Capillary pressure for the sand–CO₂–water system under various pressure conditions. Application to CO₂ sequestration

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Received 9 October 2006; received in revised form 21 May 2007; accepted 22 May 2007
Available online 8 June 2007

Abstract

Accurate modeling of storage of carbon dioxide (CO₂) in heterogeneous aquifers requires experiments of the capillary pressure as function of temperature and pressure. We present a method with which static drainage and imbibition capillary pressures can be measured continuously as a function of saturation at various temperature (T) and pressure (P) conditions. The measurements are carried out at (T, P) conditions of practical interest. Static conditions can be assumed as small injection rates are applied. The capillary pressure curves are obtained for the unconsolidated sand–distilled water–CO₂ system. The experimental results show a decrease of drainage and imbibition capillary pressure for increasing CO₂ pressures and pronounced dissolution rate effects for gaseous CO₂. Significant capillary pressure fluctuations and negative values during imbibition are observed at near critical conditions. The measurement procedure is validated by a numerical model that simulates the experiments.

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Keywords: Capillary pressure; Carbon dioxide; Quasi-static; High pressures; Mass transfer; CO₂ sequestration

1. Introduction

There is increasing evidence that the emission of CO₂ contributes to the global warming problem. Geological storage of CO₂ in deep (saline) aquifers, abandoned hydro-carbon reservoirs and unminable coal seams (Enhanced Coal Bed Methane) has the potential to reduce the problem of global warming. Sequestration of CO₂ in aquifers is achieved by the following processes: (1) storage of CO₂ as free-phase gas in the pore spaces (hydrodynamic and capillary trapping), (2) dissolution of CO₂ in the formation water and (3) mineral trapping through geochemical reactions [1–3]. According to Kumar et al. [1], the residence time of the CO₂ in aquifers for sequestration applications is of the order of 10,000 years and different times scales for the different processes must be considered. Dissolution of CO₂ in water is rapid and strongly depends on the contact between the phases, whereas the time scale for trapping of CO₂ as free gas is much longer (the life time of the project) and strongly depends on the reservoir properties. Geochemical reactions (e.g., mineral trapping) are in general very slow, however, under some conditions the rate may be comparable to other transport processes [1].

One of the key-issues considered in CO₂ sequestration are the capillary pressure related properties of porous media. Kumar et al. [1] concluded that capillary trapping of CO₂, i.e., as residual gas or as gas trapped below an internal layer, is the most relevant mechanism for underground storage of CO₂. Other mechanisms for which the capillary pressure behavior is important, are the alternate imbibition and drainage processes in heterogeneous media [4], which results in capillary hysteresis. This non-uniqueness in capillary pressure can be explained by irreversible fluid redistributions [5] and the difference between specific area of the fluid–fluid interface per unit of injected volume [6,7]. For sequestration applications, the hysteresis is of relevance when the fluid displacement leads to residual saturations [1]. Furthermore, capillary pressure is a direct

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measure for wetting effects [8,9]. This wetting behavior is relevant for the integrity of the caprock as a geological seal [1,10]. The seal capacity of the caprock during the project’s life time is therefore a measure of the sustainability of CO₂ sequestration. From literature it is found that CO₂ can alter the wettability of the rock [11–13]. These wetting alterations are observed for shaly caprocks by determining the contact angle between brine and CO₂ on a mica and quartz surface [11]. Similar behavior is reported for coal by Siemons et al. [13,14] and Plug et al. [12]. They concluded, from contact angle measurements and capillary pressure data, that the system becomes CO₂-wet near critical conditions.

Therefore, understanding of the capillary pressure behavior is essential in assessing the suitability and potential of CO₂ sequestration in aquifers. In the literature there is a lack of experimental data of capillary pressures for the rock–water–CO₂ systems in the relevant temperature and pressure range. The only reference with data on capillary pressures at relevant conditions are the indirect (relative permeability) measurements reported by Bennion and Bachu [15,16].

