ENTRY PRESSURE MEASUREMENTS USING THREE UNCONVENTIONAL EXPERIMENTAL METHODS

P.F. Boulin, P. Bretonnier, V. Vassil, A. Samouillet, M. Fleury, and J.M. Lombard
IFP Energies nouvelles

This paper was prepared for presentation at the International Symposium of the Society of Core Analysts held in Austin, Texas, USA 18-21 September, 2011

ABSTRACT

In CO_2 geological storage, porous rocks with very low permeabilities (k_w < 100 nDarcy, 10^{-19} m^2) play an important role as cap rock formations. It limits any CO_2 migration from the reservoir to the local environment. Caprocks efficiency relies on its entry pressure (or threshold pressure P_E) which is related to the capillary barrier generated by nanometric pores. This study focuses on the comparison of four different techniques (standard approach and three unconventional methods) of P_E measurement. Each of them has pros and cons which are important to take into consideration.

Two samples were studied. One was a carbonate rock and the other one was a clay stone, Permeability of the carbonate was estimated at 1.5 µDarcy (1.5 10^{-18} m^2) and 15 nDarcy (3 10^{-20} m^2) for the caprock. The samples were confined in a Hassler cell bounded by two reservoirs (closed or open to pumps that control flow rate or pressure depending of the experimental method). Four different entry pressure measurement methods were carried out on each sample: 1. standard method. Upstream gas pressure is increased step by step until water displacement at the outlet [1]. 2. Dynamic approach. Gas is injected upstream at a constant pressure Pg. Upstream, gas displaces water until gas is in contact with the sample surface. Downstream pressure is maintained constant, two different flow rates are observed: before and after gas entry. The two flow rate difference is related to the P_E value [2]. 3. The racking method is similar to the dynamic approach, downstream reservoir is connected to a pump racking at a constant flow rate. Downstream pressure decreases until gas displaces water in the sample. P_E is estimated from the minimum pressure observed downstream [3]. 4. Residual Pressure method based on Hildenbrand's experiment [4].

On the carbonate sample, methods 1, 2 and 3 provided a value of the P_E at 11 bar. Experiment 4 gave a P_E of 4 bar. Both experiment 2 and 3 were fast (lasted one to two days) and accurate. On the Caprock sample, experiments were much longer. The P_E value was around 120 bar. The method 1 lasted three weeks whereas method 2 lasted three days. Method 2 can be the most accurate and the quickest methods but attention should be paid to the mechanical stresses endured by the sample. Especially in low permeability media (P_E > 100 bar), pressure gradients can be high in method 2. Methods 1 and 3 should be preferred when samples sensible to stress are characterized. Method 3 requires good control of water leakage. Method 4 should be avoided since it underestimates entry pressure value.

INTRODUCTION

Geological storage of CO_2 (CCS projects) is considered a valuable option to reduce anthropogenic emissions of greenhouse gases. Because caprocks are barriers to gas migration from the reservoir to the biosphere, they have an important role in such a storage. The caprock sealing efficiency relies on its very low permeability and its high entry pressure (P_E) value [5]. Low permeabilities limit any CO_2 leakage from the reservoirs. P_E corresponds to the gas pressure required to displace water within the rock. If gas pressure does not overcome capillary forces, generated by the caprock nanopores, gas cannot penetrate further in the formation and does not leak. CO_2 pressure within the reservoir is related to the gas column weight. Caprocks with high P_E can hold high gas column weight and the reservoir has thus a high storage capacity. Therefore, this value is crucial to assess CCS potential sites. The higher the P_E value, the more gas can be stored. Assessing P_E value is also a point of interest in nuclear waste disposal [6] and natural gas storage.

Evaluating P_E values in caprocks can be a very long process. Especially when a good accuracy is required and when caprocks with very low permeability are involved. The main technique used to characterized caprocks is the step by step approach initially proposed by [7]. The residual pressure method proposed in Hildenbrand's experiments [4] can be found in the recent literature [8]. A first study by [2] had compared different P_E measurement methods in different kind of rocks and proposed a new one called the dynamic method. The present study completes the work of [2] with very low permeability samples (permeability around 15 nD for the less permeable, $P_E > 100$ bar). Attention will be focused on method accuracy and duration. In addition, a fourth method was tested. It is the racking method proposed by [3]. It has never been used, to our knowledge, in CCS research program.

