An experimental methodology to assess the impact of desaturation on gas diffusion in clay based materials

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Abstract. The transport of gas in clay-based materials is dominated by diffusion. SCK CEN has studied and recorded an extensive data set of diffusion coefficients of gases in various saturated clays (Boom Clay, Opalinus Clay, Callovo-Oxfordian claystone and bentonites) used in Europe as host formations or in engineered barrier systems in the context of deep geological disposal of high and intermediate level nuclear wastes. However, partially saturated conditions may exist during the life cycle of a radioactive waste repository. The current study aims at establishing an experimental method to measure the diffusion coefficients of various gases in partially saturated clay-based materials by means of double through diffusion tests (cross diffusion of gases across the porous sample, driven by concentration gradients) and to assess the impact of desaturation on gas diffusivity. Historically, gas diffusion measurements have been performed under dissolved conditions with continuous water and dissolved gas flow around the clay sample. However, since the saturation degree of the sample has to be constant, a novel setup has been designed and optimized to operate under a pure gas phase under controlled relative humidity (RH). The experimental concept consists of cross diffusion of gas mixtures from two reservoirs at a fixed relative humidity on either side of the sample cell, namely, the upstream and downstream reservoirs. The RH is controlled using the same saturated salt solutions in both reservoirs. During the experiment, gases will diffuse from the upstream to the downstream reservoir. By measuring the change in gas composition in the downstream reservoir with a gas analyzer equipped with a mass spectrometer (which expresses the gas composition in terms of partial pressure), the gas flux and hence the diffusion coefficient is estimated by applying steady state Fick's first law. The experimental methodology has been validated by performing an experiment on a sandy-clay sample of known petrophysical properties, at full saturation.

1 Introduction

In various European countries, low permeability clay formations are currently being considered or have already been selected as potential host formations for the geological disposal of radioactive wastes [1]. Deep geological disposal is currently deemed as the best solution for the final disposal of high and intermediate level radioactive wastes around the world. One such example of a low permeability clay formation is Boom Clay, a poorly indurated plastic clay, found at depths between 200 and 400 metres in Belgium [1,2]. However, the permanent geological disposal of radioactive waste comes with its own challenges, one of which is the evacuation of gas generated by various mechanisms in the disposal system, such as corrosion of metallic components in the waste and packaging or radiolysis of water and subsequent microbial conversion of organic components in the waste forms [3,4]. In the case of gas production by anaerobic corrosion of metal components, the escape of gas from the repository is possible by diffusion, dilatant pathway flow, two phase flow, or fracturing of the backfill, host formation or EBS (Engineered Barrier System) components. While some of these mechanisms are reversible, fracturing, for example, can lead to potential preferential pathways for radionuclide transport, which could be permanent. The imminent production of gases in a waste repository bears the concern that the pore water of the host formation and the backfill become saturated with gas after the initial diffusion stage, which may potentially lead to a free gas phase formation. This could cascade into a gas pressure build-up within the repository environment, if the rate of gas generation is not offset by the diffusive gas transport through the host formation. However, the transport of these gases is then primarily driven by diffusion [5,6].

As diffusion is the transport phenomenon of interest in this particular setting, it then becomes important to determine gas diffusion coefficients, to provide a view on the absolute rate of transport of different diffusing species through the clay formations [7]. While gas diffusion coefficients have been measured and characterized for fully saturated clay based materials (porous materials with relatively higher clay content in terms of mineralogy), there is little to no information on

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gas diffusivities in unsaturated clays. This is a significant knowledge gap, given that unsaturated conditions are expected to exist at some points during the life cycle of the waste repository [8–10]. Unsaturated conditions in the host clay (and clay based EBS) can also result from temperature and pressure changes emanating from the conditions in and around the radioactive waste packages [11] Thus, for improving gas diffusion process understanding, it is also important to study gas diffusion in partially saturated clay based materials as well as to understand and link the processes that affect these gas diffusivities in partially saturated conditions. It is worth noting that the overall water content of the partially saturated zones within the radioactive waste repository is not expected to be strongly below full saturation [12]. Therefore, an interest range of 70-100% water saturation (weight/wet weight) has been fixed to study the effects of desaturation on gas diffusivity.

