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P. Bachaud[1,2], Ph. Berne[1], P. Boulin[1,3,4], F. Renard[5,6], M. Sardin[2], J.P. Leclerc[2]

[1] *CEA, LITEN, L2T, F-38054 Grenoble, France*
[2] *LSGC, Nancy-Université, CNRS - 1 rue Grandville, BP 20451, 54001 Nancy Cedex, France*
3 *Agence nationale pour la gestion des déchets radioactifs (Andra), Parc de la Croix Blanche, 92298 Châtenay-Malabry, France*
[4] *Laboratoire d'étude des Transferts en Hydrologie et Environnement, CNRS/INPG/IRD/UJF-UMR 5564, BP n° 53, 38041 Grenoble Cedex 9, France*
[5] *LGCA-CNRS-OSUG - University Joseph Fourier, Grenoble I BP 53, 38041 Grenoble, France*
[6] *Physics of Geological Processes, University of Oslo, Oslo, Norway*

Abstract: It is shown how a simple gas tracer technique can contribute to the determination of transport characteristics of tight rock formations. Main obtained parameters are intrinsic permeability and the Klinkenberg coefficient; permeability as low as 10^{-21} m^2 is easily attainable. Some information is also gained on diffusion characteristics and porosity. An example of application is given using caprocks from a deep saline aquifer in the Paris basin.

Introduction

Storage of carbon dioxide in deep saline aquifers is a promising technique to reduce greenhouse gas emissions. To be accepted by the public, long-term safety has to be proven. Safety predominantly depends on the sealing efficiency of the caprock formation above the aquifer, hence the need to thoroughly determine the physico-chemical properties of that formation. Among these properties, *permeability* is obviously important since it will largely control the flux of CO_2 that may escape under the influence of the pressure excess in the CO_2 bubble. Determination of the *diffusion properties* is also required since they will govern how dissolved CO_2 may migrate through the pore water to the outside.

Measurement of permeability is quite a routine procedure in high permeability rocks such as hydrocarbon reservoirs or aquifers. However, the permeability of caprocks is so low that conventional techniques are difficult to apply, not to say wholly inadequate. The aim of the present study is to illustrate how the use of a particular gas tracer technique can contribute to the measurement of low permeabilities and, to some extent, of diffusion coefficients. This technique is applied to measure the transport properties of a carbonate caprock with permeability lower than 10^{-19} m^2.

Material

The samples used here come from the Charmottes oilfield located about 100 km south-east of Paris (France). They are part of the top of the Dogger (Bathonian and Callovian geological units) and were taken at four different depths between 1900 and 2000 m.

The samples are compact and highly consolidated micritic marls. Mineralogical analysis showed that they contain carbonates (calcite and ankerite) with various proportions of quartz and minor clays. Mercury porosimetry tests were made and yielded low values of about 2 to 5 %. Pore size distributions were found unimodal with a peak well under 100 nm.

Whether these carbonated rocks can actually be considered as a good confining medium for CO_2 sequestration is unsure. Working with these samples is nevertheless interesting because one of the problems with caprocks is the complex chemical interactions with the fluid that are expected to produce both dissolution and precipitation of minerals.

These interactions will be enhanced and made more easily observable by the nature of the samples. In addition, the samples are used as a model system to develop measurement methodologies.

"Conventional" techniques for permeability measurement
"Conventional" techniques for the measurement of permeability involve imposing a pressure gradient across a sample and measuring the resulting flux. They can be divided into:

- steady-state tests: the pressure gradient is kept constant and the flow rate is measured once a constant value is reached,
- pulse tests: the sample is placed between two closed reservoirs; a pressure step is applied to one of them and the fluid is let to flow into the second one while the pressure difference is monitored.

According to Davy et al. (2007), the former technique can be used down to 10^{-19} m^2; below that value, the latter technique should be preferred; the price to pay is that the tests are more complicated to make and to interpret.

Both techniques can be used with liquids or gases. In our case, gases are advisable because i) we are indeed interested in permeability to a non-wetting fluid (supercritical CO_2) ii) this implies working with dry samples, which are much easier to prepare and handle than water-saturated ones.

The samples porosity and pore size values reported above suggest that:

- permeability will indeed be low, probably in the 10^{-19} to 10^{-20} m^2 range (the latter value can be obtained for example using the Kozeny-Carman porosity-permeability relationship),
- a wide class of pores have sizes close to the mean free path of the gas molecules, which means that molecular (as opposed to viscous) flow will occur.

