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6 **Well injectivity during CO₂ storage operations in deep saline aquifers**

7 **1: Experimental investigation of drying effects, salt precipitation and**
8 **capillary forces**

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Abstract

Carbon Capture and Storage (CCS) is a technique that can potentially limit the accumulation of greenhouse gases in the atmosphere. Well injectivity issues are of importance for CCS because the gas injection rate must be maintained at a high level (a million tonnes of CO₂ per year and per site) during the industrial operation period (30 to 40 years). The risk of altered permeability must therefore be determined in order to guarantee the sustainability and the security of the CO₂ geological storage. Injection of dry gas in deep saline aquifers might lead to near wellbore drying and salt precipitation. The solid salt might then reduce the rock permeability by clogging pores or by pore throat restriction. The objective of this paper is to present new experimental results on the drying of rocks induced by continuous injection of large amount of dry gas (N₂). The main goal of the study was to understand and model the physical processes that govern the decrease in water saturation in reservoir rocks.

Two types of sandstone were used to study slow and fast drying rates and capillary effects on drying. The experimental results evince the main physical parameters that control the key mechanisms. In a companion paper in this issue (André et al., 2013), we show that the continuous approach in the context of a compositional two-phase flow model can fairly well predict the saturation evolution in the near wellbore and the alteration in permeability due to salt precipitation.

Keywords: drying-out effects, coupled modelling, relative permeability, salt precipitation, capillary processes.

1. Introduction

Geological sequestration of CO₂ into deep saline aquifers is of interest because these geological formations represent a huge storage volume. However, they have been studied much less than mature oil & gas reservoirs. Injection of carbon dioxide into saline aquifers might involve some specific effects that could limit the gas injectivity. Different mechanisms could alter the permeability. One of the first studied is geochemical reactions due to CO₂ injection (Kaszuba et al., 2003; Jonhson et al., 2004; Brosse et al., 2005; lagneau et al., 2005; André et al., 2007, 2010). The dissolution of the carbon dioxide in water can induce mineral precipitation and dissolution. The rock porosity and permeability can then be modified depending mainly on the rock type but also on injection conditions (Bacci et al., 2011a). Another mechanisms, much less studied, is drying and salt precipitation at the near wellbore. The dry injected gas, at low water-vapour partial pressure, will equilibrate with the groundwater and water mass transfer will occur leading to the desiccation of the rock. Drying effect has been studied in the context of oil & gas to estimate *water blocking* in the case of gas production well (Mahadevan et al., 2006, 2007) but drying can also induce salt precipitation in the case of saline aquifer. The solid salt might reduce the rock permeability by clogging pores or by pore throat restriction. This effect has been reported for gas producing wells in reservoirs of high salinity brine (Kleinitz et al., 2003). In the context of CO₂ geological storage, injectivity alteration by salt precipitation has been analytically and numerically studied by Giorgis et al. (2007), Pruess and Müller (2009), Pruess (2009) and Zeidouni et al. (2009). They showed that skin factors due to salt precipitation effects can be evaluated. Flow models have been used to study drying and precipitation dynamics in simplified well bore geometry taking into account a larger set of parameters (Spycher et al., 2003; Spycher and Pruess, 2005; André et al., 2007). The results reveal large drying zones in certain cases. Recent experimental work has attempted to measure the change in permeability under controlled drying conditions and has shown that permeability can alter significantly (Bacci et

al., 2011b; Ott et al., 2011; Peysson et al., 2011a; Peysson, 2012; Golghanddashi et al., 2013).

The expansion with time of dried zones near injection wells has been studied for the most part numerically, and field-scale comparison is not yet possible because few large-scale pilots have been built. Experimental studies are therefore very useful for determining the key parameters involved so that we can correctly model well injectivity in the context of CO₂ storage. We studied the effect of long-term injection of dry gas in brine-saturated rock samples having different porosities and permeabilities in order to understand and quantify the main parameters needed to develop a comprehensive model of CO₂ injection in real situations. We specifically looked at different drying rates and capillary effects that might limit the drying by using rock samples with very different permeabilities. In a companion paper in this issue, we describe the use of reservoir numerical models to simulate drying and precipitation dynamics. The numerical results are in good agreement with the experiments described in this paper.

