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## **DETERMINATION OF DIFFUSION COEFFICIENTS OF DISSOLVED GASES IN BOOM CLAY AND OPALINUS CLAY**

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### **ABSTRACT**

Diffusion coefficients of gases in Boom Clay and Opalinus Clay are investigated in the framework of characterisation of the formations and performance assessment of potential geological disposal of radioactive waste in these formations. The diffusion coefficients of Ne and Ar in Boom Clay were measured in a cross through diffusion experiment to verify if a relation exists between the diffusion coefficient and the size of the diffusing gas. This relation could then be used to determine the diffusion coefficient of H<sub>2</sub>, which has proven difficult to measure experimentally. Apparent diffusion coefficients of  $5.1 \cdot 10^{-10} \text{ m}^2/\text{s}$  for Ne and  $2.0 \cdot 10^{-10} \text{ m}^2/\text{s}$  for Ar were obtained. In a 2<sup>nd</sup> experiment, the diffusion coefficient of He in Opalinus Clay was measured. Profiles of natural tracers, like He, are used to characterise transport properties of argillaceous rock formations on a large spatial and temporal scale. An apparent diffusion coefficient of  $4.0 \cdot 10^{-10} \text{ m}^2/\text{s}$  was obtained for He.

### **Keywords**

Boom Clay, Gas Diffusion Coefficient, Geological Disposal, Opalinus Clay, Natural Tracer, Nuclear Waste, Through Diffusion

## 1 INTRODUCTION

Storage of radioactive waste is an important modern-day topic. Even if nuclear energy is abandoned in the near future, the waste that is currently being produced still needs a destination. Interim storage facilities have the disadvantage that they need continuous monitoring, their security cannot be guaranteed for the centuries needed for waste to reach acceptable radiation levels through radioactive decay. The most promising solution currently under investigation is the deep geological disposal of the high-level and long-lived nuclear waste. The idea behind this concept is that the soil where the waste is stored in, functions as a last barrier for transport of radioactive isotopes when the engineered barriers fail. The goal is to delay transport long enough to ensure that radio-active decay substantially reduces the level of activity by the time the pollutants reach the environment. (Nagra, 2002) (ONDRAF/NIRAS, 2011)

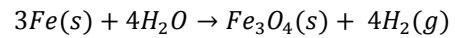
Good knowledge on the transport behaviour of radionuclides through the host formation is essential for safety assessment. This transport behaviour can be disturbed by for instance the presence of a free gas phase. In a geological repository, gas will be generated locally and if the gas cannot diffuse away fast enough, a free gas phase will be formed and gas flow may occur. This gas flow could influence the safety functions of a repository. Therefore knowledge of gas diffusion coefficients is important for a good evaluation: will the gas be transported away by diffusion or will a free gas phase be formed?

SCK·CEN has developed a straightforward method to determine the diffusion coefficient of dissolved gases. This method has been validated on Boom Clay samples by Jacobs et al. (2013). Boom Clay is studied in Belgium as a potential host rock for the geological disposal of radioactive waste. (ONDRAF/NIRAS, 2011) This paper describes 2 diffusion experiments with dissolved gases using the technique developed by SCK·CEN, but the rationale for both experiments is different. The first experiment was conducted with neon and argon on a Boom Clay sample to verify if a relation exists between the diffusion coefficient and the size of the diffusing gas. This relation could then be used to estimate the diffusion coefficient of hydrogen gas in Boom Clay. Furthermore Ne has a similar size as H<sub>2</sub> molecules. Diffusion experiments on H<sub>2</sub> have proven difficult in the past due to contamination of the set-up with methanogenic bacteria which use the H<sub>2</sub> to produce CH<sub>4</sub>.

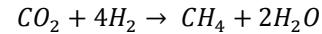
The second experiment was performed with helium on an Opalinus Clay sample in the framework of the ‘natural tracer research program’ of the University of Bern. (Mazurek, et al., 2011)

Gas diffusion experiments are being conducted on Boom Clay to enable the evaluation of the formation of a free gas phase in a repository. Several different processes are responsible for gas generation at or near a nuclear waste repository. (Yu & Weetjens, 2009) Anaerobic corrosion of metals in waste and packaging and radiolysis of water and organic materials in the waste mainly produce hydrogen. Microbial degradation of organic material produces a.o. methane and carbon dioxide.

The anaerobic corrosion reaction of iron is:



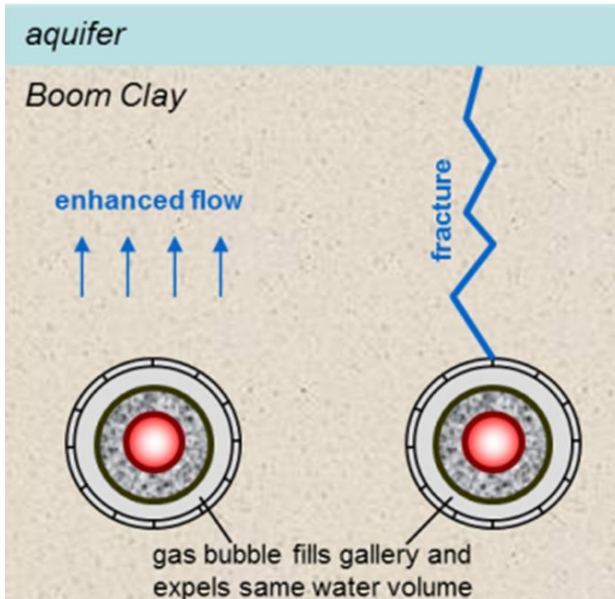
Radiolysis of water is the decomposition of water molecules into hydrogen and hydroxide radicals under the influence of nuclear radiation. After recombination a number of reaction products are formed, mainly hydrogen gas and hydrogen peroxide. Methanogenesis is the microbial degradation of organic material under anaerobic circumstances. Carbon is used as electron acceptor instead of oxygen. A common reaction is the conversion of hydrogen into methane:



The generated gas will dissolve in the pore water and is transported away from the repository by diffusion as dissolved species. If the gas generation rate is larger than the diffusive flux, the porewater in the near field will exceed the solubility limit and a free gas phase is formed. Initially, isolated gas bubbles will accumulate until a continuous gas phase is formed and gas flow may occur which may be accompanied by a release of radionuclides (see figure 1). Whether gas flow will occur in the Boom Clay depends on many factors: a.o. the gas generation source term, the (dissolved) gas diffusion coefficient, gas entry value of the concrete EBS materials and total storage volume, characteristics of the seals etc. (Jacobs, et al., 2013) (Yu & Weetjens, 2009)

The goal of the second experiment is to determine the diffusion coefficient of helium in Opalinus Clay. Opalinus Clay is studied as a potential host formation for the geological disposal of radioactive waste in Switzerland. Information on the transport properties of radionuclides through the host rock can be obtained from small scale lab experiments and on a larger scale by looking at natural tracer profiles. Helium is one such natural tracer. (NEA, 2009) An example of a He-concentration profile (measured at the Mont-Terri underground rock laboratory) is presented in figure 2. To

obtain more accurate model calculations on the He concentration profiles found over the entire stratigraphic column, information on the diffusion coefficient of helium through Opalinus clay is required.

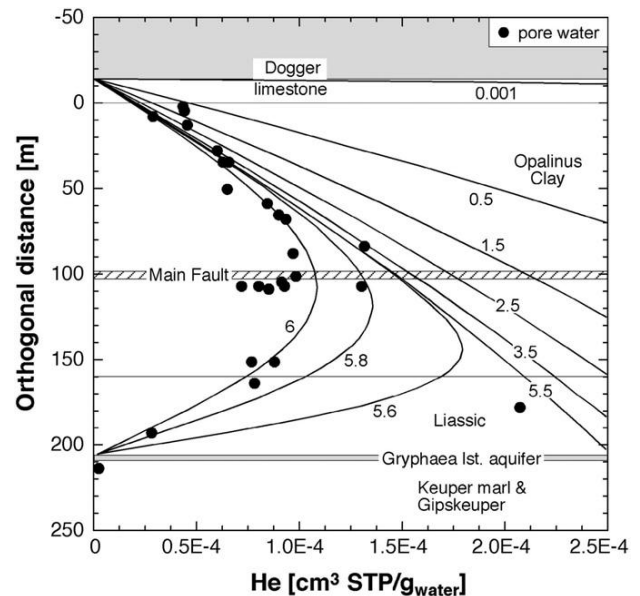


**Figure 1: Production of gas in a radioactive waste repository and the possible consequences**

Profiles of natural tracers dissolved in pore water form an important step for performance assessment of a potential host rock for radioactive waste disposal. They are used to characterise the transport properties of argillaceous rock formations on a much larger spatial and temporal scale than is possible with laboratory experiments. The goal is to prove that diffusion is and will be the main transport mechanism for at least a million years in the entire stratification. The distribution of several different natural tracers (anions, water isotopes and noble gases) is measured via boreholes. These data are compared to model calculations based on transport parameters derived from a variety of laboratory and field experiments and based on a set of different initial and boundary conditions. The uncertainty on initial conditions often determines the accuracy of the model. Models take into account diffusion, advection and in the case of  $^4\text{He}$  production rates due to radioactive decay of thorium and uranium, both of which are present in Opalinus Clay. A good match between the measured data and model simulations indicates the input parameters could be appropriate. Studies indicate that diffusion coefficients determined in laboratory experiments are applicable for large scale transport modelling. (Mazurek, et al., 2008) (Mazurek, et al., 2011)

Research concerning the diffusion coefficient of helium in Opalinus Clay is limited in literature. (Gómez-Hernández, 2000) conducted an in situ in- and out-diffusion experiment with He parallel to the bedding plane in the Mont-Terri Rock Laboratory. In the in-

diffusion experiment, the accumulation of  $^4\text{He}$  which is naturally present in the formation is measured. In the out-diffusion experiment, a pulse concentration of  $^4\text{He}$  is injected into the borehole and the concentration decrease due to diffusion is measured. An effective diffusion coefficient of  $2.1 \cdot 10^{-10} \text{ m}^2/\text{s}$  was obtained, but an estimated porosity of 30% was used because an excavation disturbed zone was created around the borehole. This estimate was not verified through measurements and is roughly double the value of undisturbed Opalinus Clay. (Rübel, et al., 2002) obtained a value for  $D_{\text{app}}$  of  $3.5 \cdot 10^{-11} \text{ m}^2/\text{s}$  from the helium profile in an outgassing experiment. However, this value is likely not very accurate due to an overly simplified model (Mazurek, et al., 2011). So no reliable diffusion coefficient for He in Opalinus Clay was available. Therefore, a collaboration between the University of Bern and SCK·CEN was set up to determine the diffusion coefficient of He in Opalinus Clay.