The latter effect requires that a correction (the so-called Klinkenberg correction – Klinkenberg, 1941) be introduced in Darcy's law (written here for a perfect gas):

$$J = -\frac{k}{\mu}\left(1+\frac{b}{p}\right)\frac{p}{RT}\frac{\partial p}{\partial z} \qquad (1)$$

where J is the molar flux, k the intrinsic permeability, μ the dynamic viscosity, p the pressure, b the Klinkenberg factor, R the gas constant, T the temperature and z the abscissa along the sample axis.

In the case of a steady-state test, equation (1) is easily integrated into:

$$J = \frac{k}{\mu RTe}\left(1+\frac{b}{p_m}\right)\frac{p_1^2 - p_0^2}{2} \qquad (2)$$

where p_1 and p_0 are respectively the upstream and downstream pressure, p_m their arithmetic mean and e the thickness of the sample. Plotting the apparent permeability k_{app} defined by:

$$k_{app} = J\frac{2\mu RTe}{p_1^2 - p_0^2} \qquad (3)$$

against $1/p_m$ should therefore yield a straight line:

$$k_{app} = k\left(1 + \frac{b}{p_m}\right) \tag{4}$$

from which the coefficients k and b can easily be estimated.

To give an example, the flux of air through a sample 1 cm thick and 3 cm in diameter with $k = 10^{-20}$ m^2, $b = 10^6$ Pa, $p_1 = 10^6$ Pa, $p_0 = 10^5$ Pa, $T = 300$ K, is only about *2 standard cubic centimetres per hour,* which makes accurate measurements challenging.

An alternative "tracer" technique
Basic principle

The "tracer" technique differs from the previous ones by the use of two different gases: the first one, say helium, is used to maintain a pressure gradient upstream the sample, while the other one, e.g. nitrogen, flushes the downstream side with a known and constant flow rate (Figure 1). If the mole fraction of gas 1 in gas 2, x, can be measured, the molar flux of gas 1 through the sample, J_1, is simply given by:

$$J_1 = \frac{x}{1-x} J_2 \tag{5}$$

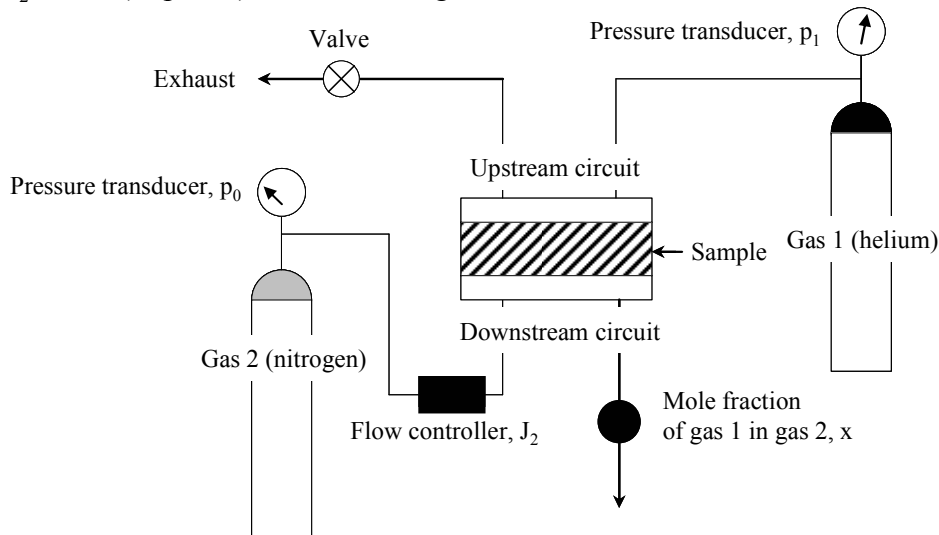where J_2 is the (imposed) molar flux of gas 2.

Figure 1: "Tracer" technique for the measurement of permeability.

This technique is an adapted version of the "continuous dilution method" commonly used to measure flow rates with tracers (AIEA, 1990), with the sole difference that the objective here is to measure the flow rate of the "tracer" (gas 1). It is also often used to measure transport properties through polymers (Flaconneche et al., 2001).

Using a mass spectrometer, mole fractions of helium in nitrogen down to 50 ppm (5.10^{-5} mol/mol) can be measured fairly easily. An helium flow rate of 0.2 standard cm^3/hr, one order of magnitude lower than the one mentioned above, is then measurable if a reasonable nitrogen flow rate of about 50 standard cm^3/min is used. In other words, a permeability of 10^{-21} m^2 is easily measured.

