GAS MIGRATION THROUGH SELF-SEALED OR INTACT CLAYSTONE

Yang Song, C. A. Davy, F. Skoczylas
Ecole Centrale de Lille, LML UMR CNRS 8107, CS20048,
59651 Villeneuve d'Ascq Cedex, France

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ABSTRACT

This contribution investigates gas migration through fully water-saturated Callovo-Oxfordian (COx) claystone.

Our originality is to evidence the nature of progressive passage through initially macro-cracked and water-saturated (i.e. self-sealed) claystone, or through intact (undisturbed) matter. The sample is subjected to hydrostatic pressure, identical to the mean *in situ* principal stress. We use a mix of gases detected on the sample downstream side by a mass spectrometer accurate to 2-5 ppm (i.e. 2-5 10^{-6} particles). We show that gas breakthrough occurs first, by discontinuous capillary passage, i.e. *snap off*, followed by continuous breakthrough (i.e. permeation), whether the upstream pressure value is increased or kept constant. *Snap off* is characterized by small amounts of gas detected at the outlet at random frequency and amplitude, until all gases in the mix are detected continuously and simultaneously.

At continuous breakthrough, gas permeability is on the order of 10^{-21} m^2 (1nD). For self-sealed claystone, gas breakthrough pressure (GBP) varies hugely in the low range 1.45-3 MPa. For undisturbed claystone, GBP ranges between 4.38 MPa (20 mm thickness) to 5.43 MPa (30 mm thickness), in good accordance with former research. It is concluded that *self-sealed* COx claystone has significantly weaker gas breakthrough properties than undisturbed matter.

INTRODUCTION

This contribution was originally devised for engineering applications related to deep underground nuclear waste storage. In France, the latter is planned at 420-550 m depth, and represents a network of horizontally-drilled galleries of several kms long, starting from a main vertical shaft and an auxiliary vertical shaft [1]. Storage tunnels are made within a claystone of Callovo-Oxfordian age (the so-called COx claystone), which has an undisturbed water permeability of the order of 10^{-21} to 10^{-23} m^2 (0.01 to 1 nanoDarcy). In the Excavated Damaged Zone (EDZ) around the tunnels, macro-fracturing is observed. However, underground water seepage is shown to allow *self-sealing* [2], whereby water permeability recovers values on the order of 10^{-21} to 10^{-23} m^2, similar to undisturbed claystone.

Further, after drilling, filling and closure of storage tunnels, hydrogen gas may develop and progressively pressurize inside the repository, due to varied physico-chemical phenomena (anaerobic corrosion of carbon steel canisters, water radiolysis, etc.).

The industrial issue is to ensure the conditions for proper gas immobilization within the underground site, both in the self-sealed zone and in the undisturbed claystone, away from the repository: this is investigated here by identifying the Gas Breakthrough Pressure (GBP) across fully water-saturated claystone. This study can be extrapolated to the migration of a non wetting fluid (e.g. gas here, or oil in the petroleum engineering context) through a wetting fluid filling the pores (water here, and water too in the petroleum engineering context).

Extensive research has been performed on gas migration (or breakthrough) through COx claystone with the step-by-step method [3, 4, 5] or with quicker, transient techniques [6,7].

With the step-by-step method, progressive gas passage through water-saturated matter is identified, so that both discontinuous and continuous migrations can be observed [8]. Through the test series presented here, our aim is to assess:

1. the difference between discontinuous and continuous gas passage: does the former occur consistently before the latter?
2. is discontinuous passage mainly a feature of our experimental set-up, so that argon gas detected in the downstream chamber is due to argon accumulation by diffusion phenomena, or is discontinuous passage a capillary phenomenon, the so-called *snap off* (or discontinuous capillary digitation)? For this part of our experimental campaign, gas detection on the downstream side uses a mass spectrometer accurate to 2-5 ppm, and gas is either 100% argon or a mix of 50 mol% argon/50mol% helium.
3. is discontinuous or continuous GBP repeatable, *i.e.* after a first breakthrough at a given gas pressure, whenever claystone is re-saturated with water until being self-sealed, does it have the same GBP again?

MATERIALS AND METHODS

Table 1: Main features (sample size, water permeability at saturation) and GBP test results for COx claystone sample series S3.