MATERIALS AND METHODS

Sample description

Two samples were chosen for P_E experiments. The first sample is a carbonate sandstone from the TAVEL location in France. The plug used for P_E experiment was 4.9 cm in diameter and 4 cm thick. The TAVEL sample has been characterized by high pressure mercury intrusion capillary pressure measurements (MICP) and its porosity was 14% with a mean pore diameter of 250 nm. The mercury, as non-wetting phase, invades the porous media like a gas would when its pressure increases. The intersection of the tangents of the curve of saturation versus logarithm of the mercury injection pressure gives the pressure value at which the mercury significantly penetrates the sample. Using MICP results, P_E can be estimated [9][10] and corresponded for the TAVEL sample to 8 bar. It is only a first guess that provides only the order of magnitude of the P_E [2]. The second sample was extracted from the caprock formation (claystones) of the KETZIN CSS research project in Germany [11]. The plug used for P_E experiment was 4.1 cm in diameter and 2.95 cm thick. The MICP porosity was around 15% with a mean pore diameter of 10 nm. A first estimation of the P_E value, based on the MICP results, was 120 bar. All P_E values available in this paper are defined for nitrogen displacing brine.

P_E measurement methods

The experimental set up used to performed the P_E experiment is composed of a Hassler cell (to confine the sample), a pump for water which controlled pore pressure and measured the water going out of the sample or imposed water flow rate, and a 1L bottle to ensure a good gas pressure stabilization when it was required. For all the experiments, the sample was supposed completely saturated with water.
Four experimental methods were investigated (summarized in Figure 1):

- The standard method based on the step by step approach [7]. Gas is in contact with the sample surface at the inlet. Initially gas pressure is equal to pore pressure. Then gas pressure increases by steps. Each pressure amplitude and step duration depends on the accuracy required on P_E and the sample permeability. When the capillary pressure (gas pressure minus pore pressure) is higher than P_E, water is displaced out of the sample. The pump placed downstream provides this information.
- The dynamic approach [2]. Gas is injected upstream at a constant pressure P_g. Upstream, gas displaces water until gas is in contact with the sample surface. Downstream pressure is maintained constant at P_w through all the experiment. Gas pressure should be high enough to allow gas to penetrate the sample. Two different flow rates are observed: before and after gas entry. Before gas entry, water is produced due to a pressure gradient within the sample equal to $\Delta P_1 = P_g - P_w$. When gas enters the sample, pore pressure drops due to capillary forces. Upstream pressure drops from P_g to P_g-P_E. Pg should be higher than P_w, otherwise water stops to move and no flow rate is observed. The new pressure gradient is then $\Delta P_2 = P_g - P_E - P_w$. The flow rate being continuously measure and P_g, P_w being known values, P_E can be estimated from Q_2 (the second observed water flow rate), by :

$$P_E = P_g - P_w - \frac{e \cdot \mu}{S \cdot k} \cdot Q_2 \qquad \textbf{(1)}$$

k is the sample permeability, S sample surface, e sample length and μ the water viscosity)

- The racking method [3] is similar to the dynamic approach. The difference here is that the pump is placed downstream extracting water at a constant water flow rate. This method is a three step process. First, water moves from the upstream reservoir to the downstream reservoir. Like a simple steady state experiment, downstream pressure reaches equilibrium. After that, when gas starts to be in contact with the sample surface, pore pressure is still too high to allow gas to enter within the sample. Downstream pore pressure starts to decrease due to the constant flow rate extracted by the pump. In porous media, pressure wave propagation is a fast process even in very low permeability rocks such as Ketzin caprocks [12]. Therefore, when downstream pressure starts to decrease, pore pressure within the sample decreases too. The third step happens when pore pressure is low enough to permit gas penetration. Gas displaces water and downstream pressure stops to decrease. The downstream pressure drop is equal to P_E.

- The residual experiment is based on the principle of a pulse decay experiment with gas [13] [4]. The upstream pressure is elevated instantaneously to a high value (estimated at least twice higher than the actual P_E). Downstream and upstream reservoirs are closed. Gas moves from the upstream reservoir to the downstream reservoir. When downstream pressure is high enough an imbitibition process starts and stops gas migration. The pressure difference between upstream and downstream reservoir is called residual pressure and is assumed to be the P_E value.