Elementary model for data interpretation

Interpretation of this tracer experiment however requires some caution since the gases are now submitted to an extra gradient due to the concentration difference between the upstream (pure helium) and the downstream (almost pure nitrogen) sides of the sample. Gas diffusion may therefore play some role and should be taken into account.

A simple way is to break the gas flux into convective and diffusive parts, respectively J_c and J_{1d} (gas 1) and J_{2d} (gas 2). J_c is again given by equation (1), where μ now is the viscosity of the mixture and, strictly speaking, dependent on volume fraction x. A simple expression for J_{1d} and J_{2d} could be the following form of Fick's law:

$$J_{1d} = -D\frac{\partial}{\partial z}\left(\frac{px}{RT}\right) \quad J_{2d} = -D\frac{\partial}{\partial z}\left(\frac{p(1-x)}{RT}\right) \tag{6}$$

where D is an effective molecular diffusion coefficient that should be inversely proportional to pressure according to the kinetic gas theory (Bird et al., 1960):

$$D = D_0\frac{p_0}{p} \tag{7}$$

D_0 being the value of D at reference pressure p_0, taken for instance as the downstream pressure. The system is completed by the molar balance equations for gas 1 and for the mixture:

$$\frac{\partial}{\partial t}\left(\frac{\varepsilon xp}{RT}\right) = -\frac{\partial}{\partial z}(xJ_c + J_{1d}) \tag{8}$$

$$\frac{\partial}{\partial t}\left(\frac{\varepsilon p}{RT}\right) = -\frac{\partial}{\partial z}(J_c + J_{1d} + J_{2d}) \tag{9}$$

where ε is the accessible porosity.

This model is certainly oversimplified since it does not account for all the phenomena of gas diffusion in porous media (Boulin, 2008). It is however adopted here because it is mathematically manageable and yet able to capture the main trends.

Suppose now that a steady-state tracer experiment is performed where the flux of gas 1, J_1, is measured. It is again possible to derive an apparent permeability:

$$k_{app} = J_1\frac{2\mu RTe}{p_1^2 - p_0^2} \tag{3bis}$$

The steady-state version of equations (8) and (9) yields an analytical solution provided that the concentration dependence of μ is neglected, which is not a strong assumption in the case of helium and nitrogen since their viscosities are very similar (respectively 1.9 and 1. 8.10^{-5} Pa.s at ambient temperature). This solution reads:

$$k_{app} = k\left[\left(1 + \frac{b}{p_m}\right) + \frac{2\alpha}{\left(p_1\big/p_0\right)^2 - 1}\log\left(\frac{p_1}{p_0}\right)\right]\frac{\exp(\xi)}{\exp(\xi) - 1} \tag{10}$$

with:

$$\xi = \frac{\left(p_1\big/p_0\right)^2 - 1}{2\alpha}\left(1 + \frac{b}{p_m}\right) + \log\left(\frac{p_1}{p_0}\right) \tag{11}$$

where α is a dimensionless parameter that can be interpreted as the inverse of a Péclet number:

$$\alpha = \frac{D_0 \mu}{k p_0} \qquad (12)$$

Equations (10) looks substantially different from equation (4); however it has a particular behaviour at large upstream pressure: expression (11) grows to infinity when p_1 is much larger than p_0; the exponential terms in equation (10) therefore cancel out. At the same time, the log term in equation (10) becomes vanishingly small. Equation (10) therefore reduces to equation (4):

$$k_{app} = k\left(1 + \frac{b}{p_m}\right) \qquad (4bis)$$

The practical consequence is that the high pressure points from a tracer experiment will fit on a straight line on the k_{app} vs. $1/p_m$ graph, from which the intrinsic permeability and the Klinkenberg coefficient can again be derived very simply.

Diffusion characteristics

Diffusion is somehow present in our interpretative model. To investigate how it affects k_{app} and under which conditions is it possible to measure it, the function k_{app}/k vs. p_0/p_m has been plotted for various values of coefficients α and b (Figure 2). For low values of α, the straight line predicted by equation (4bis) is indeed observed. As α increases, the low pressure part of the curve shows some deviation from linearity. The larger α, the stronger the deviation and the shorter the straight part of the curve. This effect tends to be stronger when b is small.