2. Experimental set up

2.1 Set up

The experiment involved placing cylindrical rock samples 6 cm long and 4.9 cm in diameter in a horizontal Hassler cell (Fig. 1). The inlet of the core holder is connected to a gas reservoir and the injection pressure controller. A back pressure of 50 bars was set at the outlet. Outlet gas fluxes were measured with a gas flow meter after the back pressure and the water outlet volume had been recorded using a burette. The pressure drop across the sample was also recorded. The system temperature is thermostatically controlled. An X-ray source and detector are placed on a translation rail that records the saturation profile along the sample. Calibration under dry and fully saturated conditions allows the water saturation measurements. Each saturation profile is obtained in 12 minutes.

2.2 Rocks and Fluids

Two types of sandstone with very different petrophysical properties were used for this study.

One is a Vosges Sandstone that is representative of a reservoir rock with 20-22% porosity and a permeability of about 100 mD. The other is a Moliere Sandstone with a very low permeability 10^{-2} mD and 14% porosity. The Moliere Sandstone, which cannot be considered to be representative of a reservoir rock, was chosen to study the effect of capillary trapping on drying dynamics since capillary effects are enhanced in tight systems, and to test the model more broadly and specifically in the low drying rate regime. The rock properties are summarized in Table 1.

Non-wetting fluid (Nitrogen)

The non-wetting fluid used in this study is nitrogen (N_2) because we focused only on drying mechanisms. CO_2 might have caused ancillary geochemical reactions and water-rock interactions outside of the scope of this study. The key parameter needed to evaluate drying dynamics is the water vapour concentration in the gas phase at thermodynamic equilibrium under specific temperature and pressure conditions. The water vapour content is known for different gas and water systems and specifically for water brine/ CO_2 (Spycher et al., 2003; Spycher and Pruess, 2005). So, the results, in term of drying dynamic, obtained using N_2 can be used for CO_2 storage based on reservoir modelling with appropriate thermodynamic description of the carbon dioxide/brine system.

Brine

Various brines were prepared for the experiments. With the Moliere sandstone, we used mainly a mixture of salt representative of a Paris Basin brine at a high salinity of 160 g/L (KCl 4.12 g/L; $MgCl_2 \cdot 6H_2O$ 5.23 g/L; $CaCl_2 \cdot 2H_2O$ 22.00 g/L; NaCl 139.33 g/L; Na_2SO_4 0.52 g/L) (Azaroual et al., 1997). For the Vosges sandstone, we used a mixture of aqueous KCl and KI solutions. The latter is used to intensify the density contrast for X-ray measurements.

2.3 Methodology

The rock sample cores were initially dried in an oven at 80 °C for at least 24 hours and placed in the core holder. A first X-ray profile under dry conditions was acquired before the sample was saturated with the brine. A second X-ray profile was acquired in order to

calibrate the X-ray absorption technique for saturation measurements. The initial water permeability was then determined by measuring the flow rate and pressure. The nitrogen was then injected under controlled pressure. The inlet pressure was fixed and the outlet gas flow rate was measured. Saturation profiles were recorded repeatedly to measure the evolution of brine saturation in the samples.

3. Drying of Moliere Sandstone samples by gas injection

The dynamics of drying by gas injection have been only poorly investigated by experiments (Mahadevan et al., 2007; Peysson et al., 2011b). The main objective of our work was to measure the evolution of water saturation with time in order to quantify the drying effect. Is there a remaining water phase blocked by capillary effects? What effect does the dissolved salt have on drying dynamics and rock permeability? These questions must be answered if we wish to predict, for CO₂ sequestration, the temporal and spatial evolution of the dry zone near the injection wells. The first set of experiments was done with tight sandstone to increase the capillary effects and to investigate the drying dynamics.

3.1 Drying conditions at the lab scale and experimental results

We measured the evolution of the local and average liquid saturation in the Moliere sample. The nitrogen injection was imposed in four steps (Fig. 2). The outlet pressure was set at 50 bars and two temperatures were studied: 90 °C and 120 °C.

The pressure was increased step-wise to study the effect of gas velocity on saturation and drying dynamics. The average water saturation and the outlet gas flow rates for the two temperatures are shown in Fig. 3, and the local saturation profiles are shown in Fig. 4.