Sample n.	Core n. EST	direction	H (mm)	Initial state	Pc (MPa)	Water saturation phase (days)	K_{water} at saturation (m^2)	Migration test & GBP (MPa)
n.1	34386	horizontal	10,9	macro-cracked	12	16	$9.3x10^{-21}$	1.64
					12	63	$9.3x10^{-21}$	1.45
n.2	34386	horizontal	10,76	macro-cracked	6	68	7,1 to $7,3x10^{-21}$	2.25
n.3 undisturbed	44331	vertical	19,74	turned	6	35	$3x10^{-20}$	4.5-5.7
					6	49	$2,6x10^{-20}$	4.38
n.4 undisturbed	44140	vertical	30	turned	6	134	6,9 to $7,4x10^{-21}$	5.2-5.3
n.5	44331	vertical	9,5	turned	6	30	$1,9x10^{-20}$	2.2
					6	13	$1,6x10^{-20}$	3.0
					6	96	$1,8x10^{-20}$	2.96
					6	50	$1,7x10^{-20}$	3.6

Sample Origin and Preparation

Each of the five samples tested is cored and macro-cracked by Brasilian test (or splitting test of a circular cylindrical sample), or machined by turning to 37 mm diameter and varying height, from 9.5 to 30 mm, from horizontal core EST34386 or vertical cores EST44331 and EST44140, see Table 1. Turning allows to minimize sample damage and provides us with so-called undisturbed claystone, whereas macro-cracking provides samples similar to damaged claystone from the EDZ.

Water Saturation. Prior to GBP, full water saturation is achieved as follows. The sample is placed in a hydrostatic cell, and subjected to a confining pressure of 12 MPa (on the order of *in situ* principal stress levels). Water is injected on the upstream side at 4 MPa pressure, which is the lithostatic water pressure, until it is fully saturated. Full saturation state is achieved when water permeability K_{water} values fall below 10^{-20} -10^{-21} m^2, see Table 1. Owing to the water flow duration and to the stability in water permeability values, it is thought that either all potentially trapped gas within the pore network has evacuated, or has been dissolved in flowing water.

Single-gas GBP Experiment

Following water saturation, upstream pipes are emptied from water, while the sample is kept at a constant confinement Pc=6 or 12 MPa, in order to avoid its premature failure. The downstream chamber (of a volume of 2 cl) is closed by a dedicated valve, and its pressure $P_{downstream}$ is recorded with a pressure transducer accurate to +/-100Pa. On the upstream side, the argon gas pressure $P_{upstream}$ is increased very slowly, at a rate of 0.5-1 MPa per day (unless otherwise stated in the following), and up to 14 days for a few tests. Upstream gas pressure is given by a pressure transducer accurate to 1 kPa. Gas detection on the downstream side is performed using both the downstream pressure transducer and

a dedicated argon gas detector accurate to +/-10^{-7} l/sec. At constant $P_{upstream}$ value, gas detection is performed every 24 to 72 h as follows: the downstream chamber valve is opened and gas is detected (or not) by placing the detector nozzle at ca. 5 mm from the valve opening. Gas passage is considered discontinuous whenever gas presence is detected for less than 10-60 sec; gas passage is considered continuous when gas outflow is recorded for more than 10 sec, three times every five minutes. This method means that downstream gas pressure goes back to zero after each downstream valve opening. Also, it does not ensure whether gas actually passes through the porous medium by dissolution and diffusion in pore water, or by capillarity. Therefore, both mechanisms are accounted for in the following.

Two-gas GBP Experiment

This test aims at determining what phenomenon is at the origin of gas breakthrough, *i.e.* either percolation or dissolution and diffusion. For this purpose, a mix of gases is injected through water-saturated claystone: it is chosen to ensure a significant difference between both their solubility in water and their diffusivity, *i.e.* a significant difference in the product of their solubility and diffusivity. If the gas with the greatest solubility and diffusion migrates first, these phenomena will be privileged to explain breakthrough.

At 15 °C, the solubility is $3.00x10^{-10}$ mol/Pa for argon and $7.20x10^{-11}$ mol/Pa for helium; the diffusion coefficient is $2.00x10^{-9}$ m^2/sec for argon and $6.30x10^{-9}$ m^2/sec for helium [9]. The product of solubility and diffusion coefficient at 15 °C is of $5.92x10^{-19}$ mol/N.sec for argon and $4.48x10^{-19}$ mol/N.sec for helium: helium has lower solubility and diffusivity by a coefficient of 1.32, when compared to argon. Although this difference may not appear large enough, these gases have been chosen in a first approach given their excellent availability and harmlessness.