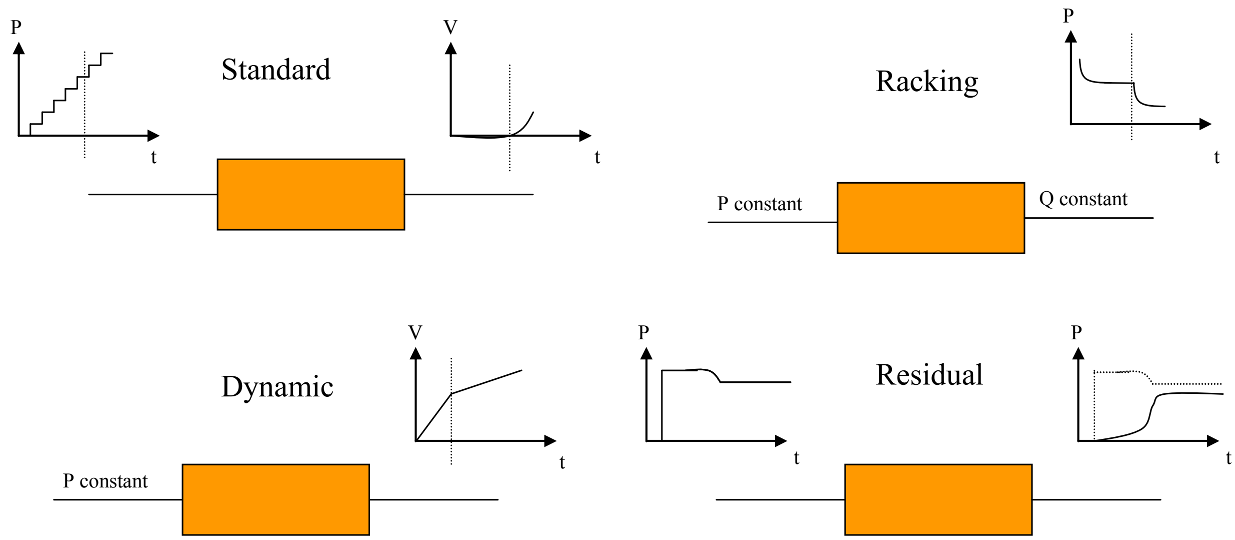

Figure 1. Description scheme of the four PE measurement methods investigated in this study (P: pressure, V: Water accumulation, Q: flow rate)

Experimental Protocol

The samples were placed in a Hassler cell. The confining pressure was 300 bar (30 MPa) for the Ketzin samples and 70/100 bar (7/10 MPa) for the Tavel sample. Temperature was maintained at 25°C +/- 0.5 to avoid any temperature fluctuations which can induce water dilatation and can affect the experiments, especially when low water flow rate are involved.

On the Tavel sample the following experiments were performed (P_{conf} = confining pressure (constant)):

- Standard method with downstream connected to the atmosphere, P_{conf} = 70 bar.
- Dynamic method with downstream connected to the atmosphere, P_{conf} = 70 bar.
- Dynamic method, P_{pore} = 30 bar, P_{conf} = 100 bar.
- Standard method, P_{pore} = 30 bar, P_{conf} = 100 bar.
- Four attempts for the racking method, P_{conf} = 100 bar.
- Three attempts for the residual method, P_{conf} = 100 bar.

On the Ketzin sample the four experiments were performed with an initial pore pressure of 50 bar (5 MPa). Owing to its very low permeability, experiment were not repeated. For the two samples, permeability was measured thanks to the steady state method described in [12], before and after each P_E experiment, in order to verify that the sample has not been damaged by the previous P_E experiment and that the sample was fully saturated from one experiment to another. Permeability was measured from Darcy's law and applied to three flow rates measured for three different pressure gradients.

RESULTS AND DISCUSSION

Permeability

The permeability of the Tavel sample was 1.5 µD +/- 15% (Figure 2) and the permeability on the Ketzin sample was 16.5 nD +/- 15% (Figure 3). Permeability remained the same throughout the experimental procedure. Therefore the samples have not been affected (mechanical fracturation for example) by the P_E experiments. Moreover, the samples have been fully saturated before all P_E tests.

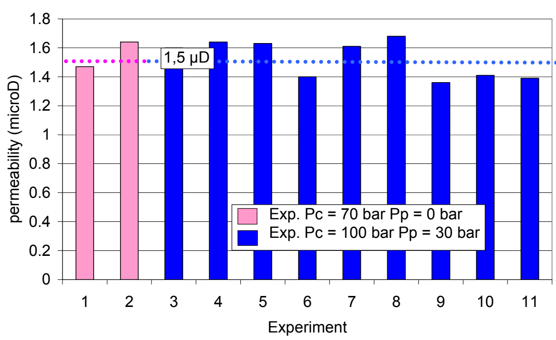

Figure 2. Permeability measured on Tavel sample after each P_E tests.