At both temperatures, the mean water saturation decreased and the gas outlet flow rate increased (Fig. 3). During the first two pressure plateaus, the predominant regime was a two-phase immiscible displacement (piston effect) as the gas flow pushed the water out of the rock sample. Thereafter, the gas flow rate was high enough to evacuate part of the water as water vapour in the gas phase (last two plateaus). In this regime, the water saturation

decreased below the irreducible water saturation level ($S_{wi} = 16\%$). At the same time, the gas flow rate increased significantly. At 90°C, water saturation reached zero, and at 120°C, it reached a “residual signal”. In both experiments, the samples were, in fact, completely dry. To check that, we removed the samples and let them dry in an oven with regular weighting. In both cases, no mass losses were observed. The “residual signal” at 120 °C corresponds to the presence of precipitated salt in the sample measured with the X-ray.

The temporal evolution of the water saturation profiles also shows two trends (Fig. 4). The first two pressure steps are characteristic of two-phase immiscible displacement with a gas breakthrough and a decrease of the water saturation with a capillary fringe. (Because of diffraction effects, the two ends of the sample are fuzzy and we do not have the water saturation measurements at the ends. However, we clearly see the increase in saturation at the end of the sample.) However, for the last two pressures steps and at both temperatures, the profiles tend to flatten out and the capillary fringe disappears. Moreover, no drying front is observed until the end of the experiments, which means that capillary flows were strong enough to homogenise the water profiles even at low saturation.

At the end of the experiments, we observe no residual signal at 90 °C aside from a small effect at the entrance ($x < 5\text{mm}$), and a flat profile with a peak at the entrance at 120 °C. In both cases, precipitated salt is present in the sample.

Permeability, measured at the end of the experiments, had decreased due to the presence of salt. The final gas permeability was 37 and 50 % of the initial permeability at 90 °C and 120 °C, respectively. Every sample was weighed at the end of the experiment, but the small mass changes just allow estimating a porosity change of about one point or less.

3.2 Quantitative Interpretation - Two phase flow immiscible displacement

The results are representative of gas injection for CO₂ storage in the sense that two coupled mechanisms contribute to the changes in wellbore water saturation: viscous displacement and drying. In order to fully interpret the experiments quantitatively, we studied the effect of two-phase flow on the total water saturation evolution. Darcy's law model for two-phase flow

(Kulkarni et al., 2009) was used to calculate the evolution in saturation caused by the injection of gas at an imposed pressure. Two closure laws are required: the gas-water capillary pressure and the gas-water relative permeability curves (Fig. 5).

The drainage capillary pressure curve was measured using the centrifuge technique and modelled with the following equation (Fig. 5a):

$$P_c(S_w) = -P_0 \ln(S^*) + P_t \quad (1)$$

where P_t and P_0 are parameters and $S^* = (S_w - S_{\min}) / (S_{\max} - S_{\min})$ is the reduced water saturation ($S_{\min} = 0.16$ and $S_{\max} = 1$). Relative permeability curves for gas and water were calculated using the Corey equation (Fig. 5b).

$$K_r^w = K_{\max}^w (S^*)^{\alpha_w} \quad (2)$$

$$K_r^g = K_{\max}^g (1 - S^*)^{\alpha_g} \quad (3)$$

Although the effect of temperature on relative permeability has rarely been studied, some measurements are available for thermal enhanced oil recovery (Hamouda and Karoussi, 2008). The relative permeability curves change little for a small range of temperatures. This can be interpreted, bearing in mind that these curves represent, for the most part, the geometrical restriction to the flow of one phase relative to the other. The distribution of the fluid in the porous structure depends on the capillarity and wettability. However, within a temperature range of 90 to 120 °C, the changes are small. We therefore considered no changes in the relative permeability curves for our experiments at 120 °C.

The capillary pressure curve can be represented as $P_c = 2\sigma \cos\theta / \langle r \rangle$, where $\langle r \rangle$ is the average pore radius saturated with water for a given saturation. The temperature variation would then be given by the surface tension variation σ and the wettability that could be locally represented by a contact angle θ (or more precisely the cosines of this angle). In general, surface tension decreases with temperature (Guyon et al., 2001). For water-air systems, the decrease is relatively small between 90 and 120°C (60 to 55 mN/m). For the

wettability, we assume, in our case, strong water wet rock and no change with the temperature. The gas is the non-wetting phase for the two temperatures. So at a first approximation, we kept the capillary pressure curve constant for the case of 120 °C.