For capillary pressure measurements involving CO₂, the complexity of the phase behavior of the CO₂–water system in porous media system requires both sophisticated theoretical and experimental investigations at conditions of practical interest [17–19]. The non-linear behavior for the CO₂ density and viscosity, as function of temperature and pressure [18] in the vicinity of the critical point, is well described by Span and Wagner [20], Duan and Sun [21] and Fenghour et al. [22]. The solubility of CO₂ in water for various pressures and temperatures is experimentally investigated by Wiebe and Gaddy [23] and a thermodynamic description is given by Duan and Sun [21]. Chun and Wilkinson [24] investigated the interfacial tension for CO₂–H₂O mixtures for a wide range of temperatures and pressures. The results showed a minimum for the interfacial tension at the critical point of CO₂. Numerical and analytical models for the prediction of CO₂ sequestration on the long term can be found in the work of Pruess and Garcia [25], Spycher et al. [17], Ebigbo et al. [18], Class et al. [19] and Nordbotten et al. [26]. For the validation and applicability of these models, experimental measurements are needed to provide the essential input parameters.

The literature describes a number of techniques, which in principle can be used to measure the capillary pressure at the relevant pressure and temperature conditions. Most techniques are based on the porous plate technique [27], the micro-pore membrane technique [28,29], mercury drainage experiments [8] and the centrifuge method [30,31]. Conventional capillary pressure studies use the multi-step method, where after a finite pressure increment an equilibrium water saturation distribution is established. Experimental data are also available in the literature where continuous phase injection is applied [32–40]. These experimental data can be considered as quasi-static because small displacement rates are applied.

In this study, we performed capillary pressure measurements on the unconsolidated sand–CO₂–distilled water system up to near critical conditions. The reason we choose to investigate the capillary behavior of unconsolidated samples is because the experimental set-up is not suitable for consolidated cores.

The objective of this work is to develop a method with which static drainage and imbibition capillary pressures for CO₂ can be measured continuously as a function of saturation at various temperature (T) and pressure (P) conditions and to investigate the effects of the dissolution of CO₂ in water during the CO₂ sequestration process. Quasi-static conditions are achieved by applying small injection rates (0.01–0.1PV/h). To understand the influence of the dissolution process for the CO₂ experiments, nitrogen (N₂) experiments are conducted for which the dissolution effects are much smaller.

From the measurements we expect to observe the mass transfer effects of CO₂ on the injection and production curves because the fluid velocities are very small compared to the mass transfer rate. To understand the effects of dissolution on capillary pressure and the cumulative water production, a quasi-1D, fully implicit numerical model is developed. Moreover, the measurement procedure is validated by this model which simulates the drainage experiments. The simulator is based on the upstream finite volume method that incorporates the CO₂–H₂O phase behavior, mass transfer and dissolution of one phase into another. The mathematical model is explained in Appendix A.

2. Experimental design

2.1. Experimental set-up

The equipment is an optimized version of the set-up presented in Plug et al. [41] and Mazumder et al. [42], and is based on the porous plate technique combined with the micro-pore membrane technique, discussed by Jennings et al. [28], Longeron et al. [29] and Christoffersen and White [27]. This set-up is suitable to measure the capillary pressure for water–gas (N₂ and CO₂) system in unconsolidated quartz sand for different fluid pressures (P_{atm}–85 bar) and temperatures. An overview of the temperature and pressure properties of each experiment performed, are listed in Table 1.

In Fig. 1, the schematic diagram of the set-up is shown and the cross section of the sample holder is shown in Fig. 2 and discussed in Section 2.2. Two syringe pumps (ISCO pump, 260D) are connected to the in- and outlet of the sample holder and can be set to a constant injection rate (accuracy ±0.005 ml/h) or a constant pressure (accuracy ±0.01 bar). The gas phase is injected or produced at the top of the sample holder and the water is collected or injected at the bottom using the water syringe pump for pressures above 1 bar. For primary drainage experiments at atmospheric conditions, valve 7 is closed and valve 8 is open and the water is produced in a beaker placed on a bal-
ance (accuracy ±0.005 g). A layer of paraffin on top of the water surface avoids evaporation. The gas pressure transducer (GPT) and the water pressure transducer (WPT) record the single phase pressures (range 0–100 bar, accuracy ±0.01 bar). The differential pressure between the gas and the water phase is measured by the pressure difference transducer (PDT, range 0–500 mbar, accuracy ±0.1 mbar), which is located at the same height as the middle of the sample, such that no correction for gravity effects is required.