Historically, experiments of diffusion of gases in clays have been performed in fully saturated conditions, with gases being transported as a dissolved species. For this purpose, the double-through gas diffusion methodology, as described in [7], has been employed to make significant advances in measuring diffusion coefficients of gases [7,13]. However, since the experimental conditions are different for measurements in partially saturated clays in this study, a novel setup has been designed and assembled to make diffusivity measurements in purely gaseous conditions under controlled RH, while following the same double through diffusion methodology. Therefore, the main objective of this study is to establish and validate the experimental methodology and test setup for measuring gas diffusion coefficients of gas mixtures in gaseous conditions using a fully saturated sample (for which reference measurements exist), which should subsequently allow for gas diffusivity measurements in the 70-100% saturation range in clay based materials.

2 Materials and methods

For the purpose of measuring gas diffusion coefficients in partially saturated clays, an approach different from the conventional dissolved gas transport is proposed. The setup is envisioned to be able to conduct experiments in a pure gas phase, to keep the saturation of the clay sample constant, without wetting or drying it during the experiment.

Since clays, in their natural state in the environment are fully saturated, a drying technique has to be employed to lower the moisture content of the clay sample, while keeping the physical integrity of the clay specimens intact. A non-destructive technique called the vapour equilibrium technique is used to lower the saturation of clay samples for the experiments in partially saturated conditions [14]. Still, the primary focus of this study is the design and the validation of the experimental diffusion setup in pure gaseous conditions.

2.1 Experimental diffusion setup

The experimental setup is based on the through-diffusion setup used in [7]. It consists of two diffusion chambers or reservoirs. As a convention, the left reservoir represents the upstream reservoir for a mixture of 50% helium in methane (gas mixture 1) and the right reservoir is the upstream reservoir for a mixture of 50% xenon in ethane (gas mixture 2). The upstream and downstream reservoirs denote the high and low concentration reservoirs, respectively. A schematic is shown in Fig. 1.

All diffusion experiments are performed at pressures at or marginally above ambient pressure, with concentration gradients being the only driving force for the transport process. The relative humidity in the reservoirs is maintained by using selected saturated salt solutions, thus keeping the moisture content of the clay sample constant throughout the experiment.
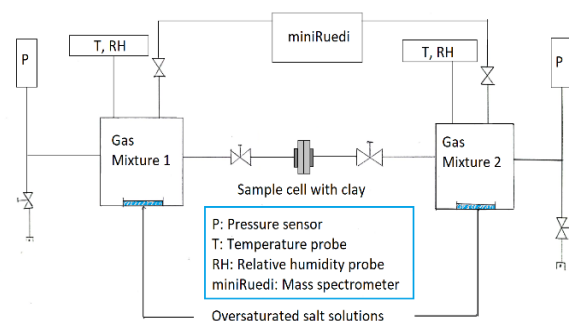
Fig. 1. Schematic of experimental setup

The gas analysis for the planned experiments makes use of mass spectrometry (MS), which is performed using a miniRUEDI (Gasometrix GmbH, Switzerland) [15]. This is a portable gas analyser, equipped with a quadrupole mass spectrometer (Standford Research Systems RGA200), with two types of detectors, namely, the electron multiplier and the Faraday cup detectors.. The mass spectrometer works on ion currents peaks measured by the detectors and maps it to partial pressures of different gas species present in a mixture relative to a reference or standard gas mixture whose composition is known and defined. A sample measurement for xenon as a major component (49.9%) and a minor component (0.1%) in two different gas mixtures is shown in Table 1 and Table 2. The number 132 signifies the peak corresponding to the analyte in the m/z scale. The F stands for the Faraday cup detector.