For the CO₂/brine system, surface tension and wettability measurements as a function of the temperature have been reported recently (Chalbaud et al., 2009, 2010).

The Darcy two phase flow equations were solved numerically. The calculated gas flow rate and the average water saturation inside the core were compared to the experimental data (Fig. 3). This confirmed that the first two pressure plateaus are essentially two-phase flow immiscible displacement. However, the two last plateaus in the experiments are dominated by drying dynamics. Indeed, with only two-phase flow, saturation should have continued to the irreducible water saturation ($S_{wi} = 0.16$ for these samples) but we observed a total desaturation of the samples. We must therefore quantitatively consider the effect of water evaporation.

3.3 Quantitative interpretation: Thermodynamic aspect of drying

To interpret the drying dynamics, we assumed that irreducible saturation was achieved after the gas displacement. The liquid water mobility was therefore zero. The dry gas was injected at a mass flow rate Q_g (Fig. 6). If we introduce the water vapour weight concentration at equilibrium C (kg of water/ kg of gas), the mass balance gives the outlet water flow rate CQ_g :

The decrease in the saturation in the sample is then directly related to the gas flow rate:

$$\frac{dS_w}{dt} = - \frac{C}{m_0} Q_{gaz} \quad (4)$$

where m_0 is the initial mass of water in the fully saturated sample.

In porous media, a classical assumption is to consider a local thermodynamic equilibrium so that the water vapour concentration can be calculated at equilibrium (Puiggali and Quintard, 1992). Indeed, the latent heat of the vaporisation is in excess in the solid phase and the

pores are small enough so that gas diffusion is fast enough to homogenise the water vapour at the pore scale.

Water vapour concentration

Water vapour concentration can be defined by the molar fraction y (mol of water vapour/mol of gas) or by the mass concentration C (kg of water/kg of gas). The relationship between the two variables is the following:

$$C = y \frac{M_{H_2O}}{M_{gas}} \quad (5)$$

where M_{H_2O} is the molar mass of water and M_{gas} is the molar mass (kg/mol) of the water vapour and gas mixture. For nitrogen:

$$C = y \frac{M_{H_2O}}{(1-y)M_{N_2} + yM_{H_2O}} = y \frac{M_{H_2O}}{M_{N_2} \left[1 - y \left(1 - \frac{M_{H_2O}}{M_{N_2}} \right) \right]} \quad (6)$$

But in the case of drying under our thermodynamic conditions, y is very small (around 10^{-3}) and the term

$$\left(1 - \frac{M_{H_2O}}{M_{N_2}} \right) = 0.36 \quad (7)$$

We could therefore simplify C to:

$$C = y \frac{M_{H_2O}}{M_{N_2}} \quad (8)$$

The water vapour molar fraction was estimated analytically using the Ideal Gas Law. Indeed, at equilibrium, we have:

$$y = \frac{P_s(\bar{T})}{P} \quad (9)$$

where $\bar{T}$ and $\bar{P}$ are the average pressure and temperature in the sample. Since we measured the volumetric flow rate in our experiments, we introduced β (kg/m³), the water vapour concentration (mass of water vapour by volume of gas), and can write:

$$CQ_g = \beta Q_{gas}^v \quad (10)$$

where β depends only on the temperature:

$$\beta = \rho_0 \frac{P_s(\bar{T})}{P_0} \frac{M_{H_2O}}{M_{gas}} \frac{T_0}{T} \quad (11)$$

For nitrogen, we calculated β as a function of temperature (Fig. 7) ($\rho_0 = 1.17$ kg/m³ at $T_0 = 20$ °C and $P_0 = 1.013 \cdot 10^5$ Pa). The vapour pressure equilibrium equation is the Duperray correlation, which represents fairly well the water vapour curve up to the critical point ($P_C = 221.2$ bar $T_C = 374.15$ °C):

$$P_s(\bar{T}) = \left(\frac{\bar{T}}{100} \right)^4 \quad (12)$$

where T is °C.

We also calculated β for the real gas equation for nitrogen with CARNOT, thermodynamic software developed by IFPEN, from the Peng-Robinson equation of state. In this case, we have a weak pressure effect (Fig. 7).