To maintain a constant temperature we cover the entire set-up with a perspex box, sealed by polystyrene. Inside the box two 60 W light-bulbs, which switch on and off, regulate the temperature in the range between 25–40 ± 0.5 °C. We allow temperature equilibration for at least two days for gaseous and liquid CO₂/N₂ and at least three days for supercritical CO₂.

2.2. The sample holder

The sample holder, as shown in Fig. 2, consists of three parts: two end-pieces and a ring that contains the unconsolidated sample. In this work, two types of rings are used: a stainless steel ring with a height of \( H = 25 \) mm and a PEEK (polyetheretherketone) ring with a height of \( H = 27 \) mm [41]. The sand pack with a permeability of \( k \approx 2 \times 10^{-10} \) m², is kept in place using a combination of plates at the top and bottom of the sample. At the bottom, two porous plates (SIPERM R, Cr–Ni-Steel basis), with a permeability of \( 2 \times 10^{-12} \) m² and a porosity of 0.32, support the sample and protect the hydrophilic Millipore membrane used in primary drainage experiments. Two stainless steel plates both with 32
perforations \((D_p = 5 \text{ mm})\) are used at the top directly above the sample in combination with a nylon filter. Between these plates, a hydrophobic membrane is placed for the primary imbibition process, prohibiting water production. To avoid leakage of gas or water over the hydrophobic or hydrophilic membranes, we seal the outer perimeters with a Viton O-ring. Concentric flow grooves in the end-pieces redistribute the injected and produced phase over the total sample area to avoid preferential flow and fast breakthrough of the injected phase.

2.3. Experimental procedure

At the start of each experiment the set-up is cleaned and the porous plates are dried. The assembly of the sample holder is from the bottom upward. For each experiment we use new Millipore filters and new O-rings. When end-piece 2, the porous plates, the hydrophilic membrane and the O-rings included, and the ring are mounted together, we pour the unconsolidated sample in the sample holder. The O-rings included, and the ring are mounted together, we pour the unconsolidated sample in the sample holder. The sample holder is placed in between valves 4 and 5 and the entire system is evacuated for 1 h. During the evacuation, valve 4 is closed.

The next step is to determine the porosity, \(\varphi\), with helium. Therefore, we measure the void volume of the empty sample holder \((V_{\text{void,empty}}\text{, situation 1})\) and the sample holder containing the sand \((V_{\text{void,sample}}\text{, situation 2})\). Both volumes and the sample volume are used and \(\varphi\) can be defined as follows:

\[
\varphi = 1 - \left(\frac{V_{\text{void,empty}} - V_{\text{void,sample}}}{\pi (D_{\text{sample}})^2 H}\right).
\]

In Eq. (1), \(V_{\text{void,empty}}\) and \(V_{\text{void,sample}}\) include the void volume between valves 4 and 5, the gas tubing (between valves 1, 3 and 4) and the gas pump (see Fig. 1). In both situations, we start with an initial helium equilibrium pressure, \(P_{g,1}\), and after moving the piston of the gas pump upwards, we measure the final equilibrium pressure, \(P_{g,2}\). From the difference in gas pump volume, \(\Delta V_{\text{pump}}\) and the two helium pressures we can determine \(V_{\text{void,empty}}\) and \(V_{\text{void,sample}}\) from

\[
V_{\text{void,empty/sample}} = \frac{P_{g,1} \Delta V_{\text{pump}}}{Z_2 \left(\frac{P_{g,2}}{Z_1} - \frac{P_{g,1}}{Z_2}\right)} - V_{\text{pump,2}} - V_{\text{tubing}},
\]

