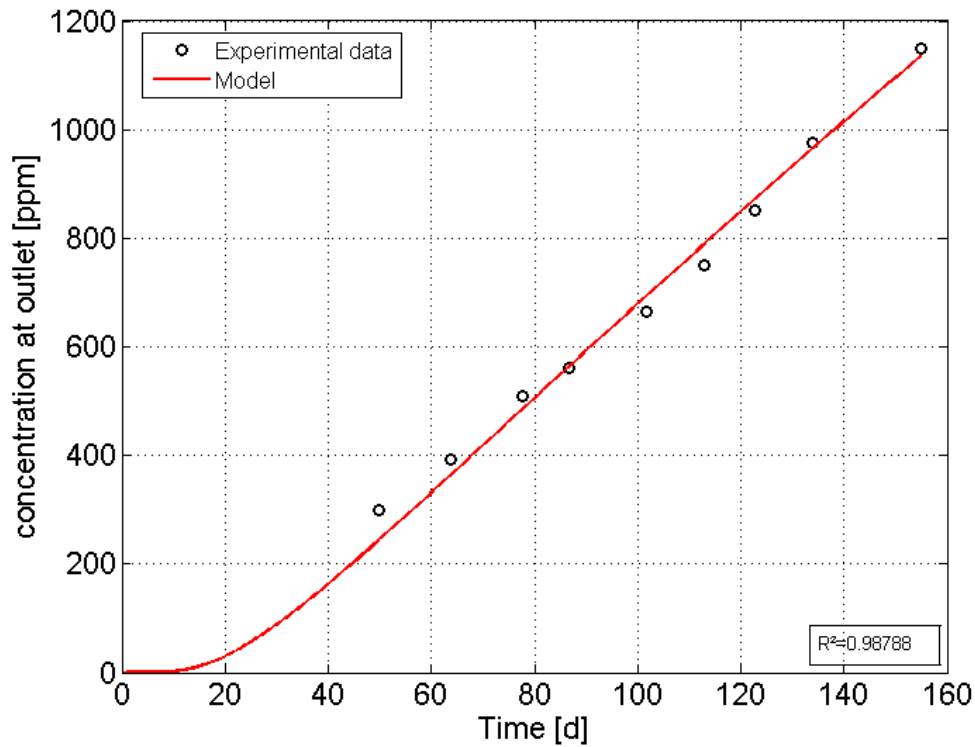


Figure 7: Fit for diffusion coefficient of Ar on sample 2 (EST51008)

## 5 Discussion and conclusions

Diffusion coefficients for He and Ar in Callovo-Oxfordian Clay have been obtained for both samples parallel and perpendicular to the bedding plane.

In order to compare the diffusion coefficients obtained in this work with those available in literature, an evaluation of the available data is made and an overview is given in Table 4. One has to consider that in literature, only diffusion coefficients for He have been reported. For argon, no data have been found.

Table 4: Overview of diffusion coefficients for He reported in literature

Formation	Reference	Type	Measured D (m <sup>2</sup> /s)	η (%)	T (°C)
COx	(Bigler et al., 2005)	D <sub>p</sub>	2.41 x 10 <sup>-10</sup>	15.4	20
COx	(Rebour et al., 1997)	D <sub>app</sub>	5±1 x 10 <sup>-11</sup>	23	50
COx	This work	D <sub>p</sub>	4.5 x 10 <sup>-10</sup>	18	21 ± 2

(Bigler et al., 2005) performed an <sup>4</sup>He outgassing experiment with a spherical sample of the Callovo-Oxfordian Clay. With the best fit between the experimental result and the analytical

solution,  $D_p = 7.5 \cdot 10^{-10} \text{ m}^2/\text{s}$  was obtained with an uncertainty of 20% (data not reported in Table 4). The diffusion coefficient obtained for the spherical sample is actually a mixed diffusion coefficient with respect to bedding plane orientation. In addition, the sample was not a perfect sphere and might have been disturbed by cutting. It is reported that this value has to be considered as a maximum value, affected by experimental artefacts (Bigler et al., 2005).

(Bigler et al., 2005) also modelled an in-situ pore diffusion coefficient based on the natural He profile in the Callovo-Oxfordian Clay. The value is  $D_p = 2.41 \cdot 10^{-10} \text{ m}^2/\text{s}$  with a range of uncertainty from  $0.8 \cdot 10^{-10}$  to  $7.2 \cdot 10^{-10} \text{ m}^2/\text{s}$ . This range of uncertainty is almost 1 order of magnitude, and the experimentally obtained value for  $D_p$  on the spherical sample is outside this range.

(Rebour et al., 1997) used a through diffusion set-up. Despite the fact that this set-up could be used for different gases, only data for He diffusion on Callovo-Oxfordian Clay were reported ( $D_{\text{app}} = 5 \pm 1 \cdot 10^{-11} \text{ m}^2/\text{s}$ ). The interpretation of the data suffered from complications such as anisotropy effects, which were not taken into account and the measured porosity (23%) did not correspond to the porosity value needed to obtain a good fit (16%) (Bigler et al., 2005). Moreover, the sample used in this experiment seems to originate from the top of the Callovo-Oxfordian Formation and contains more carbonate than samples located at the level of the underground research laboratory (like the sample used in this study). Therefore no direct comparison can be made between both experimental results.

Also the diffusion coefficients reported for the Callovo-Oxfordian Clay by (Bigler et al., 2005) and (Rebour et al., 1997) differ more than one order of magnitude. The value obtained in this work corresponds best to the value reported by (Bigler et al., 2005), but unfortunately the value of Bigler suffers from an uncertainty of more than one order of magnitude.

Currently, Andra considers for hydrogen a diffusion coefficient  $D_p = 4 \cdot 10^{-10} \text{ m}^2/\text{s}$ , based on values obtained for tritiated water HTO. This value is in good agreement with the  $D_p$  obtained for He in this work.

**Table 5: anisotropy ratio**

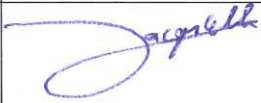


	$D_p$ (EST49109) ( $\text{m}^2/\text{s}$ ) $\perp$	$D_p$ (EST51008) ( $\text{m}^2/\text{s}$ ) //	Anisotropy ratio
He	$4.5 \cdot 10^{-10}$	$5.5 \cdot 10^{-10}$	1.23
Ar	$4.1 \cdot 10^{-11}$	$7.1 \cdot 10^{-11}$	1.74

It is generally observed in Callovo-Oxfordian Clay that solute diffusion is anisotropical: diffusion rates are higher in the direction parallel to the bedding plane compared to the direction perpendicular to the bedding plane, due to the layered structure of clay. The average anisotropy ratio measured in our work is 1.5 which is close to the average anisotropy ratio measured for HTO which is 1.6.



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