Kelvin effect - Capillary contribution to the vapour concentration

Using low permeability sandstone enabled us to study capillary effects. First, we evaluated the contribution of the Laplace pressure on the liquid-vapour equilibrium. This can be evaluated from the Kelvin equation (Eq. (13)):

$$P_s^c(T) = P_s(T)\varphi \quad (13)$$

$$\text{and } \varphi = e^{-\frac{M_{H_2O} P_c(S)}{\rho R T}} \quad (14)$$

The water liquid-vapour equilibrium curve $P_s(T)$ is modified in porous media by the capillary pressure $P_c(S)$. The water is trapped in liquid form and the vapour concentration in the gas decreases. The higher the capillary pressure, the lower the water vapour concentration. But even in the Moliere sandstone, this effect was very weak, as shown by the dashed line in Fig. 7 (the correction is made for ideal gases only). We used the capillary pressure curve measured for the Moliere sandstone (Fig. 5a).

Saturation evolution in drying regime

From Eq. (4), if drying is the predominant regime of water evacuation, we can calculate the average saturation evolution in our experiments:

$$S_w(t) = S_w^i - \frac{\beta}{m_0} \int_0^t Q_g(t) dt \quad (15)$$

where Q_g is the flow rate measured at the outlet of the core. Fig. 8 compares the average water saturation remaining in the sample and the saturation calculated with Eq. (15) (at 120 °C, we removed the residual signal due to the precipitated salt to have only the water saturation evolution). In Fig. 8a, we used different values of β ($\beta_1=0.31$; $\beta_2=0.4$; $\beta_3=0.2$) to compare with the data.

For the two temperatures studied, only one value of β enables a perfect estimation of the decrease in saturation. β could be measured by adjusting the saturation calculated with Eq. (15) and the experimental data.

This strong coupling between the measured gas flow rate and the average saturation was verified for all of the experiments and for the two rock types. For each experiment, in the predominant drying regime, Eq. (15) was used to calculate β and Fig. 9 shows the values measured for the different temperatures studied.

These results are very interesting because we see a very good match with β calculated with the Real Gas Law, and we can then conclude that the evaluation of β at equilibrium is valid

and that the Kelvin effect can be totally disregarded, as expected based on the model (Eq. (10)).

Outlet gas flow rate prediction in the drying mode

Because the average water saturation and the outlet gas flow rate are coupled in the drying mode (Eq. (15)), if we can determine the outlet gas flow rate from the imposed pressure, we can directly deduce the water saturation. For this, we need to know the shape of the gas relative permeability curve in the unusual range $[0 - S_{wi}]$.

For the two experiments at different temperatures, we could directly estimate the gas relative permeability curve from the experimental data. Indeed, as shown on the local saturation profile, in the drying stage, the saturation within the sample does not depend on the position x (Fig. 4). The average water saturation depends only on time $S_w(x,t) = S_w(t)$. Under these conditions, assuming no water mobility, we can write the Darcy law directly under weak compressibility hypotheses:

$$\frac{\Delta P}{L} = \frac{\mu_g}{K_0 K_r^g(S_w(t))} \frac{Q_g(t)}{A} \quad (16)$$

Because the pressure is constant during the plateau, we can calculate the evolution of the gas relative permeability with saturation by the ratio of Eq. (16) at two times:

$$K_r^g(S_w) = K_r^g(S_w(t=0)) \frac{Q_g(t)}{Q_g(t=0)} \quad (17)$$

The recorded data at 90 °C and 120 °C are represented in Fig. 10.

The only constraint imposed is $K_r^g(S_w=0) = 1$ (We have to recover the sample permeability in monophasic flow). The two data sets merge on a single curve (Fig. 11) that is coherent with the first set of relative permeability values estimated from the first experimental phase (two-phase flow displacement) showing that relative permeability is an effective parameter of the problem.

The results of the Fig. 11 also confirm that, as expected, relative permeability curves do not depend greatly on temperature in the 90 – 120 °C range.

3.4 Contribution of the two predominant mechanisms to the water saturation decrease

Fig. 12 shows the evolution of the average water saturation if only two-phase flow (black thin line) or only drying (bold black line) are taken into consideration. The saturation was calculated with Darcy two-phase flow model, as discussed in paragraph 3.2 (black thin line), and, using the experimental outlet gas flow rate, we calculated the equivalent water saturation evacuated through evaporation (with Eq. (11)). At the end, the mass balance of water is respected to within 3 % (water displaced through two-phase flow with water evaporated).

