CO_2 capillary entry pressure into flow barrier and caprock

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ABSTRACT

Flow of CO_2 through a partly sealing barrier like intra-formation low permeable layers or caprock will depend on characteristics like permeability and the capillary threshold of the flow barrier. Possible changes in wettability due to physical-geochemical processes could decrease the capillary entrance pressure and reduce the sealing integrity of the caprock. Changes in wettability have therefore been investigated by measuring the CO_2 contact angle on muscovite mica in the presence of brine at reservoir conditions.

Water wettability of muscovite mica at the conditions of interest for CO_2 sequestration was changed from strongly water wet to intermediate water wet after exposure to CO_2. This wettability alteration in muscovite mica brings concern regarding CO_2 leakage in shaly caprock. For more investigation, the step-by-step approach (standard method) was used to directly determine the capillary entry pressure in systems composed of dense CO_2, brine and reservoir flow barrier rock material. All the key components for determination of capillary entry pressure of CO_2 were installed in a cabinet at isothermal conditions and exact pressure control.

The core comprising the highest permeability of the tested cores (with absolute air permeability of 90 micro Darcy) was saturated with brine and water permeability was determined. The capillary entry pressure of gas in the rock was measured and determined when the gas was forced to enter the pore network of the low permeability core. The experiments were repeated to determine the impact of successive exposure of CO_2 and brine on the capillary entry pressure.

INTRODUCTION

Wettability is the tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids [1]. In CO_2 injection process into aquifer, possible changes in wettability of the caprock could decrease the capillary entrance pressure. Such a decrease could reduce the sealing integrity of the caprock. When the pressure in the CO_2 phase (P_{CO_2}) is high enough to displace the water in the caprock or flow barrier, capillary leakage occurs. This takes place at the threshold capillary entry pressure (P_{ce}) for the CO_2 phase which is defined by Equation 1 [2]:

$$P_{ce} = P_{CO_2} - P_{water} \approx 2\gamma_{w-CO_2} cos(\theta)/R \qquad \text{Equation 1}$$

Here R is the radius of the largest connected pore throats in flow barrier, γ_{w-CO_2}, the brine/CO_2 interfacial tension and θ is the contact angle of the mineral/brine/CO_2 system. P_{water}, is the pressure in water (brine) which saturates the seal layer.

Water-wettability of various inorganic (e.g., stainless steel) [3] and organic (coal) materials and shale [4], [5] have been found to change in the presence of dense CO_2. Some of these studies are referred to in the following. Chiquet *et al.* and Shah *et al.* reported that the wettability of minerals mica in the presence of CO_2 at elevated pressures (in a range of pressures extending up to 150 bar), changed from water wet to intermediate wet [5], [6]. Bikkina claims that exposure of calcite and quartz to dense water-saturated CO_2 caused a permanent shift in the contact angle [7]. Plug *et al*. found increase in CO_2 wettability of medium-rank and high-rank coals for increasing CO_2 pressure [4].

Egermann *et al.* observed that CO_2 was clearly the non-wetting phase in carbonate cores for pressures from 80 to 180 bar and temperatures from 60 to 80 °C [8]. Experiments by Wollenweber indicated that repeted CO_2 exposure resulted in a reduction of the capillary sealing efficiency [9]. Chalbaud *et al.* showed by use of pressurised micromodels that for water/CO_2 system, the CO_2 can wet a solid surface at reservoir conditions if the surface is intermediate wet or oil-wet [10], [11]. Hildenbrand *et al.* performed breakthrough experiments on pelitic rocks and showed that the capillary-sealing efficiency of the samples depends on the gas phase used in the experiments [12].

This paper presents two sets of experiments which have been performed to determine the possible changes in wettability in CO_2-brine system at reservoir conditions. The first set of experiments presents changes in wettability quantified by measuring the CO_2 contact angle on muscovite mica mineral in the presence of brine at reservoir conditions. In the second set of experiments, a core with low permeability has been selected. In the first place, the core permeability was measured with two different methods, an unsteady-state method based on the pressure fall-off technique and a conventional steady-state method with gas and with water. Afterward, CO_2 capillary entry pressure was measured by use of the step-by-step approach at typical geological CO_2 storage conditions was measured. The experiments were repeated three times to see the effect of repeated CO_2 exposure.

EXPERIMENTS

Contact angle measurement and results

The experiments are performed by the captive-needle drop method. The experimental setup is equipped with a high-pressure viewing cell with two parallel see-through windows, in which drops of CO_2 are formed at the end of a needle and contacted with the substrate (mineral) immersed in brine. To avoid the gravity effect, the CO_2 drop is positioned beneath the substrate [13]. The angle was always measured through the brine phase. Measurements have been carried out in a range of pressures extending from atmospheric pressure up to 400 bars, at temperatures of 36 °C, with CO_2 and with mineral substrate muscovite mica. The tests were performed with water with 0.8 NaCl molarity.