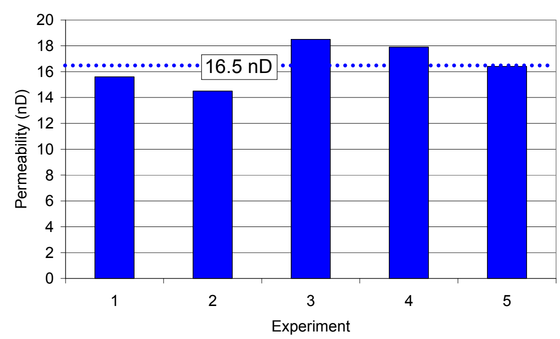

Figure 3. Permeability measured on Ketzin sample after each P_E tests.

Standard method

On the Tavel sample, upstream pressure steps lasted for a minimum of one day with an increment of approximately 1 bar (Figure 4). The experiment lasted eighteen days (initial gas pressure was 0, we had no idea at this time of the P_E value). There was a clear production of water (> 14 cc/day) when gas pressure was between 12 and 13.3 bar. A small production was observed when pressure was higher than 11 bar. If the pressure steps were longer it would have been possible to assess this production as gas displacing water within the sample. P_E value was estimated around 12.6 bar +/- 20 %. To reduce uncertainties it would have been preferred longer steps to ensure gas breakthrough and smaller pressure step to have a more restrictive range for the P_E value. Yet, those actions will increase the experiment duration. The second experiment was faster and it took seven days to observed water production. Since the P_E value was already estimated, the pressure steps were chosen accordingly.
Regarding the Ketzin sample, initial gas pressure was 100 bar, pressure was increased every three to five days with an increment of 10 bar and the experiment lasted 48 days. Despite the long time steps, It was rather difficult to estimate when the production of water started (Figure 5). A sligh volume change suggested that water production was occurring in the middle of the 159 bar step. A longer pressure step (at least 5 days more) would have been required to confirm that. At least, the gas penetrated the sample for a pressure higher than 154 bar +/- 10%. Subtracting the pore pressure, P_E was thus estimated at 104 bar +/- 15%.

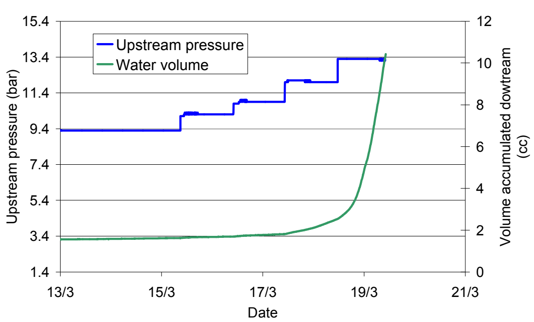

Figure 4. Standard approach on the Tavel sample

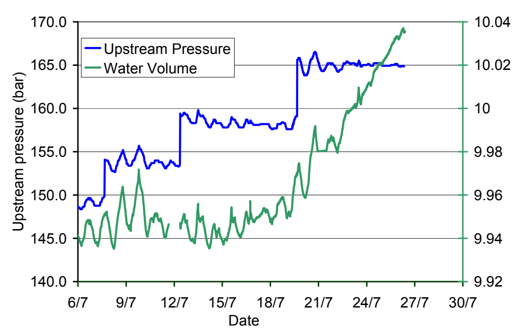

Figure 5. Standard approach on the Ketzin sample

The standard method has the advantage to reproduce what happens when gas goes into contact with the caprock. The porous media is fully saturated with water at a given in situ stress and gas pressure start to increase at one end of the sample until penetration.

Dynamic method

On the Tavel sample, the P_E value was supposed to be close to 12 bar. To be able to measure with accuracy the P_E value in this range with the dynamic method an upstream pressure of 15.6 bar was chosen (always higher than the expected P_E value). Two different flow rates were observed (Figure 6). First, a flow rate of 10 cc/day was measured, corresponding to an average permeability of 1.6 µD. The second flow rate was 1.55 cc/day, according to the previous estimation of the permeability, it corresponded to a pressure drop of 2.4 bar. The P_E value was 13.4 bar +/- 10% (fairly good accuracy to estimate the flow rate). The second dynamic experiment looked like the first one with an initial pressure gradient of 20.5 bar (upstream pressure at 50.5 bar, pore pressure at 30 bar), water flow rate dropped from 13.2 cc/day to 6.3 cc/day, it corresponded to a P_E value of 10.9 bar +/- 15 % (higher uncertainties due to higher pressures measured). Both experiment lasted less than one day.