4. Drying experiments with Reservoir rock samples (Vosges sandstone)

4.1 Experimental results

The second set of experiments was done with Vosges sandstone – a type of rock representative of a sandstone aquifer. The initial gas permeability of the sample was 74 mD and the porosity 21.8 %. The brine was 35 g/L, a mixture of KCl (55 %wt) and KI (45 %wt). In these experiments, the imposed pressure was reduced in order to stay within the range of measurement of the gas flow rate of our system. We imposed three pressure plateaus (120 mbars, 800 mbars and 1500 mbars) and measured the gas flow rate and the saturation evolution in the sample with time. The temperature was lowered a little to decrease the evaporation rate (80 °C). The outlet pressure was 50 bars. As with the experiment at 120 °C with the Moliere sandstone, a residual absorption was obtained by the end of the drying. This time, we used this as the calibration signal for the dry state. We could then represent the evolution of the average (Fig. 13) and local liquid saturation in the sample with time (Fig. 14).

The average water saturation (Fig. 13) follows the same trend as for the Moliere samples. The first plateau is purely two-phase flow displacement with a rapid gas breakthrough (at $t=5$ hours) and a low gas flow rate. The second plateau is mixed, with a significant contribution of drying. For the highest pressure, drying is very rapid, lasting only a few hours.

The saturation profiles along the sample also show the same trend as for the Moliere sandstone (Fig. 14). The first profiles are typical of two phase flow displacement with a capillary fringe close to the outlet of the sample. The profiles are then flatter and at the end of the drying, we clearly see a drying front that moves from the sample inlet to the outlet. This is due to the fact that the drying rate is much higher than in the previous cases and the water flow does not have time to re-equilibrate the water saturation in the sample.

The drying front is observed only at the very end of the drying stage. At higher water saturation, capillary back flows are strong enough to flatten the water saturation profiles. The dissolved salt is transported in the water and accumulates near the injection surface. At the end of the experiment, the X-ray absorption signal is very heterogeneous throughout the rock sample (Fig. 15).

There is a very pronounced peak in the first 5 millimetres of the sample. The residual signal is due to the salt precipitation induced by the drying. The permeability decreases 70 % due to this salt deposition (22 mD at the end compared to an initial 74 mD).

This case was numerically modelled in detail, with the full coupling of drying and two-phase flow displacement (André et al., 2013).

We also injected gas at a constant imposed pressure of 300 mbars into a sandstone core initially fully saturated with a 150 g/L of KCl brine (Fig. 16). This caused total plugging of the sample. No gas flow was observed after 46 h, which confirms the previous interpretation of a salt accumulation near the injection surface that can be strong enough to block the gas flow. This has also been confirmed by modelling (André et al., 2013).

4.2 Interpretation - Discussion

The drying of the brine-saturated cores was forced by a driven gas flow. The main mechanisms can be divided into two steps, as already mentioned in the literature (Mahadevan et al., 2007):

- 379 - **Step 1:** Dry gas pushes the pore water by a piston effect. The flows of the two
380 phases (gas and brine) are controlled by Darcy equations. This is observed
381 regardless of the initial permeability of the porous medium (Figs. 3 and 12). First,
382 most of the water is pushed out from the core (to the outlet), then water can flow in
383 the other direction (toward the column inlet) due to capillary effects. This process re-
384 equilibrates the water saturation inside the core and explains the flattening of the
385 curves observed mid-way through the experiments (Figs. 4 and 14). During this first
386 phase, water turns also to vapour in the gas because thermodynamic equilibrium is
387 reached as already emphasized. However, this process contributes little to the water
388 transport compared to advection. As a consequence, in this first step, there is only
389 little evaporation, therefore no oversaturation and salt does not precipitate.
- 390 - **Step 2:** The water saturation in the core is close to the irreducible water saturation.
391 Darcy brine flows are not predominant and evaporation becomes the main process
392 within the core causing the water to be evacuated. During this phase, most of the
393 water mass exchange takes place at the injection surface where the gas comes into
394 contact with the water. The decrease in water saturation at the injection surface
395 induces brine capillary back flow that transfers the brine toward the injection surface.
396 Salt accumulates near the injection surface and precipitates when saturation is
397 reached. This is observed in each experiment, although to a lesser extent with the
398 Moliere sandstone (see the residual X-ray profiles for both samples at the end of the
399 drying in Fig. 4 where there is also a small peak in the first 5 millimetres). Salt
400 precipitation is not homogeneous because drying can cause the dissolved ions to
401 flow toward evaporating surfaces (Huinink et al., 2002; Sgair et al., 2007; Guglielmi et
402 al., 2008; Peysson, 2012). The salinity of the brine plays a crucial role in the amount
403 of salt precipitated even if this mechanism is observed for all the salinities tested. In
404 the experiment with Vosges sandstone, the brine salinity is 5 times higher than in the