**Figure 2: Base-case tracer model for He at Mont-Terri (considering diffusion and in situ production)** (Figure taken from Mazurek, et al., 2011)

## 2 BOOM & OPALINUS CLAY PROPERTIES

Natural claystones like Boom and Opalinus Clay have a number of advantageous properties that make them a potentially suitable geological formation for hosting a repository for radioactive waste. They have a very low hydraulic conductivity (order of magnitude  $10^{-12} - 10^{-13} \text{ m/s}$ ). Therefore the main transport mechanism for solutes is molecular diffusion driven by concentration gradients. This is a very slow transport process, which means that any radioactive pollutants that are released in the host rock will migrate very slowly. (Yu, 2013) Both clays also have good sorption capabilities for pollutants as evidenced by studies by PSI (Paul Scherrer Institute) (Lauber, et al., 2000) and SCK·CEN (Maes, et al., 2004) on Opalinus and Boom Clay respectively. The clays are self-sealing, which means that cracks of excavation

disturbed zones (EDZ) are closed in time due to swelling of the rock when in contact with water. (Van Geet, et al., 2008) (Thury, 2002)

### 2.1 Boom Clay

Boom Clay is a plastic clay located in north-east Belgium and part of the Netherlands, deposited during the Tertiary (32.7 – 28.5 million years ago). The thickness of the Boom Clay layer at the Mol site is about 100 m and starts at a depth of 186 m. Extensive research is done at the HADES underground laboratory at SCKCEN in Mol, Belgium, to discern the hydrogeological, geochemical and mechanical properties of the rock and to analyse changes caused by excavation, heat generated by waste and engineered barriers. The clay has a porosity of approximately 37% and is saturated with water containing low concentrations of  $\text{NaHCO}_3$ . The composition of Boom Clay is fairly homogeneous. It consists of about 60% clay minerals (mainly illite, illite-smectite interlayered, kaolinite) and further quartz, pyrite, carbonates, K-feldspar ( $\text{KAlSi}_3\text{O}_8$ ) and Na-plagioclase ( $\text{NaAlSi}_3\text{O}_8$ ). (Wemaere, et al., 2008) (De Craen, et al., 2004)

### 2.2 Opalinus Clay

Opalinus Clay is a clay stone found in Switzerland and southern Germany. It was deposited as marine sediment about 180 million years ago during the Mesozoic. Extensive research has been done, and is still ongoing, at the Mont Terri Underground Rock Laboratory in north-western Switzerland to discern the hydrogeological, geochemical and mechanical properties of the rock and to analyse changes caused by excavation, heat generated by waste and engineered barriers.

Opalinus Clay is very heterogeneous, meaning its characteristics are location-dependent. At Mont Terri the porosity is approximately 18%, depending on the depth and clay content. The clay content rises slightly with increasing depth. The sample used in this experiment originates from the Schlattingen borehole. It has a porosity of 12% (Wersin, et al., 2012) and was taken perpendicular to the bedding plane. Opalinus Clay is saturated with pore water which has a similar composition to sea water, but diluted ( $\text{Na-Cl-(SO}_4)_2$ -water) The clay consists of 40-80% clay minerals, 10-40% quartz ( $\text{SiO}_2$ ), 5-40% calcite ( $\text{CaCO}_3$ ) and small amounts of siderite ( $\text{FeCO}_3$ ), pyrite ( $\text{FeS}_2$ ) and organic carbon. (Mont Terri Project, 2012)

## 3 TRANSPORT IN SATURATED MEDIA

Transport properties of solutes in the clay are determined by the network of micro, meso and macro pores. Extensive research has been done about the transport mechanisms in Boom Clay and Opalinus Clay. Diffusion was determined to be the dominating mechanism due to the low hydraulic conductivity of the rock. Advective transport is at best similarly slow as diffusion, if not slower. (Mazurek, et al., 2008) (Wemaere, et al., 2008) Diffusive transport of gases is described by two fundamental laws: Henry's law describes the solubility of gases and Fick's law describes the diffusion of the dissolved gases. (Marschall, et al., 2005)

Fick's 1<sup>st</sup> law of diffusion applied to porous media describes the diffusive flux  $F$  ( $\text{mol/m}^2\cdot\text{s}$ ) as the result of a concentration gradient. (Sandler, 2006)

$$F = -\varepsilon D_{pore} * \frac{\delta c}{\delta x} \quad (1)$$

With  $\varepsilon$  the diffusion accessible porosity,  $c$  the concentration ( $\text{mol/m}^3$ ) and  $D_{pore}$  the pore diffusion coefficient ( $\text{m}^2/\text{s}$ ). The pore diffusion coefficient is proportional to the diffusion coefficient  $D_0$  in pure water, with the proportionality factor depending on the geometry of the porous medium. The pore water concentration  $c$  is related to the bulk soil  $c_b$  by

$$c_b = \varepsilon R c \quad (2)$$

with  $R$  the retardation factor, which takes into account interactions between the diffusing solute and the medium (e.g. sorption). For most gases  $R$  equals 1 (Horseman, et al., 1996)