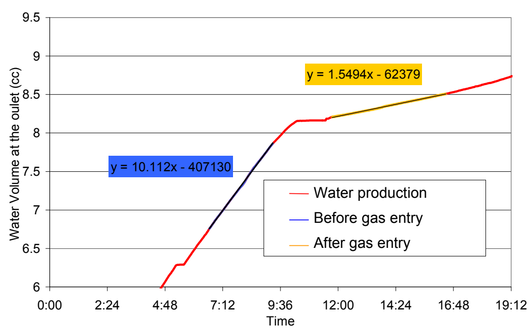

Figure 6. Dynamic method on the Tavel sample

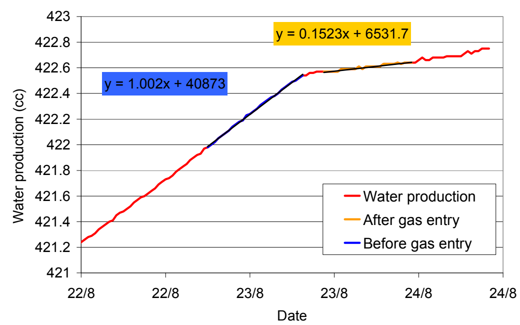

Figure 7. Dynamic method on the Ketzin sample

Concerning the Ketzin sample, gas pressure was increased to 186 bar ($\Delta P = P_g - P_w = 160$ bar). Water was displaced before and after that gas made contact with the sample surface. Two different flow rates were observed (Figure 7). The first flow rate measured was 1 cc/day, corresponding to a permeability of 18 nD. The second flow rate was 0.15 cc/day. The pressure drop associated to this flow rate can be estimated from Darcy's law using the permeability estimated from the first flow rate. To deduce P_E a reference permeably is necessary. Actually, this permeability (18 nD) is higher than the permeability measured before the test (14.5 nD). Those two different permeabilities can be used to estimate P_E. In fact, when high gas pressure is used in the dynamic experiment the sample is subject to mechanical stresses that are much different from the ones in the permeability test. In fact, pore pressure decreased from 186 bar (imposed upstream pressure) down to 26 bar (initial pore pressure) all along the sample. Effective pressure (confining pressure minus pore pressure) is thus lower before gas breakthrough than after. After gas breakthrough, pore pressure drops due to capillary forces. The sample is, in term of mechanical stress, closer to the state when permeability test were performed. Therefore the value of 14.5 nD was used to estimate the pressure drop. It corresponded to a ΔP of 30.1 bar and therefore the P_E value was 130 bar +/- 12%. This value would be 136 bar using the 18 nD as permeability. This slight difference can become a problem in the case of samples notably affected by mechanical stress changes. The experimental lasted three days.

In the case of very low permeability porous media, e.g. a 1 nD sample, it would take several days, even weeks, in order to push 1 cc of water through the sample to let the gas be in contact with the sample surface. To reduce experimental duration, it would be advantageous to flush the water out of the upstream reservoir once the first flow rate is stabilized.

Racking method

The racking method was tested four times in order to check the repeatability of this experiment using a constant flow rate of 0.15 cc/h and a downstream reservoir of 200 cc. For the third attempt, the racking flow rate was reduced from 0.15 cc/h to 0.04 cc/h. The fourth experiment was carried out with downstream reservoir of 5 cc instead of 200 cc in order to understand the pressure drop observed during downstream reservoir decompression. Experiments lasted one day in order to obtain the P_E value. The results were very similar. The third experiment looked like the previous ones time delayed by a factor 3. The initial pressure drop was around 6.6 bar (Figure 8). When gas was in contact with the sample surface, pressure decreased linearly with the time until the pressure drop was around 18.3 bar. The P_E value was 18.3 – 6.6 bar = 11.7 +/- 10%. As the racking test involved only pressure measurement, it is thus a very accurate method. Interestingly, downstream pressure dropped linearly at a constant rate of 85 bar/day. When the downstream reservoir was reduced from 200 cc to 5 cc, the pressure drop rates were roughly similar. There was no clue in [3] on how pressure decreased in the downstream reservoir. The first hypothesis we made was to believe that pressure will drop due to the decompression of water within the downstream reservoir. For a reservoir compressibility of 10^{-9} Pa^{-1}, a constant rack of 0.15 cc/h yields to a pressure drop of 7200 bar/day in a 5 cc reservoir and 7 bar/day in a 180 cc reservoir. It was thus believed that the pressure drop would be very fast in the racking method. In fact, the downstream pressure decrease was slower than expected. It can be explained by pore pressure decompression within the sample or water displaced by gas during breakthrough.