Table 1 MS measurement error of xenon as a major component (49.9%)

Sample	Partial pressure (mbar)*	Absolute error (mbar)	Relative Error (%)
SampleGas1	499.42	0.42	0.084
SampleGas2	501.07	2.07	0.414
SampleGas3	500.64	1.64	0.328

*at m/z 132_F peak

Table 2 MS measurement error of xenon as a minor component (0.1%)

Sample	Partial pressure (mbar)*	Absolute Error (mbar)	Relative Error (%)
SampleGas1a	0.981	-0.019	-1.9
SampleGas2a	1.004	0.004	0.4
SampleGas3a	1.08	0.08	8

*at m/z 132_F peak

Tables 1 and 2 show the analysis of standard gases containing 49.9% xenon in ethane, with 0.1% helium in methane and 0.1% xenon in ethane, with 49.9% helium in methane, respectively. It can be seen from the measurements that the accuracy for even trace amounts of gases at ambient pressure is quite high. The advantage of miniRUEDI is that it has been designed to work with low pressure gases, with a low limit of detection and a very low gas consumption rate.

2.2 Test sample

To validate the diffusion setup, a test sample is selected with characteristics similar to those in reference literature with available diffusivity values [16]. A sandy clay material called Eigenbilzen sand is used, which is a glauconite-rich, fine to medium grained sandy clay found in the layer just above Boom Clay, in Belgium [16]. The sandy clay sample used in this study stems from the ON-Mol-2A-189 core, drilled perpendicular to the bedding plane in November 2014, at a depth of nearly 296 metres, in Mol, Belgium.

The sample was extracted from the drill core and shaped to dimensions 38 mm in diameter and 20 mm in height. This was done using a dedicated cutting tool, with the help of a hydraulic press. The sample was shaped and smoothened by hand with a knife and then pressed into the sample cell, which was subsequently fitted into the setup. Traditionally, diffusion setups measuring dissolved gas diffusivities take advantage of the swelling potential of the clay plugs on contact with water to seal the sample cell interface. However, in this study, the sealing was achieved by using a high relative humidity to keep the sample from shrinking and creating a gas pathway along its perimeter. This was confirmed with a pressure test where a pressure gradient of 0.1 bar was applied across the two reservoirs using the same gases. The lack of pressure convergence meant that there was no distinct pathway between the sample and the cell that could be accessed by the gases.

2.3 Experimental methodology

In preparation for the diffusion measurement, the reservoirs were flushed with pure nitrogen to remove traces of atmospheric gases remaining in the reservoirs and/or the tubing connecting them to the cell. The nitrogen was then flushed out using the test gases in each reservoir. For the left reservoir, a mixture of 50% helium in methane was used for flushing and filled up to a pressure of 0.1 bar above ambient pressure. The same procedure was followed for the right reservoir using a 50% mixture of xenon in ethane.

The standards used for calibration of the mass spectrometric gas analyser are as follows:

- Left reservoir: 49.9% helium in methane, 0.1% xenon in ethane.
- Right reservoir: 49.9% xenon in ethane, 0.1% helium in methane.

All test gases were procured from Air Products, Belgium. The relative humidity in each reservoir was monitored via temperature sensitive dew point probes (Indigo 520) from Vaisala.

Before starting the experiment and allowing the gases to diffuse across the sample, a zero or baseline reading is performed to quantify background noise, residual traces or fragment interferences. The experiment starts when the test gases come into contact with the sample, dissolve in the pore water of the sample and are transported as a dissolved species across the sample in the case of water saturated samples and once again migrate into the free gas phase on the way to the downstream reservoir. On the other hand, if the sample is only partially saturated, there is a combined effect of diffusion of gases in water filled pores as a dissolved species, as well as diffusion in the gas phase in pores which are de-saturated or partially saturated. The sampling is done in the downstream reservoirs, where the composition of the gas mixture is analysed by the mass spectrometer. Thus, information about the concentration increase with respect to time is obtained for each diffusing component, from which the flux, and hence, diffusivity can be calculated by using Fick's first law of diffusion.

This work is more focused on providing a validation step for the novel setup and methodology. Hence, the natural step is to perform an experiment under conditions for which reference data exists. For this purpose, the validation experiment was performed at full saturation (>99% water saturation), with 50ml of water in each reservoir to keep a high relative humidity.