experiment with Moliere sandstone. The consequence is a massive precipitation of salt close to the inlet of the core with a full clogging preventing any gas injection.

The processes occurring during this second step are complex because many have opposite effects. To better understand the different processes, a Péclet number can be calculated to provide information concerning the ratio between advective and diffusive transport (Huinink et al., 2002; Sgair et al., 2007; Guglielmi et al., 2008):

$$Pe = L\beta V/\rho\phi D \quad (18)$$

where L is the characteristic length, D the diffusion coefficient ($D = 10^{-10} \text{ m}^2/\text{s}$ for salt in water), and V the gas velocity ($V = Q_g/S$). β is taken from Fig. 9.

During step 2 (i.e., the drying period) of the experiments with Moliere sandstone, the low mean gas velocity (about 2-3 L/h) caused a very low evaporation rate. Capillary flow continuously re-equilibrated the water saturation inside the core (water flowed toward the sample inlet). At the same time, because of water evaporation near the injection surface, the salt concentration increased, creating a salt gradient inside the column. However, the low Péclet number (about 4 and 15 at 90 °C and 120 °C, respectively) suggests that salt diffusion occurred inside the core (from the inlet toward the outlet) resulting in a rather homogeneous distribution of salt throughout the column.

For the experiment with the Vosges sandstone, the mean gas velocity (Q_g) was about 3 L/min (Fig. 13). Consequently, the Péclet number is about 360, which suggests the predominance of advective processes. Massive capillary flow carried salt toward the injection surface where the water evaporation was very rapid because of the gas injection flow rate. Like for the previous experiments, a salt gradient was created inside the core. However, because the diffusive fluxes were negligible compared to the evaporation rate, salt precipitated close to the injection surface, leading to heterogeneous salt deposits.

Conclusion

We ran experiments to study the mechanisms governing the saturation evolution at the near wellbore of CO₂ injection wells. During the first stage of gas injection, two-phase flow immiscible displacement is the main mechanism and water is pushed in the aquifer. This phase could be modelled with Darcy two-phase flow models. Thereafter, the residual water at the near wellbore might be transferred to the gas phase by thermodynamic exchanges. Drying is then the predominant mechanism controlling the decrease in water saturation. The drying rate is proportional to the gas velocity and the water vapour concentration in the gas had to be estimated at equilibrium.

Any dissolved salt in the water can be transported by capillary flows induced by drying and can even accumulate near the injection surface. The permeability can then be altered by pore clogging. To correctly determine well injectivity, all of these mechanisms must be included in models to calculate the near wellbore permeability and porosity changes with time.

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Fig. 1

Fig. 2

Fig. 3

(a)

(b)

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11

Fig. 12

Fig. 13

Fig. 14

Fig. 15

Fig. 16

623 Table 1: Sample characteristics for each experiment.

<i>Rock Sample</i>	<i>Temperature</i>	<i>Brine</i>	<i>Initial Porosity</i>	<i>Initial permeability</i>	<i>Final permeability</i>
Moliere Sandstone	90°C	Paris basin brine (160g/l TDS)	14%	8 10 ⁻³ mD	3 10 ⁻³ mD
Moliere Sandstone	120°C	Paris basin brine (160g/l TDS)	14%	12 10 ⁻³ mD	6 10 ⁻³ mD
Vosges Sandstone	80°C	KCl + KI (35g/l TDS)	21.8%	74 mD	22 mD
Vosges Sandstone	60°C	KCl (150g/l TDS)	21.8%	160 mD	0 mD

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