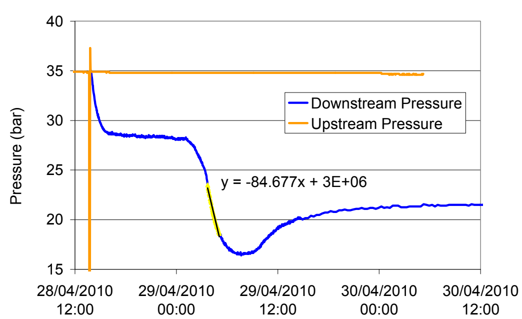

Figure 8. Dynamic method on the Tavel sample

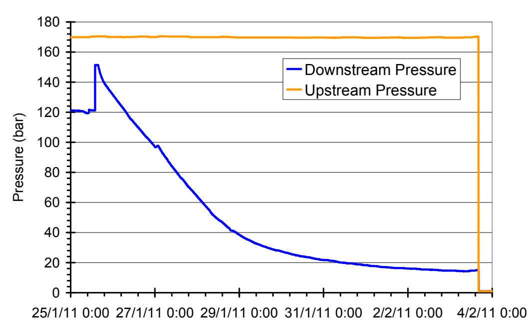

Figure 9. Dynamic method on the Ketzin sample

The gas pressure was set to 170 bar on the Ketzin sample experiment. The pump racked at a constant rate of 0.004 cc/h. This very low flow rate was performed by a Quizix pump, the flow rate was controlled by the recording of the piston displacement. Firstly, water is displaced from the upstream reservoir to the downstream reservoir, the pressure should equilibrate around 150 bar (permeability of 16 nD). An average volume of water of 1 cc has to be racked though the sample in order to have gas in contact with the sample surface. This should have taken at least 10 days with a constant racking rate of 0.004 cc/h. During this time, downstream pressure dropped every time above 120 bar and it was impossible to maintain a constant pressure. It can be due to very small leaks in the downstream reservoirs although the experimental set up was checked prior to and during the experiment. After ten days the pressure was raised to 150 cc and the experiment was conducted until the end. Pressure dropped below 20 bar within six days and never stopped to decrease. There was a slight change in the pressure drop around 30 bar. If this change is due to possible gas entrance within the sample it would lead to a P_E value of 130 bar (with the hypothesis of initial pressure equilibrium at 150 bar). However there is no clear evidence of this fact. In very low permeability rocks, the racking method can be hard to perform due to possible leakage. In term of mechanical stresses, when high P_E value is expected, high effective pressure changes are expected between the first stage of the experiment and the last one.

Residual Method

For the residual experiment, the upstream pressure was maintained constant and the downstream volume was 25 cc. The residual pressure observed after three days of experiment is 5 bar +/- 10% (Figure 10). The accuracy here is quite good since only pressure measurement is required. During previous attempt, the observed residual pressure was zero, downstream pressure reached upstream pressure at the end of the experiment. It was believed that the imbibition process was not taking place properly due to too fast experiments. The residual method on the Ketzin sample lasted 19 days (Figure 11). The pressure equilibrium was not totally achieved. A first estimation of the P_E value was 60 bar +/- 10%.