The diffusion equation describes the concentration  $c(x,t)$  of the solute as a function of the position ( $x$ ) in the clay core and of the time ( $t$ ). (Rebour, et al., 1997)

$$\frac{\delta c(x,t)}{\delta t} = D_{app} \frac{\delta^2 c(x,t)}{\delta x^2} \quad (3)$$

with  $D_{app} = \frac{D_{pore}}{R}$  the apparent diffusion coefficient. The apparent diffusion coefficient is the diffusion coefficient of a diffusant which is retarded in the porous medium (Horseman et al., 1996)

A through diffusion experiment (see figure 3) allows to measure the transport parameters  $\varepsilon R$  and  $D_{app}$ . A clay sample with length  $L$  is positioned between two continuously stirred water volumes, each with a length  $L_1$ . Initially, a tracer is injected in the water volumes at the inlet. The initial concentration of the injected tracer in this inlet volume is  $C_0$ . Elsewhere, the concentration is zero. Next, the concentration in the outlet volume is measured as a function of time.



**Figure 3: Configuration of the through diffusion model**

Assuming that both the inlet and outlet volume are very large, the change of concentration as a function of time can be neglected. Thus the boundary conditions become:

$$\begin{aligned} c(x = 0, t) &= C_0 \\ c(x = L, t) &= 0 \end{aligned} \quad (4)$$

The initial condition is

$$\begin{aligned} c(x = 0, t = 0) &= C_0 \\ c(x > 0, t = 0) &= 0 \end{aligned} \quad (5)$$

The diffusion equation was solved by (Aertsens, 2011) with these boundary and initial conditions:

$$c(x, t) = C_0 \left[ 1 - \frac{x}{L} - \frac{2}{\pi} \sum_n \frac{1}{n} \sin\left(\frac{n\pi x}{L}\right) \exp\left(-\left(\frac{n\pi}{L}\right)^2 D_{app} t\right) \right] \quad (6)$$

The flux at the outlet volume is

$$F(x = L, t) = -\varepsilon R D_{app} \left( \frac{\delta c}{\delta x} \right)_{x=L} \quad (7)$$

The quantity  $Q_{out}(t)$  that has diffused out of the clay is

$$Q_{out}(t) = S \int_0^t F(x = L, t') dt' \quad (8)$$

with  $S$  the clay core cross section. Substitution gives

$$\begin{aligned} Q_{out}(t) &= \\ \varepsilon R C_0 S L &\left[ \frac{D_{app} t}{L^2} - \frac{1}{6} - \right. \\ &\left. \frac{2}{\pi^2} \sum_n \frac{1}{n^2} (-1)^n \exp\left(-\left(\frac{n\pi}{L}\right)^2 D_{app} t\right) \right] \end{aligned} \quad (9)$$

The ratio of  $Q_{out}(t)$  and the outlet volume is the concentration in the outlet volume, which should remain much smaller than the concentration in the inlet volume according to the boundary conditions. Due to sampling, the concentration at the inlet decreases, so the boundary conditions are not fixed. With these changing boundary conditions the above analytical solution is no longer valid and the diffusion equation is solved numerically in COMSOL Multiphysics version 3.5a Earth Science

Module. A least squares fit of the outlet concentration versus the experimental data (performed with the MATLAB Optimization Toolbox) allows to determine the apparent diffusion coefficient  $D_{app}$  and the product  $\varepsilon R$ .

The initial concentration  $C_0$  can be calculated with Henry's law, which determines the solubility of a gas in pore water: at constant temperature the concentration of a substance in solution is proportional to the partial pressure of the substance in the gas phase which is in equilibrium with the liquid phase. (Oxtoby, et al., 2003)

$$c_i = H * p_i$$

with  $c_i$  the concentration of substance  $i$  in the liquid phase (mol/l),  $p_i$  the partial pressure of substance  $i$  in the gas phase (atm) and  $H$  Henry's constant (mol/l.atm).

## 4 MATERIALS AND METHODS

### 4.1 Experimental set-up

#### 4.1.1 Principle: Through diffusion test

Diffusion coefficients of dissolved gases are determined here in a cross through diffusion experiment. A clay core is mounted in a stainless steel diffusion cell and is connected at both sides to a water vessel. Both sides are pressurised with a gas at equal pressure to avoid advective transport. Gas saturated water (Henry's law) is circulated along a filter in contact with the rock core. The dissolved gases will diffuse through the core due to a concentration gradient. The changes in gas composition at both sides are monitored by micro gas chromatography ( $\mu$ GC), and so the through-diffusion fluxes of the gases can be quantified.

#### 4.1.2 Diffusion cell

The diffusion cell is a cylindrical stainless steel vessel which can be filled with a cylindrical block of clay with a diameter of 80 mm and a height of 25 mm for Opalinus Clay and 30 mm for Boom Clay. The top and bottom of the diffusion cell contain grooves to ensure good water circulation. Stainless steel filters were inserted between the clay and the top and bottom of the vessel to prevent the clay from clogging the grooves. These filters are thin (2 mm) and porous (40% porosity) so that their influence on the experiment is negligible.