What is observed here is obviously the effect of the diffusion flux. Figure 2 shows that, provided the adequate pressure range is explored, the k_{app}/k versus p_0/p_m curve is actually sensitive to α, or, in other words, that the diffusion coefficient D_0 can be obtained by parametric adjustment. Using the tracer technique, one can therefore get information not only on the permeation parameters, but also on the diffusion properties of the studied material.
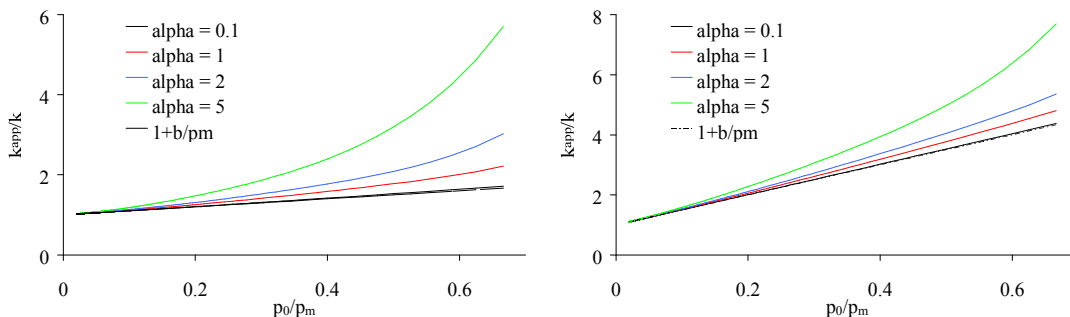

Figure 2: k_{app}/k versus p_0/p_m for different values of α
Left: $b/p_0 = 1$ - Right: $b/p_0 = 5$.

For this information to be really exploitable, a more realistic model for diffusion should be used. In that case, determination of the actual coefficient of mutual molecular diffusion of the gases is possible. This quantity does however not correspond to the initial problem: the transport of dissolved CO_2 in the pore water of caprocks. One possible way to bridge this gap is to introduce the notion of formation factor, equal to the ratio of the molecular diffusion coefficient of a species in a porous medium to its equivalent in a free fluid (Bear, 1972). Provided that all the species involved (helium and nitrogen under gas form, dissolved CO_2) have access to the same porous network, the formation factor should be the same for all. The gas tracer experiment enables to determine it; the desired diffusion coefficient is then just the product of this value by the diffusion coefficient of dissolved CO_2 in brine. The equal formation factor assumption is however a very strong one, and there are indications that it might not be generally valid (Boulin, 2008).

Two examples from experiments

The first experiment shown here was conducted on a very low porosity sample (less than 3 %) composed chiefly of carbonated materials. The sample was placed in a triaxial cell and an isotropic confinement pressure of 200 bar was applied. Downstream pressure p_0 was atmospheric pressure; upstream pressure varied from 2.5 to 125 bar. The main objective of this experiment was to measure intrinsic permeability k.

The results are shown on Figure 3. Visually, the data points group along a straight line on a k_{app}/k vs. p_0/p_m graph; they are actually well represented by a linear equation ("linear fit" on Figure 3). The parameters of the linear fit yield $k = 2.1 \ 10^{-19}$ m^2 and $b = 19$ bar (or $b/p_0 = 19$).

As demonstrated in the previous section, the diffusion coefficient D_0 is related to curvature of the k_{app}/k vs. p_0/p_m line, which means that D_0 cannot be determined from this experiment (or lower values for the upstream pressure should have been used). The k and b parameters from the linear fit were however combined with various values of D_0, ranging from 10^{-9} to $2. \ 10^{-8}$ m^2/s, to yield the group of dotted curves on Figure 2. Upon examination, it appears that the actual D_0 coefficient should be less than 10^{-9} m^2/s; coefficient α should therefore be less than 0.9, which is indeed in the lower range in Figure 2.
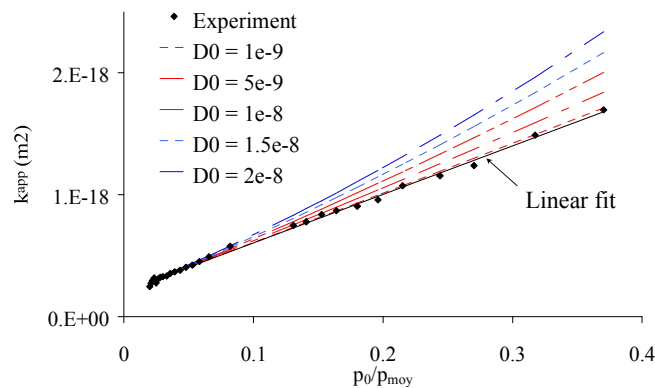

Figure 3: k_{app}/k versus p_0/p_m, 1st sample.