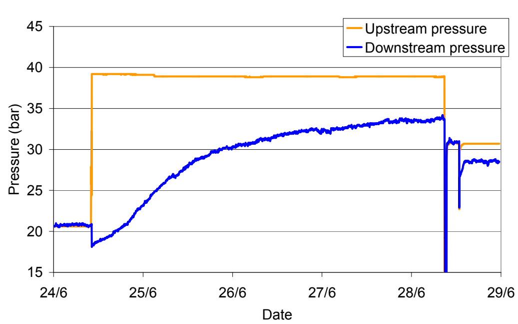

Figure 10. Residual method on the Tavel sample

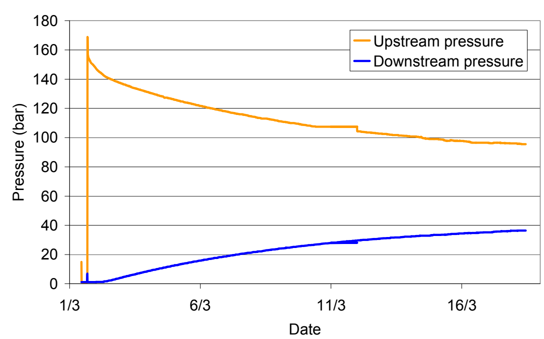

Figure 11. Residual method on the Ketzin sample

Summary on the Tavel and the Ketzin samples

Figure 12 shows the different P_E values obtained on the Tavel sample. The P_E value average is 11 bar. There is a small difference between experiments performed at 100 bar of confining pressure and 70 bar even if the effective stress remains the same. All experiments, excepted for the residual method, provides a suitable P_E value. It means that the sample is correctly resaturated after each experiments and that its structure is not noticeably affected by the experiments.
The Ketzin sample shows a P_E value close to 120 bar for both standard and dynamic method. The other methods are not able to provide a suitable value.
For both samples, the residual method is unable to provide a good P_E value, and underestimated, in average, the P_E value by a factor 2.

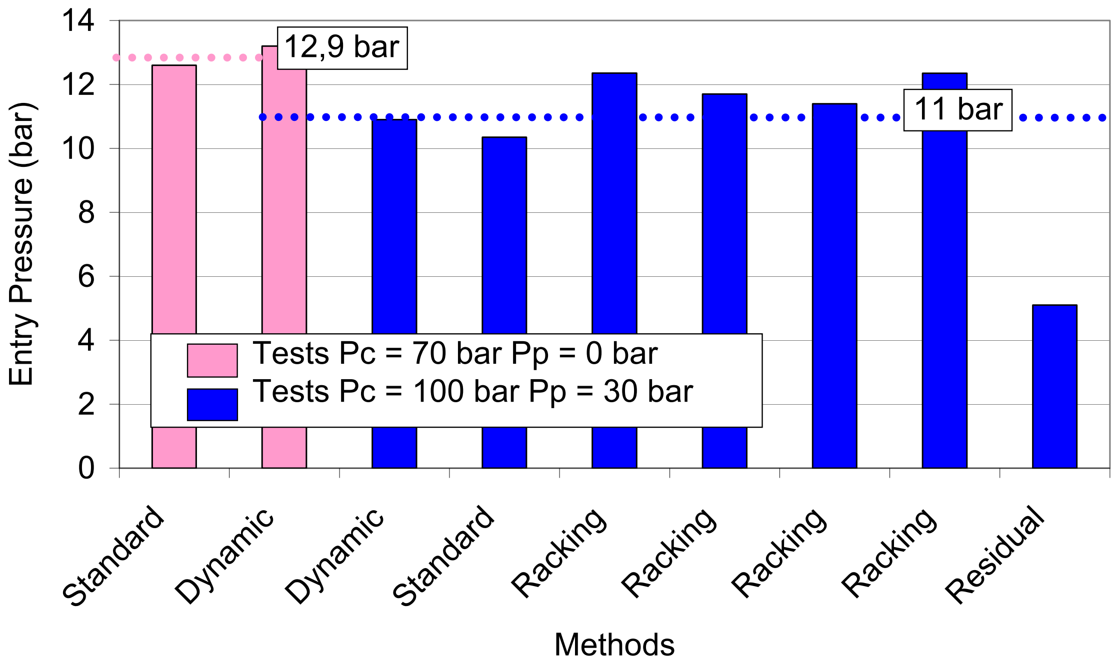

Figure 12. Summary of the P_E measurements on the Tavel sample

CONCLUSION

The main conclusions are summarized in Table 1. The information in bold refers directly to the experiment performed on very low permeability rocks (not investigated in [2]). Experiment representativeness corresponds to the fact that mechanical stresses applied on the sample can be close or far from the in situ condition. Accuracy is related to experimental errors on the sensors / experimental devices used to estimate the P_E.
The standard method is the longest experiment with the lowest accuracy. Higher accuracy would require even longer. Yet, P_E is poorly determined due to too short pressure steps and big pressure increments. The main interest of this experiment is the sample state and

the gas penetration process which are very close to in situ gas migration through caprocks.
The racking method is a good alternative to the standard approach. The P_E measurement is straightforward, very accurate and requires only pressure measurement. However, in very low permeability rocks, the experiment can be difficult to perform due to possible leakage and the very low racking flow rate required. In addition, the experimental duration was longer than expected due to decompression or motion of water within the sample that slow down the downstream reservoir decompression.