After imposing the gas mix on the sample upstream side at given pressure, the presence of each gas is detected individually on the downstream sample side by a mass spectrometer accurate to 2-5 ppm.

RESULTS AND DISCUSSION

In the following, all pressure values are expressed in MPa abs.

Evidence of Discontinuous and Continuous Gas Passage

When the GBP test starts, whatever the initial $P_{upstream}$ value chosen (as low as 0.2 MPa), $P_{downstream}$ increases. This is attributed to water expelled on the downstream side, pushed by gas on the upstream side. Therefore, potentially, gas entry may have begun, yet no device is available in this experiment to check it with adequate accuracy. The argon detector does not record any gas passage after 24 h at $P_{upstream}$ = 2.02 MPa, whereas it detects a discontinuous argon passage after 24 h at $P_{upstream}$ =2.25 MPa. Simultaneously, at each $P_{upstream}$ value, downstream pressure data display a linear increase with time (Fig. 1a), until going back to zero as soon as the downstream valve is opened. Therefore, the rate of increase of downstream pressure is plotted vs. imposed upstream gas pressure (Fig. 1b). An inflexion point is observed in these data, at $P_{upstream}$=2.22 MPa. This is attributed to the start of an additional phenomenon, which induces a greater rate of increase in

downstream pressure. As it occurs at a very close $P_{upstream}$ value as that when the argon detector evidences gas passage, it is attributed to the same phenomenon. This means that we have two independent means of detecting gas passage: the argon gas detector, and the rate of increase in downstream pressure, both occurring due to gas passage from the upstream side (where gas pressure is imposed) and downstream side (where all measurements are made).

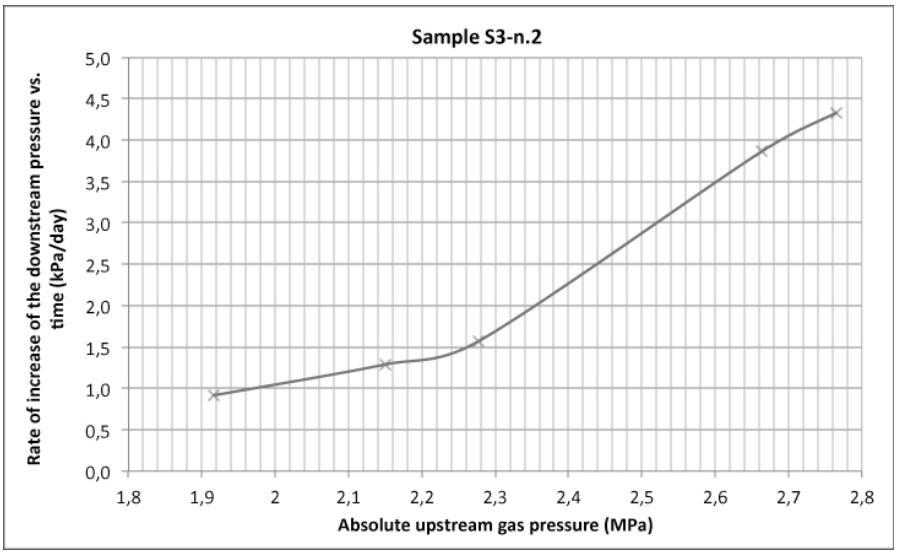

Figure 1 : Sample S3-n.2: rate of increase of downstream pressure (in kPa/day) vs. imposed upstream gas pressure (MPa).

After discontinuous passage has been observed, $P_{upstream}$ is increased regularly until continuous breakthrough (Fig. 2). Continuous breakthrough is measured by (1) the argon detector, (2) the rate of increase of $P_{downstream}$ and also (3) when the rate of decrease in upstream pressure is greater than that due to thermal variations. This second criterion allows for measuring gas permeability K_{gas}, as described in [Davy *et al.* 2007] (with an assumption of quasi-static gas flow). As for discontinuous passage, an inflexion point is observed in the rate of increase in $P_{downstream}$ *vs.* $P_{upstream}$, which occurs at a slightly greater $P_{upstream}$,=3.59 MPa than continuous passage measured by the argon detector (at $P_{upstream}$=3.35 MPa). The upstream pressure transducer allows for gas permeability measurement at an even greater $P_{upstream}$,=4.24 MPa than with the two other devices: K_{gas} is of 1.6×10^{-21} m^2 at $P_{upstream}$,=4.24 MPa. Whenever $P_{upstream}$, is increased further, K_{gas} increases monotonously [4].