To investigate wettability alteration with time, the muscovite mica mineral was exposed to the CO_2 drop at 105 bar and 36 °C in the presence of saline water for 48 days.

Prior the experiment, the mineral was washed with Deconex solution under ultrasonic bath and cleaned with distilled water at the end and then muscovite mica sheets was attached to a glass plate by wrapping Teflon tape around the edges. As the pressure increased from 10 to 300 bar, the contact angle increased from 16° to 36°. The major increase in contact angle occurred when the pressure increased above critical pressure of 73 bar. For pressures higher than 100 bar, the change in contact angle was not significant. At higher pressure, the water wettability of muscovite mica is clearly decreased. This reduction continued as muscovite mica was exposed to CO_2 drop for 48 days at constant pressure of 105 bar and temperature of 36 °C. The CO_2 contact angle increased from 35° to 60.5° over 48 days [14].

Figure 1 shows the change in CO_2 contact angle on muscovite mica surface with increasing pressure and with time. As concluded before by Broseta, et al., [15], the wettability alteration of mica could be explained by changes in intermolecular forces controlling the stability and thickness of the water film that is sandwiched between mineral and CO_2 drop at lower pH. When the drop is formed on substrate surface, it covers a certain length of the substrate. Then drop size is increased until the triple line starts to move. During 48 days of exposing muscovite mica to CO_2 drop, the length of substrate covered by CO_2 drop increased by a factor 2.7 with time as shown in Figure 2.

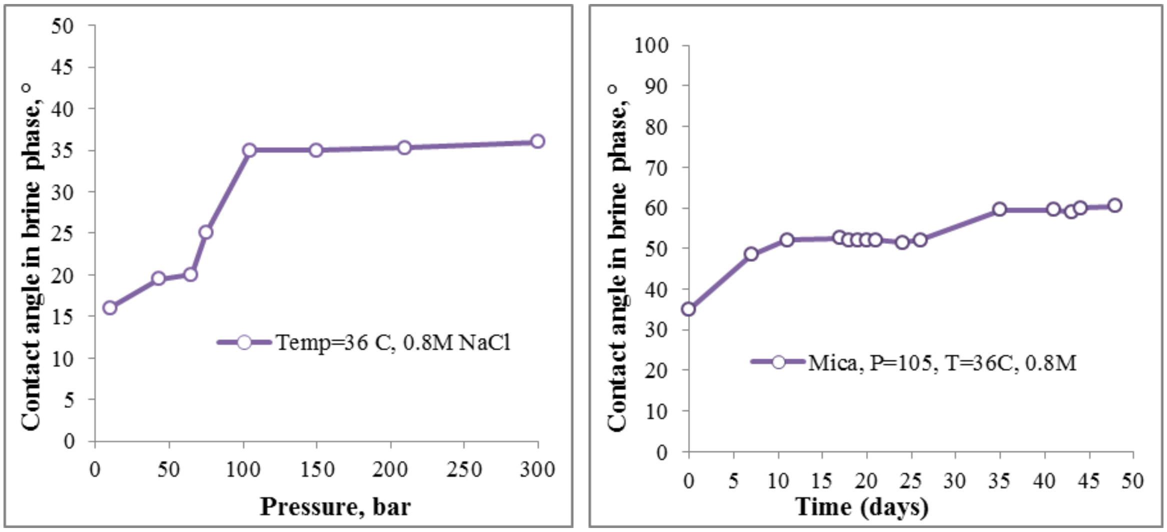

Figure 1: Left) CO_2-brine contact angle on muscovite mica surface versus pressure right) contact angle as function of time for brine-CO_2-mica system