Table 1: Main conclusions on P_E experimental methods (bold characters for very low permeability rocks)

Methods	Standard	Racking	Dynamic	Residual
Duration	7/18 days **47 days**	1.5 days **> 11 days**	1 day **3 days**	3 days **19 days**
Order of magnitude of P_E	Not required	High importance	Medium importance	Low importance
Accuracy	**Bad** to medium	High	**Medium** to high	High
Main issue	Duration	**Leaks and low racking flow rate**	Change of slope noticeable	Don't seem to work
Representativeness	High	**Bad** to Medium	**Bad** to Medium	bad

The standard method is the longest experiment with the lowest accuracy. Higher accuracy would require even longer. Yet, P_E is poorly determined due to too short pressure steps and big pressure increments. The main interest of this experiment is the sample state and the gas penetration process which are very close to in situ gas migration through caprocks. The racking method is a good alternative to the standard approach. The P_E measurement is straightforward, very accurate and requires only pressure measurement. However, in very low permeability rocks, the experiment can be difficult to perform due to possible leakage and the very low racking flow rate required. In addition, the experimental duration was longer than expected due to decompression or motion of water within the sample that slow down the downstream reservoir decompression. The dynamic approach can provide a good P_E estimation and is the most effective technique in terms of experimental duration. In very low permeable rocks (permeability near 1 nD), the experimental duration exceeds ten days. The main drawbacks are the mechanical stress changes throughout the experiment, especially when high P_E is involved.

AKNOWLEDGEMENT

The authors would like to thank Ben Norden and Cornelia Schmidt-Hattenberger from GFZ for providing the sample from the Ketzin site within the framework of the COSMOS2 program funded by the ANR.

REFERENCE

1. Al-Bazali T.M., J., Zhang, M.E. Chenevert, and M.M. Sharma, "Measurement of sealing capacity of Shale Caprocks," SPE Annual technical conference and exhibition held in Dallas, Texas, 9-12 october 2005
2. Egermann, P., Lombard, J.-M., and Bretonnier, P., " A fast and accurate method to measure threshold capillary pressure of caprocks under representative conditions," International Symposium of the Society of Core Analysts, Trondheim, Norway 12-16 September 2006
3. Meyn, "Die Bedeutung des sperrdrucks (threshold pressure) fur den uidtransport in neidrigstpermeablen Gesteinen: Experimentelle und theoretishe Aspekte", (1999), DGMK Spring Conference, 255-264
4. Hildenbrand, A., S. Schlömer and B. Krooss, "Gas breakthrough experiments on finegrained sedimentary rocks," *Geofluids,* (2002) **2**, pp 3-23.
5. Bachu, S. "CO2 storage in geological media: Role, means, status and barriers to deployment," *Progress in Energy and Combustion Sci.,* (2008) **34(2)**, 254-273.
6. Gallé, C., “Gas Breakthrough pressure in compacted Fo-Ca clay and interfacial gas overpressure in waste disposal context”, *Applied Clay Science,* (2000) **17**
7. Thomas, L.K., D.L. Katz and M.R. Tek, "Threshold pressure phenomena in porous media," *SPE Journal,* **243,** 174-184
8. Wollenweber, J., S. Alles, A. Bush, B.M. Krooss, H. Stanjek, and R. Littke, "Experimental investigation of the CO2 sealing efficiency of caprocks," *International Journal of Greenhouse Gas Control,* (2010) **4**, 231-241.
9. Carles, P., P. Egermann, R. Lenormand, and J.M. Lombard, "Low permeability measurements using steady state and transient technics," International Symposium of the Society of Core Analysts, Calgary, Canada, 10-14 September 2007.
10. Monicard, R., "Caractéristiques des roches réservoir - Analyse des carottes, ÉditionsTechnip", Paris, France (1981), 168 p.
11. Förster A., R. Giese, C. Juhlin, B. Norden, N. Springer, and CO2SINK Group, The Geology of the CO2SINK Site: From Regional Scale to Laboratory Scale Energy Procedia (2009) 1 2911–2918.
12. Boulin, P.F., P. Bretonnier, N. Gland, and J.M. Lombard, "Low permeability measurements with water on clay sample. Contribution of steady state method compared to transient methods," SCA 2010 Symposium, Halifax, Canada, October, 2010.
13. Brace W.F., J.B. Walsh and W.T. Frangos, "Permeability of Granite under High Pressure." *J. of Geophysical Research,* (1968) **73(6),** 2225-2236.