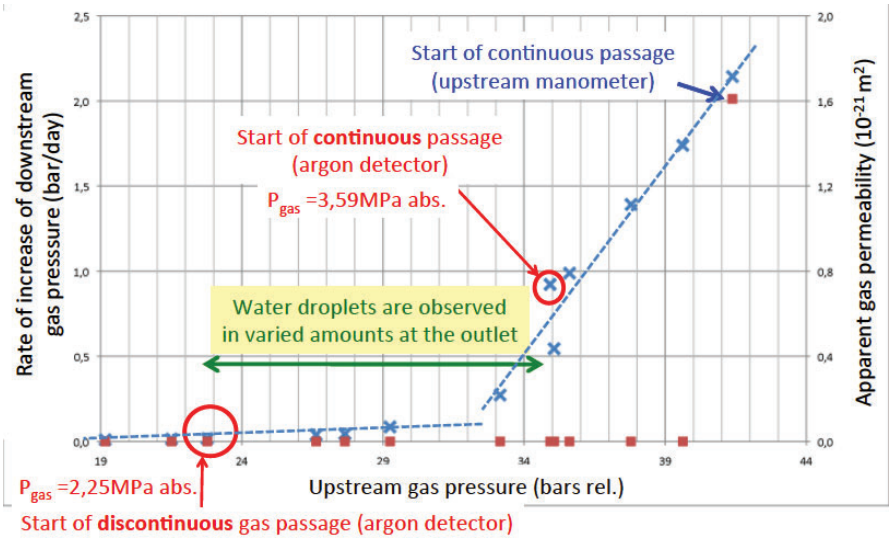

Figure 2. Sample S3-n.2: Evolution of downstream pressure increase rate (red markers) and gas permeability (blue markers) measured on upstream side vs. applied upstream gas pressure

Repeatability of GBP

Samples S3-n.1, S3-n.3 and S3-n.5 have been subjected to several water-saturation phases followed by a GBP test (Table 1). It is observed that GBP values are not repeatable, with greater or lower values after a first GBP test. For instance, for sample S3-n.1, GBP is of 1.6 MPa after a first water saturation phase, whereas it is at a lower 1.45 MPa value after a second water saturation phase. For sample S3-n.5, GBP is of 2.2 MPa after the first water saturation phase, whereas it is at a greater 2.9-3MPa value after the second and third water saturation phases. This is attributed to different gas pathways from one GBP test to the other, in relation with statistically-varying capillary digitation.

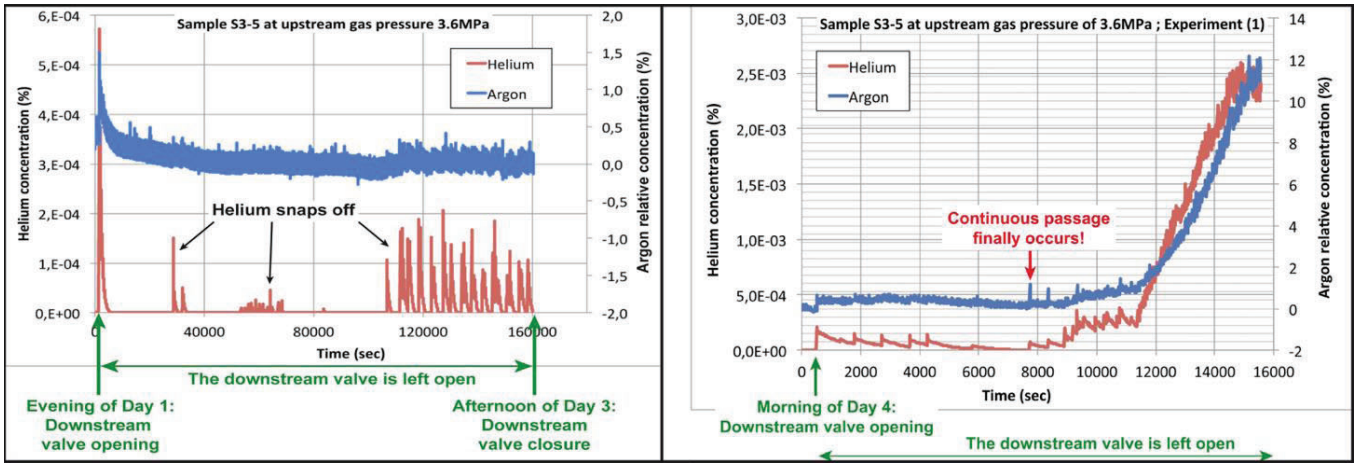

Figure 3 : Sample S3-n.5: (left): Helium and argon concentrations (in %) *vs.* after 24 h at $P_{upstream}$=3.7 MPa and downstream valve opening (at 10 sec); (right): Argon and helium concentrations (in %) *vs.* time, when the downstream valve has been kept closed for 24 h at a value of 3.555 MPa down to 3.504 MPa. The downstream valve is open at time t=500 sec.