2.4 Diffusion modelling

The diffusion model is built on Fick's first law, to obtain the effective diffusion coefficients of different diffusing gases. Contrary to the diffusion modelling performed in previous studies in this domain [16], the fitting of diffusion coefficients is based on steady state Fick's first law and not Fick's second law. This is because the bulk concentrations in the upstream and downstream reservoirs in the current pure gas phase experiment are nearly constant since the rate of consumption of miniRUEDI is very low.

The fitting is done based on an analytical solution of Fick's first law, with gas A diffusing into static bulk B. While the bulk B (upstream composition) is not exactly static, the concentration drop in the upstream reservoirs is so small that for all purposes, can be considered

negligible. Therefore, the estimation of diffusion coefficients is based on equation (1) .

$$N_A = \left(\frac{D_{eff}P}{RTz}\right) \ln\left(\frac{1\text{-}y_{A2}}{1\text{-}y_{A1}}\right) \tag{1}$$

In equation 1, D_{eff} stands for diffusivity (m^2 s^{-1}), N_A is the gas flux (kmol m^{-2} s^{-1}), P is the total pressure (kPa), R (m^3 kPa kmol^{-1} K^{-1}) is the gas constant, T (K) is the absolute temperature and z (m) is the diffusion distance. y_{A2} and y_{A1} are the concentration values (in terms of mole fraction) of the diffusing species in the downstream and upstream reservoir, respectively. In equation (1), the term D_{eff} represents the effective diffusion coefficient of gases across the porous sample.

The porosity η of the Eigenbilzen sand samples has been estimated to be 40% from a previous study [7,16].

2.5 Water permeability measurements

An important step in the experimental scheme before the diffusion experiment is the determination of water permeability K (m/s), also known as hydraulic conductivity. It is a measure of the ease of migration of water through a porous sample under an applied external pressure.

The experimental setup for measuring permeability is the same as the one used on a similar sandy clay sample in a previous study [17]. This setup has not been modified because it is highly reliable and has been used to make K measurements for different samples [17]. Hydraulic conductivities are generally measured by imposing constant pressure gradients across the faces of the sample. However, the pressures are not required to be as high since the sandy clay used in this study is of higher permeability than engineered barrier systems (EBS) materials like concretes. Synthetic pore water (0.014M NaHCO$_3$) is continuously circulated through the sample until a stable K value is obtained. This particular composition is used in order to mimic the geochemistry of the pore water of Boom clay found in the region of Mol [18]. Darcy's law is used to calculate the hydraulic conductivity.

3 Results and discussion

3.1 Water permeability measurements

The K measurement is done on a sample from the same drill core as the sample used in the diffusion experiment. The variability between samples from the same core is minimal. The results, compared with a previous reference sample K17 [16] are shown in Table 3. The reference sample K17, considered throughout this paper for permeability and diffusivity comparisons, was taken from the core ON-Mol-1 39b, drilled perpendicular to the bedding plane, in 1997, in Mol, Belgium [16].

The permeability values of Eigenbilzen sands have been reported to be higher than those of Boom Clay [16]. This is attributed to the presence of a larger sand content and larger pores than Boom Clay, leading to a different pore size distribution.

Table 3 Water permeability measurement for analysed and reference samples [16]

Sample type	name	orientation	K (×10^{-10} m s^{-1})
Eigenbilzen sand	K17 (ref)	Perpendicular	4.2 ± 0.2
Eigenbilzen sand	Mol2 A-189a	Perpendicular	3.4 ± 0.7