For the Opalinus Clay experiment, a 2-component epoxy resin (Sikadur-52 Injection Normal) was applied between the clay and the side wall to prevent water from flowing along the interface. During the curing process the clay cell was put on a heating plate at 30°C, so that polymerisation starts at the bottom and propagates upward. This method reduces the risk of shrinkage cracks as a result of a slight volume decrease. In the case of Boom Clay, the application of a resin is unnecessary because Boom Clay is a plastic clay, which swells sufficiently when saturated with water, as opposed to the more indurated Opalinus Clay. (Tsang, et al., 2011)

After the curing process the diffusion cell was carefully welded shut. The welding was done with regular pauses to allow the clay to cool off in order to avoid changing the clay properties under the influence of heat.

Prior to the start of the diffusion experiments, the hydraulic conductivity of the clay samples was measured. The hydraulic conductivity is a measure of the ease at which water moves through the pores of a soil when subjected to a hydraulic gradient. Water is injected in the clay cell under a constant pressure of about 6 bar and the amount of water that enters the clay is measured. This is also a good test to detect potential leaks and preferential paths. Low salinity Pearson water was used for the Opalinus Clay, which approximates the composition of the pore water naturally present in the Opalinus Clay (Pearson, et al., 2003). The exact composition is given in table 1. Similarly, demineralised water was used for the Boom Clay. The hydraulic conductivity is determined by Darcy's law, which describes advective flow:

$$K = \frac{1}{A} \frac{dV}{dt} \frac{l}{\Delta P}$$

with A the area of the cross-section of the clay sample in m<sup>2</sup>, dV/dt the water flow rate in m<sup>3</sup>/s, ΔP/l the pressure gradient over the length of the sample (l). The pressure ΔP is expressed in m water column. The experiment lasted 25 days. (Jacops, et al., 2009)

**Table 1: Pearson water composition used for the experiments on Opalinus Clay (Pearson, et al., 2003)**

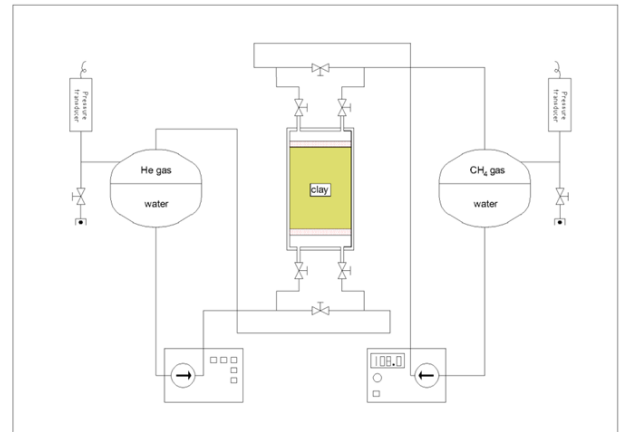
	mg/l
NaCl	6132
Na <sub>2</sub> SO <sub>4</sub>	1632
CaCl <sub>2</sub> ·2H <sub>2</sub> O	1020
MgCl <sub>2</sub> ·6H <sub>2</sub> O	1004
SrCl <sub>2</sub> ·6H <sub>2</sub> O	84
KCl	60
NaHCO <sub>3</sub>	50

#### 4.1.3 Set-up

The clay cell is located between two 1-litre stainless steel water reservoirs, each of which are filled with 0.5 litre water and pressurised with a different gas (see figure 4). An initial pressure of 10 bar was chosen so that the experiment could be concluded in a reasonable time frame (Henry's law: gas dissolves better at higher pressure). O<sub>2</sub> and CO<sub>2</sub> are removed from the water by passing the water through a Teflon tube in a vacuum space (Alltech water degasser). Gases diffuse out of the water through the tube and the water is stored in a N<sub>2</sub> atmosphere. Water was used similar to in situ conditions of the clay. In the Boom Clay experiment, water with 0.014 mol/l NaHCO<sub>3</sub> was used, which mimics the ionic strength and main constituents of the Boom Clay pore water (De Craen, et al., 2004). Low salinity Pearson water was used for the Opalinus Clay experiment. The

ambient temperature was kept constant at 21±2°C during the experiment in order to keep the pressure constant. Each reservoir is equipped with a pressure gauge (Druck, PTX 510) to monitor the pressure.

The water is circulated over the stainless steel filters by means of a magnetically coupled displacement pump (Ismatec) at a flow of 3 ml/min. This type of pump was chosen to reduce the risk of leakage due to the absence of a direct coupling between pump drive and pump head. All connections consist of metal-metal connections (Swagelok) to avoid leakage. (Jacops, et al., 2009)



**Figure 4: Diagram of experimental set-up used to measure diffusion of dissolved gases**

#### 4.1.4 Workflow

The pressure sensors (Druck, ptx 510) were installed on the water reservoirs and calibrated, and the clay cell and water reservoirs are connected. At this point the cell is still isolated from the rest of the system so diffusion through the clay cannot start yet. Both reservoirs are pressurised at 15 bar with their respective gases during 48 hours and the pressure is monitored to detect leaks. When a leak is present, it can be found using a gas leak detection spray or, in the case of small leaks, a helium detector. When the set-up was found leak proof, it was thoroughly rinsed several times by filling it with gas and subsequently evacuating the gas with a vacuum pump. This was done to remove residual gas from previous tests and avoid air-contamination. Next a sample of reservoir 1 was analysed to ensure no gas of reservoir 2 was present and vice versa.