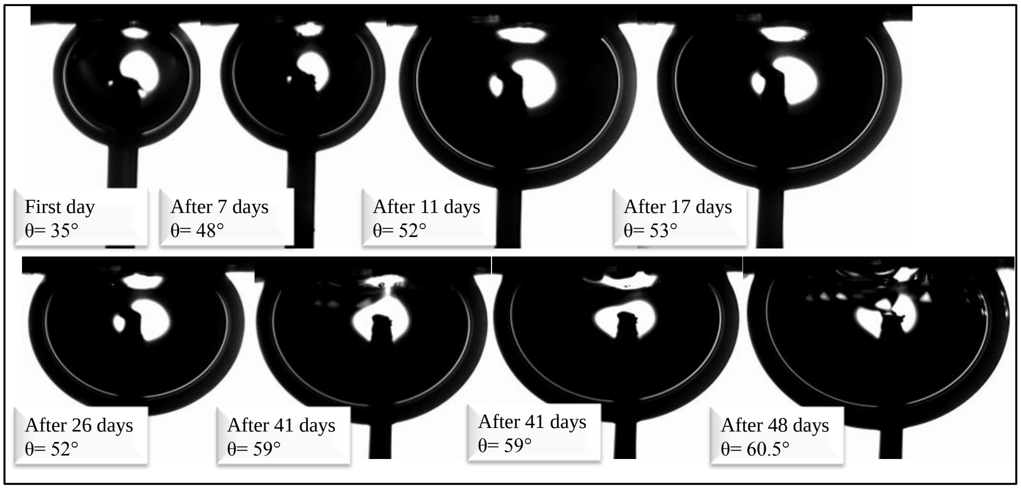

Figure 2: CO_2 drop on muscovite mica surface in 0.8 M NaCl brine over 48 days at 105 bar and 36 ^{o}C

Capillary entry pressure measurements

In this work, sample permeability was measured with gas using two different methods, an unsteady-state method based on the pressure fall off technique and a conventional steady-state method. Transient pressure fall-off measurements employ fixed-volume gas or liquid reservoirs, in this case a 1 liter tank filled with copper tubes and nitrogen gas at maximum 10 barg pressure, which is connected to the upstream end of the core subjected for gas flow [16]. The pressure in the upstream nitrogen tank declines with time when gas flows through the core. The permeabilities achieved by transient method (from late time data) were consistent with the measured permeabilities from steady state methods. The steady state permeability was measured by using constant head permeameter method and nitrogen gas as a flowing gas and it was corrected by Klinkenberg effect. Absolute permeability to brine was measured at the 100% water saturation level and stabilized pressure drop and by using Darcy equation. Table 1 shows the core properties. The porosity of the core was measured by helium (gas expansion method) and by saturating the core with brine (4% salt) and weighting the dry and wet core.

Table 1: Samples properties

Length, cm	*Diameter, cm*	*Helium porosity*	*Water saturated porosity*	*Transient Permeability, md*	*Absolute N_2 permeability, md*	*Absolute water permeability, md*
1.421	3.833	15.2 %	10.7 %	0.09	0.09	0.0017

Experimental procedure

The method allows for measurement of threshold capillary pressure of rock materials by the step by step injection approach at representative storage site pressure and temperature conditions. The following procedures were applied for each set of the experiments:

1. The core was placed vertically in the core testing apparatus and was evacuated to remove trapped gas and net reservoir overburden pressure of 150 bar was applied. Then the samples were saturated with sea water;
2. Pore pressure was increased to desired reservoir value above 75 bar while the working temperature was maintained at 20 °C;
3. The pressure at production outlet was fixed at 75 bar to keep CO_2 as liquid phase. A Quizix pump controlled water pressure at the outlet. The pump is composed of two pistons cylinder with volume of 5 cc each and was connected to the outlet side of the Hassler cell. The pistons moved in a "push-pull" configuration to keep the outlet pressure constant at 75 bar (pump worked at constant pressure receiving mode). The water flow rate was monitored by the movement of piston and also by a balance.
4. CO_2 injection began at a constant pressure of 76 bar and temperature of 20 °C. CO_2 was injected from top to avoid the gravity effect (at P=75 bar and T=20 ºC, CO_2 is lighter than brine, brine density =1.03 g/cm^3 and CO_2 density = 0.82 g/cm^3). CO_2 injection pressure was increased step by step (every 24 hours) and continued until CO_2 displaced brine and brine production at the outlet of core was increased. The inlet pressure during the experiment was monitored.
5. The sample was flooded by brine until no more gas produced and until the same stabilized baseline permeability at the 100% brine saturation level was obtained. Then the procedures 3 and 4 were repeated and CO_2 capillary entry pressure was measured;
6. By repeating procedure number 5, CO_2 capillary entry pressure was measured by successive exposure of the sample to CO_2 and brine.

Capillary entry pressure results and analysis

Table 2 shows the results for N_2 and successive CO_2 capillary entry pressure. After each test, the core was flooded by brine for two days and stabilized baseline permeability at the 100% brine saturation level was obtained.