3.2 Diffusivity measurements

The diffusion experiment was run for a total of 62 days, with enough points to ensure a linear concentration evolution and hence, a steady state solution of Fick's law as shown in equation 1 can be used to fit the data. A sample data fit is shown in Fig. 2.
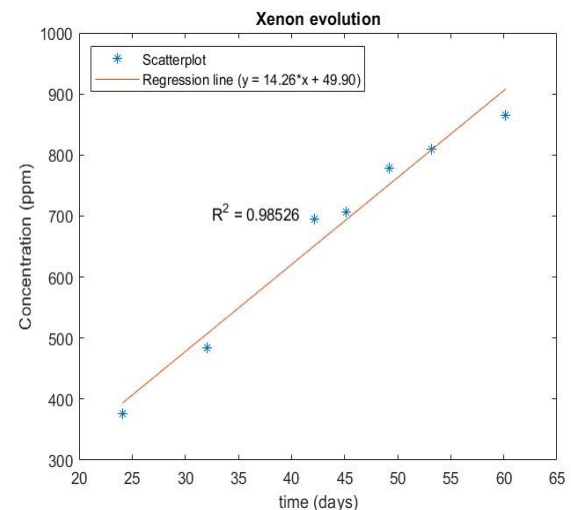
Fig. 2 Data fit for xenon diffusion in test sample

The total flux, given by the term N$_A$ in equation 1 can be calculated using the slope of the curve in Fig. 2. Equation (1) is then solved to estimate the effective diffusion coefficient of the diffusing gases.

The gas diffusivities measured are shown in Table 3, along with reference values and D$_0$ (m^2/s) values, which represent the diffusion coefficient of the gasses in water.

Table 4. Overview of diffusion coefficients for the test sample along with reference data from Jacops et al., 2017 [16], and diffusion coefficients in water (D_0).

		He	CH$_4$	Xe
D_0 (×10^{-10} m^2 s^{-1})		72.8	18.4	14.7
Sample	η (-)	D_{eff} (×10^{-10} m^2 s^{-1})		
K17 (ref)	0.4	5.82	2.44	N/M*
Mol-2A-189b	0.4	4.67	1.94	2.01

*N/M – not measured

The diffusion coefficients of gases in the test sample are in general, an order of magnitude or thereabouts lower than diffusion of the same gases in water, as shown in Table 4. This could be explained by the fact that gas diffusion only occurs through the pores of the clay sample, which has a certain tortuously connected pore network. The diffusion coefficients are however, in line with previous measurements made in a similar fully saturated sample, under dissolved conditions. The experimental study with Eigenbilzen sand sample K17 measured ethane instead. While an ethane measurement was also described in the experimental methodology, this was hampered by the presence of trace amounts of nitrogen captured at the same m/z peak in the mass spectrum. This problem of interfering fragments of the same m/z peak in the mass spectrum has been described in detail in the deconvolution methodology described in the work by Brennwald et al., 2020 [15].

While only the validation experiment performed at full saturation has been described in this work, the general principle was to establish a methodology which would allow for diffusion measurements in partially saturated clay samples. Clays, in particular, those with large proportions of swelling clay minerals, exhibit shrinking behaviour on exposure to low relative humidity, which corresponds to higher suction. Performing gas diffusion experiments on partially saturated clay samples, for example, 70% water saturation, is not possible with the classical dissolved diffusion setup. Thus, further work involves measurement of diffusion coefficients in unsaturated clays.

For the purpose of measurement of gas diffusivities in partially saturated clays, the samples will be conditioned in lower relative humidity desiccators to correspond to saturation levels depending on the material under consideration. Meanwhile, the entire experimental setup described in Fig. 1 will be maintained at the same relative humidity as the sample conditioning step throughout the experiment by placing the same saturated salt in both reservoirs, thus keeping the saturation of the sample constant.

4 Conclusions

The gas diffusion coefficients of three gases were measured in a novel experimental setup designed to handle unsaturated clay samples. Three gases have been used to demonstrate that diffusivity measurements can be made across a range of gas molecular sizes from helium to xenon. The methodology will be adapted to clay samples of lower saturation, with the working principle remaining the same. The data measured by employing the methodology presented in this study are in close agreement with previous reported experimental measurements despite the different methods of analysis and the usage of a pure gas phase instead of dissolved gases.

The use of the new gas analyser with a mass spectrometer allows for precise measurements of even minute traces, with a low detection limit, with minimal pressure loss. Hence, the experiment has been designed and validated at pressures as low as ambient pressures. A diffusion model based on steady state Fick's first law has been used to determine effective gas diffusivities.

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