At the start of the through diffusion experiment, both reservoirs are pressurised just above 10 bar with their respective gases. Next the by-pass valves are closed and the valves leading to the clay core are opened. The pressure changes a bit at this point because the clay core is still at a lower pressure and the solubility of the gases changes due to the change in pressure. When the pressure has stabilised, the pressure in both reservoirs is lowered to 10 bar. It is important to keep these pressures equal to



avoid advective transport as a result of a pressure gradient.

## 4.2 Sampling

Samples were taken with 6 ml stainless steel samplers which are thoroughly rinsed previous to sampling by cycles of flushing with gas (that has no impact on the measurement) and subsequent evacuation of the gas by means of a vacuum pump. Small volume samplers were used to avoid disturbing the gas pressure inside the reservoirs too much. A small pressure drop as a result of sampling is inevitable. The pressure of the sample is reduced to approximately 2 bar (absolute pressure) by expanding the gas into a 25 ml sampler (vacuum). Next the sample is analysed with a micro gas chromatograph ( $\mu$ GC) (Varian).

## 4.3 Gas chromatography analysis

Diffusion of a gas from the high concentration reservoir to the low concentration reservoir through the clay core is observed by measuring the concentration in the low concentration reservoir with micro gas chromatography. Argon and helium serve as carrier gas, depending on the gas that has to be measured. The column consists of a molecular sieve, a material with very small and uniform pores (5Å), which separates molecules based on their size; small molecules pass through the sieve more easily than large ones. (Hjertén & Mosback, 1962)

A Thermal Conductivity Detector (TCD) is used to analyse the sample qualitatively and quantitatively. It consists of a Wheatstone bridge with two temperature-dependent resistors in a temperature-controlled cell. The carrier gas flows over one resistor, while the column flow flows over the 2<sup>nd</sup> resistor. When the column flow consists exclusively of carrier gas, the Wheatstone bridge is balanced. When the column flow also contains another gas, the thermal conductivity changes, causing the resistance to change and consequently an electrical signal is generated. (BUCK scientific, 2012)

Prior to each measurement, the  $\mu$ GC was calibrated with a standard gas of known concentration. The retention time of a peak identifies which element the peak belongs to (qualitative indicator), while the peak area is proportional to the concentration.

Argon is a special case. Measurement of Argon is sensitive to oxygen contamination of the sample, because Argon and oxygen pass through the column at similar speeds, their peaks measured by the  $\mu$ GC overlap. Oxygen contamination occurs by attaching the sampler to the set-up and the chromatograph. Therefore a special sampling procedure was devised, which enables rinsing of the sampler and tubing connected to the experimental set-up and the  $\mu$ GC as described above while avoiding air contact, by connecting a vacuum pump. The downside of this method is that an extra vacuum section was introduced between sampler and  $\mu$ GC, causing a pressure drop and consequently a reduction of total number of replicate measurements for one sample, because the GC

can only measure as long as the sample is in overpressure.

## 5 RESULTS & DISCUSSION

### 5.1 Hydraulic Conductivity

A hydraulic conductivity of  $3.3 \cdot 10^{-12} \text{ m/s}$  for Boom Clay and  $1.8 \cdot 10^{-13} \text{ m/s}$  for Opalinus Clay was measured. These results are consistent with literature data which are in the order of  $10^{-12} - 10^{-13} \text{ m/s}$  (Van Loon, et al., 2003) (Yu, et al., 2013). These low values for the hydraulic conductivity mean that the clays are practically impermeable for groundwater flow and led to the conclusion that the main transport mechanic for solutes is diffusion, and that advective pore water flow is negligible. This is confirmed by in situ diffusion experiments conducted at the Mont Terri Underground Rock Laboratory. (Mazurek, et al., 2008)

### 5.2 Boom Clay experiment

The experiment lasted three months. Figures 5 and 6 show the results of the neon and argon measurements. Using COMSOL to fit the theoretical model to the measured data, apparent diffusion coefficients of  $(5.1 \pm 0.1) \cdot 10^{-10} \text{ m}^2/\text{s}$  and  $(2.0 \pm 0.1) \cdot 10^{-10} \text{ m}^2/\text{s}$  were obtained for neon and argon respectively. Multiplied by the clay's porosity (0.37), this results in effective diffusion coefficients of  $1.9 \cdot 10^{-10} \text{ m}^2/\text{s}$  for neon and  $7.4 \cdot 10^{-11} \text{ m}^2/\text{s}$  for argon.