Table 2: Experimental results for capillary entry pressure and permeability to the water after each test

Test number	Mean pressure, bar	Temperature, ºC	Capillary entry pressure, bar	Water permeability before test, md
Test 1	25	20	$P_{ce,N_2} = 7.05$	After first brine flooding, k_1=0.0017
Test 2	79	20	$P_{ce,CO_2} = 5.04$	After second brine flooding, k_2=0.0007
Test 3	78.5	20	$P_{ce,CO_2} = 4.56$	After third brine flooding, k_3=0.0012
Test 4	78	20	$P_{ce,CO_2} = 4.00$	After fourth brine flooding, k_4=0.0017

First N_2 capillary entry pressure was measured ($P_{ce,N_2} = 6.05$ bar) and then the sample was flooded by brine for two days. Afterward, CO_2 capillary entry pressure test was performed for three times and after each time, the core was flooded by brine and the permeability to the brine was measured. According to Table 2, the permeability changed after the core was flooded by CO_2 and brine. This could be explained by fines migration inside the core.
For $P_{ce,N_2} = 6.05$ bar, the expected capillary entry pressure for CO_2 was:

$$\frac{P_{ce,CO_2}}{P_{ce,N_2}} = \frac{\gamma_{CO_2}}{\gamma_{N_2}} \rightarrow P_{ce,CO_2} = 0.43\, P_{ce,N_2} = 3.01\, bar \qquad \text{Equation 2}$$

Equation 3 assumes $\gamma_{N_2} = 70.8$ mN/m for P = 25 bar and T=20 ºC [17] and $\gamma_{CO_2} = 30.3$ mN/m for P = 79 bar and T=20 ºC [18]

However, the experiment yielded $P_{ce,CO_2} = 5.04$ bar. Equation 2 is valid when the pore throat size is constant. Change in core permeability indicates that the assumption of constant pore throat size may not be valid.

$$\frac{P_{ce,CO_2}}{P_{ce,N_2}} = \frac{\gamma_{CO_2}}{\gamma_{N_2}} \times \sqrt{\frac{k_1}{k_2}} \rightarrow P_{ce,CO_2} = 1.56\, P_{ce,N_2} = 4.69\, bar \qquad \text{Equation 3}$$

$P_{ce,CO_2} = 4.69$ bar is very close to the measured CO_2 capillary entry pressure. In the tests 3 and 4, CO_2 capillary entry pressure had decreased to 4.56 and 4.00 bar respectively. According to Equation 3, the expected capillary entry pressures are;

$$\boldsymbol{\frac{(P_{ce,CO_2})_2}{(P_{ce,CO_2})_1} = \sqrt{\frac{k_2}{k_3}} = \sqrt{\frac{0.0007}{0.0012}} \rightarrow (P_{ce,CO_2})_2 = 0.76\,(P_{ce,CO_2})_1 = 3.85\ bar}$$

$$\frac{(\mathrm{P}_{ce,CO_2})_3}{(\mathrm{P}_{ce,CO_2})_2} = \sqrt{\frac{k_3}{k_4}} = \sqrt{\frac{0.0012}{0.0017}} \rightarrow (\mathrm{P}_{ce,CO_2})_3 = 0.84\,(\mathrm{P}_{ce,CO_2})_1 = 3.83\ \mathrm{bar}$$

The values above are even lower than the measured values, probably because of the error in pore throat size calculation and ± 2% experimental errors.
The decrease in CO_2 capillary entry pressure is mainly caused by change in permeability and pore structure and it is hard to see the effect of wettability. With reference to Equation 1, any change to capillary entry pressure is due to change to wettability, IFT and the size of pore throat. For the CO_2-water system while pressure and temperature are constant, IFT is also constant. On the other hand, since the permeability had changed during the experiments, without any visualized evidence, it is not possible to see what the wettability behavior is and how it affects capillary entry pressure.

CONCLUSION

1. Exposing muscovite mica mineral to CO_2 for 48 days at fixed conditions showed a marked increase in contact angle and mineral became significantly less water wet.

2. This wettability alteration in muscovite mica brings concern regarding CO_2 leakage in shaly caprock. Depending on shale composition, this could be a serious concern for long term CO_2 storage. For further investigation, the capillary entry pressure for CO_2-water system in the core scale was measured.
3. Exposing the core sample to brine and CO_2 and successive CO_2 capillary entry pressure measurements resulted in reduction in capillary entry pressure.
4. The permeability measurements after each test showed significant change in the absolute permeability to the brine. CO_2 dissolution in brine forms a weak carbonic acid and this acid changed pore structure and consequently permeability by reacting (eg. iron-minerals) or dissolving (eg. some minerals such as calcite cement or carbonate).
5. The CO_2 capillary entry pressure reduction was dominated by a decrease in permeability and with the employed apparatus and method; it is not possible to see the wettability effect.

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