The second experiment involved a rock sample from the same geological layer, but extracted at a different location. Porosity and clay content were much higher (about 18 and 50 % respectively). The same experimental set-up was used. Downstream pressure was 2 bar, confinement pressure 90 bar and upstream pressure ranged from 2.4 to 44 bar. This time measurement of the complete set of parameters (k, b and D_0) was desired.

The results are given by Figure 4. The effect of diffusion is now clearly visible in the low pressure part of the graph. Non-linear fitting of equation (10) proved quite successful and yielded $k = 6.5 \ 10^{-19} \ m^2$, $b = 43$ bar and $D_0 = 8.4 \ 10^{-9} \ m^2/s$.
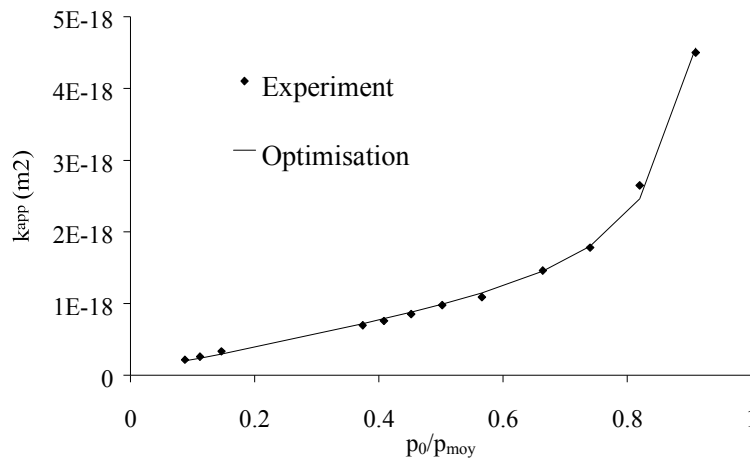

Figure 4: k_{app}/k versus p_0/p_m, 2nd sample.

Exploitation of the transient part of the tracer experiment

So far only the steady-state part of the tracer experiment has been exploited. The experiment is however by nature a transient one (successive pressure steps are applied on the upstream side). If the tracer flux is continuously monitored, a graph like the one on Figure 5 is obtained.
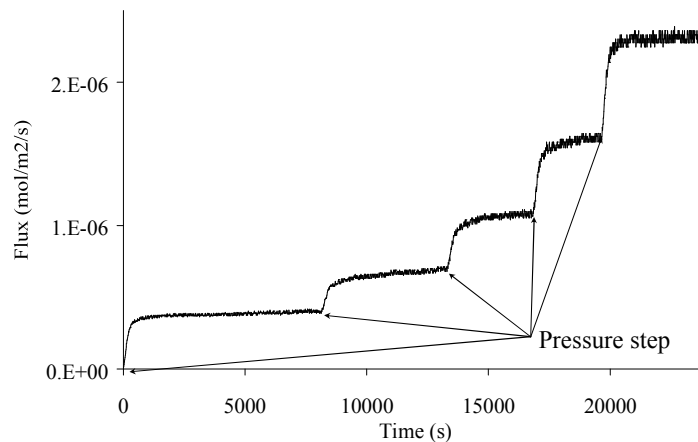

Figure 5: Tracer flux as a function of time.

Response after each pressure step comprises a transient part followed by a plateau. The transient part is governed by equations (8) and (9). In these equations, all the parameters connected with fluxes J_c, J_{1d} and J_{2d} can be known thanks to the analysis of the plateaux in Figure 5. The only remaining unknown is therefore the accessible porosity ε, that can be determined by a suitable model adjustment technique.

This method was successfully used by Boulin (2008) and has provided valuable results. It needs however further investigation, since the relationship between the porosity values yielded by this method and by other techniques like mercury intrusion remains to be confirmed.

Conclusion

The main findings of this work are the following:

- using a laboratory experiment based on a simple tracer technique, it is possible to measure very low gas permeabilities; in the numerical example given, permeability down to 10^{-21} m^2 was found easily attainable but lower values can certainly be measured with more optimised operating parameters (i.e. larger samples);
- provided the adequate pressure range is used, data are quite easy to exploit in terms of intrinsic permeability taking into account the Klinkenberg correction;
- experimental data at low pressure gradient also provides information on diffusion processes, but their processing is more difficult and requires a reliable model;
- if transient responses are monitored, accessible porosity can in addition be estimated.

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