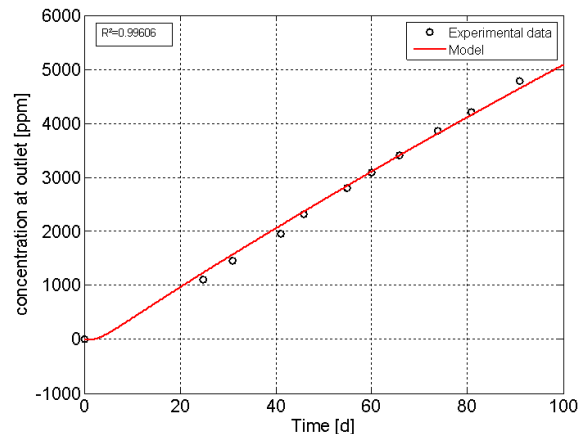
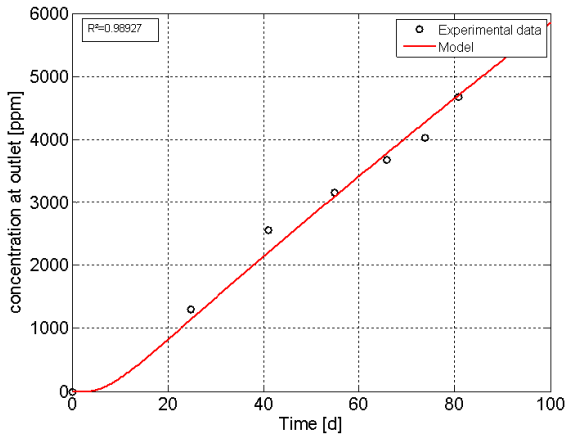


Figure 5: Neon diffusion through Boom Clay: measurements and fit



**Figure 6: Argon diffusion through Boom Clay: measurements and fit**

The obtained diffusion coefficients of Ne and Ar are used to investigate the relationship between the size of the gas molecule and the diffusion coefficient. Combined with the values for the other gases (He, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and Xe) measured by SCK-CEN in previous experiments (see table 2), following relation was found (excluding He as it shows deviating behavior):  $D_{app} = 5 \cdot 10^{-9} e^{-0.834x}$  with  $x$  the kinetic diameter of the gas molecule in Angström (see figure 7). By using this relationship, the diffusion coefficient of other gases like hydrogen can be predicted. The results also indicate that neon might be a better proxy for hydrogen than helium, because helium deviates from relation described above.

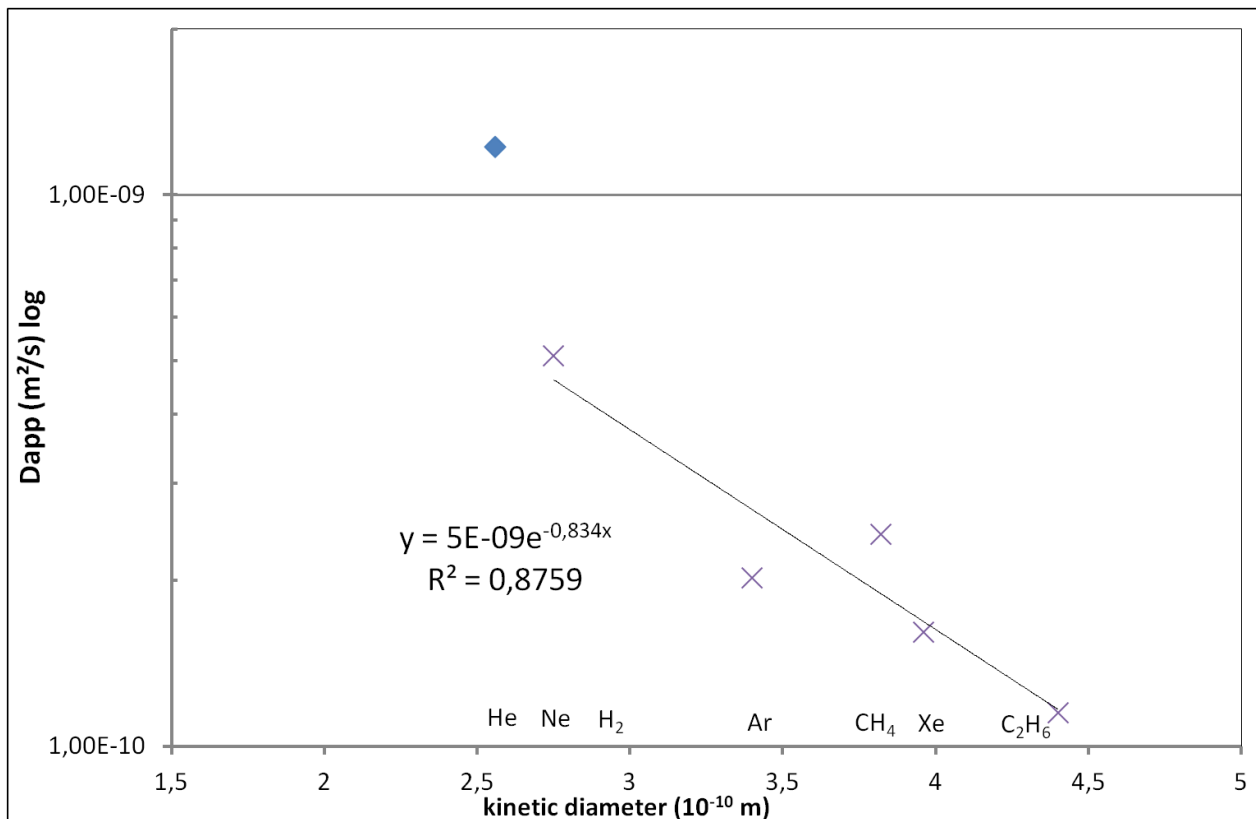
**Table 2: Apparent diffusion coefficients for gases in Boom Clay and their kinetic diameters as found in (Hirschfelder, et al., 1954)**