Effect of Sample Thickness and Damage State Upon GBP

For test series S3 (Table 1), GBP is below 3 MPa for 9.5-10.9 mm thick samples, below 5.8 MPa for 19.7 mm thick sample, and below 5.4 MPa for 30 mm thickness. Let us compare these results with existing data. GBP results on so-called undisturbed COx claystone have been obtained by BGS (UK) and Laego (France) on 55-85 mm long samples machined by turning, at values ranging between 5.5 and 6 MPa [4]. For 18 mm long COx samples, studies at RWTH (Germany) measure GBP values at 4.8-5.3 MPa, which are also attributed to undisturbed matter [4]. Results by [10] on macro-cracked claystone range between 0.8-2 MPa for 75-103 mm thickness. This means that all the values of our test series S3, and those of test series S1 and S2 (given in [5]) correspond to initially macro-cracked claystone. Higher GBP values observed for thicker samples are attributed to too quick an increase in $P_{upstream}$, which does not allow for sufficient time to record gas breakthrough, rather than to actual unability for gas to breakthrough.

Evidence of the Nature of Discontinuous Gas Passage

After a first GBP test, sample S3-n.5 has been re-saturated with water until $16x10^{-21}$ m^2 water permeability, and further injected with the mix of gases (argon+helium). At $P_{upstream}$=2.96 MPa, the presence of helium is recorded as a peak concentration value upon downstream valve opening, which decreases down to zero after several minutes: it is a first evidence of discontinuous gas passage. Argon concentration is too noisy to show any significant concentration difference upon valve opening. In order to allow for shorter experimental duration, $P_{upstream}$ is then increased slightly, up to 3.7 MPa and kept at that value for 24 h. Fig. 3a shows argon and helium concentrations *vs.* time after valve opening (at 10 sec): a peak in concentration is observed for both gases upon valve opening, with a regular decrease down to zero for helium after 5500 sec (i.e. 1 h 31 min), and with a highly fluctuating decrease for argon, down to ca. 2.8%. After 8 h at $P_{upstream}$ =3.7 MPa with the downstream valve kept open, the mass spectrometer records a peak in helium concentration, which decreases down to zero. This peak in helium concentration is followed by other evenly distributed peaks of varying amplitude, which frequency increases with time. These peaks are attributed to progressive gas passage by a discontinuous phenomenon, which cannot be attributed to progressive dissolution and diffusion through the claystone pore network: no physical reason justifies discontinuity due to dissolution and diffusion (continuous phenomena). Rather, it is the demonstration of capillary *snap off*, *i.e.* of gas passage by a discontinuous progression through pores of sufficiently varying size (gas is regularly blocked in its progression through the pore network by smaller pore throats, which requires an increase in gas pressure to be overcome [11]. Further to this, $P_{upstream}$ is kept at its value of 3.5 MPa +/- 0.05 (no increase back to 3.7 MPa is performed here), and the downstream valve is closed for 24 h. Upon re-opening (Fig. 3b), helium passes again in a discontinuous manner, with several peaks in concentration, which decrease progressively with time, yet not back to zero due to a higher frequency of occurrence. After a total of 64 h 19 min at $P_{upstream}$ =3.7 -> 3.5 MPa, helium finally passes continuously through to the downstream sample side, together with argon (Fig. 3a) again. It is a continuous capillary gas breakthrough.

CONCLUSION

This contribution has shown that gas migration through initially water-saturated and macro-cracked COx claystone occurs consistently by discontinuous capillary *snap off*, followed by continuous passage (*i.e.* percolation) (answer to the first question in the introduction). Discontinuous passage is not related to dissolution and diffusion of gas through to the downstream chamber, which is opened every 24 h (answer to question 2) in the introduction). GBP values are significantly below those of undisturbed claystone, which is evidence of its inability to self-heal, despite excellent self-sealing ability (answer to 3rd question in the introduction).

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