	Kinetic diameter (Å)	$D_{app}$ (m <sup>2</sup> /s)
He	2.56	$1.22 \cdot 10^{-9}$
CH <sub>4</sub>	3.82	$2.42 \cdot 10^{-10}$
C <sub>2</sub> H <sub>6</sub>	4.40	$1.15 \cdot 10^{-10}$
Ar	3.40	$2.02 \cdot 10^{-10}$
Xe	3.96	$1.61 \cdot 10^{-10}$
Ne	2.75	$5.10 \cdot 10^{-10}$

### 5.3 Opalinus Clay experiment

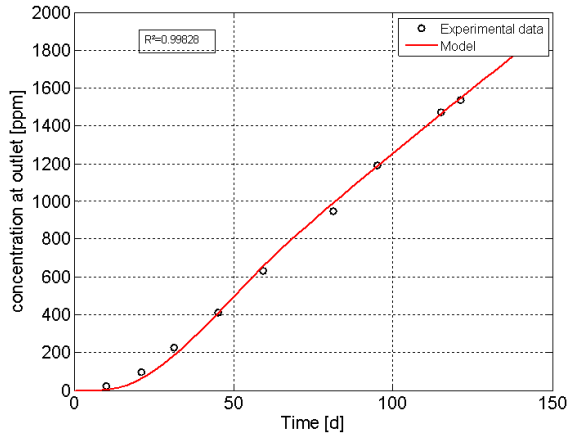
The experiment lasted four months and measurements were done about every two weeks. Figure 8 shows the results for helium. During the first week(s) of the experiment, one of the pumps failed regularly. This failing causes retardation of the diffusion process because the pumps are needed for mixing the gas and water phase. Using COMSOL to fit the theoretical curve to the measured data, the fit therefore resulted in a retardation factor of 12.3, but no sorption of noble gases is expected. This apparent retardation is only due to the malfunctioning pump at the start of the experiment.

The apparent diffusion coefficient  $D_{app}$  of helium in Opalinus Clay (recalculated as if no retardation took place) perpendicular to the bedding plane was determined to be  $5.4 \cdot 10^{-10} \text{ m}^2/\text{s}$  with a 95% confidence interval of  $5.1 \cdot 10^{-10} - 5.6 \cdot 10^{-10} \text{ m}^2/\text{s}$ . Multiplied by the clay's porosity (0.12), this results in an effective diffusion coefficient  $D_{eff} = 6.5 \cdot 10^{-11} \text{ m}^2/\text{s}$ .



**Figure 7: Relation between the apparent diffusion coefficient of gases in Boom Clay and their kinetic diameter**





**Figure 8: Helium diffusion through Opalinus Clay: measurements and fit**

As there are no independent data to compare, the soundness of the data is verified otherwise. The ratio of apparent diffusion coefficients for tritiated water (HTO) and iodide tracers in Boom and Opalinus Clay is 2.80 in both cases (see table 3). This ratio is function of the pore structure of both materials, hence it is a proportionality factor which can also be used for other elements, hence He. Using this ratio and the diffusion coefficient of He that is determined for Boom Clay, an estimation for the apparent diffusion coefficient of He in Opalinus Clay of  $12.2 \cdot 10^{-10} / 2.8 = 4.36 \cdot 10^{-10} \text{ m}^2/\text{s}$  can be made, which is relatively close to the experimental result above

**Table 3: Apparent diffusion coefficient ratio's in Boom and Opalinus Clay** <sup>a</sup>(Bruggeman, et al., 2010) <sup>b</sup>(Bruggeman, et al., 2009) <sup>c</sup>(Van Loon, et al., 2003) <sup>d</sup>(Van Loon, et al., 2004)

	I	HTO
$D_a$ Boom Clay ( $\text{m}^2/\text{s}$ ) Samples from Mol	1.4 * $10^{-10}$ <sup>a</sup>	2.3 * $10^{-10}$ <sup>b</sup>
$D_a$ Opalinus Clay ( $\text{m}^2/\text{s}$ ) Samples from Mont Terri URL	5.0 * $10^{-11}$ <sup>c</sup>	8.2 * $10^{-11}$ <sup>d</sup>
Ratio $D_a$ BC/ $D_a$ OC	2.8	2.8

## 6 CONCLUSION

The apparent diffusion coefficients for Ne and Ar in Boom Clay were determined with good precision:  $5.1 \cdot 10^{-10} \text{ m}^2/\text{s}$  for Ne and  $2.0 \cdot 10^{-10} \text{ m}^2/\text{s}$  for Ar. Combining these data with data obtained for other gases, a relationship between the diffusion coefficient and kinetic diameter of the gas was obtained, which allows prediction of the diffusion coefficient of other gases like hydrogen.

The diffusion coefficient for He in Opalinus Clay was determined to be  $5.4 \cdot 10^{-10} \text{ m}^2/\text{s}$ . The measured value for He corresponds well to an estimated value based on the ratio of diffusion coefficients for unretarded species obtained on Boom Clay and Opalinus Clay and should allow for a better interpretation of He natural tracer transport profiles in Opalinus Clay.

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