where \(Z_1\) and \(Z_2\) are the compressibilities of helium, \(V_{\text{pump,2}}\) is the final gas pump volume and \(V_{\text{tubing}}\) is the volume of the gas tubing. For both \(V_{\text{void,empty}}\) and \(V_{\text{void,sample}}\) this procedure is repeated five times and the average volume can be obtained. The average volume of the sample holder filled with sand is denoted as \(V_{\text{helium}}\) and presented in Table 1. For the sand samples we found a porosity in the range of 0.36–0.38 (Table 1). Subsequently, the total system is again evacuated for 1 h and filled with water from the water pump by closing valve 4 and opening valve 5 (Fig. 1). The values for the water volume, \(V_{\text{water}}\), are presented in Table 1. Comparison between \(V_{\text{helium}}\) and \(V_{\text{water}}\) shows small deviations (~1%), which can be explained by systematic measurement errors and the accuracy of the measurement devices. Since we use helium the system is leak-tested before each experiment.

When an experiment starts with the primary drainage process, the hydrophobic filter is left out. This makes it easier to pressurize the system. Due to the high pressure, small air bubbles carried along with the distilled water are dissolved. Similar to the primary drainage process, the hydrophilic filter is removed for primary imbibition tests. In this work, we consider three types of experiments: A. Primary drainage experiments at atmospheric pressure \((P_{\text{atm}})\). B. primary drainage and C. secondary imbibition experiments at pressures above \(P_{\text{atm}}\):

(A) The total sample holder is initially filled with water between valve 4 (closed) and valve 5 (see Fig. 1). Subsequently the water pump is used to apply a pressure of 10 bar to remove all possible air and to obtain 100% water saturation. When the pressure becomes 10 bar, the water pump is stopped and valve 7 is closed. Subsequently, valve 8 is opened and the water pressure decreases towards the atmospheric pressure. The gas tubing and the gas pump are filled and flushed with either \(N_2\) or \(CO_2\). Finally, we set a constant temperature and let the system equilibrate for 48 h. The primary drainage experiment starts when a constant gas injection rate is applied and valve 4 is opened. Due to operational restrictions of the ISCO pumps for pressures below 1 bar, no imbibition tests are conducted for atmospheric conditions.

(B) For high pressure experiments the sample holder is initially filled with water and the water pump is set to the fluid pressure we apply during the drainage measurement. Valve 4 is closed and the gas tubing and pump are filled with \(CO_2\) (or \(N_2\)). A gas booster, connected to valve 1 (Fig. 1) is used to bring up the gas pressure. We set a constant temperature and let the system equilibrate. Subsequently, when both the water and gas pressure are equal, a constant gas injection rate is applied, the water pump is set to a constant pressure and valve 4 is opened.

(C) After the primary drainage process, the secondary imbibition process starts when the water pump is set to a constant injection rate and the gas pump is set to a constant production pressure.

3. Data analysis procedure

The water saturation \((S_w)\) is obtained by the mass of water produced for the atmospheric conditions and by
the change in volume of the water pump for high pressure conditions \((P > 1 \text{ bar})\). At the end of the experiment, the integral mass balance is checked by weighing all the separate parts of the sample holder, from which an estimation of the final water saturation in the sample can be obtained.

For the high pressure drainage experiments the amount of water in the pump is measured to validate whether only negligible amounts of ‘free’ gas are produced. For imbibition tests we apply essentially the same procedure to validate that there is only negligible water production. It turns out that the gas volume in the water pump never exceeds one percent of the volume [28]. The capillary pressure curves are obtained based on the following:

1. The decrease (increase) in water saturation can be obtained from the mass/volume produced (injected).
2. The initial water (gas) saturation for primary drainage (imbibition) is 1.
3. For small injection rates (<1 ml/h), the viscous pressure drop over the sample holder is negligible (~0.04 Pa).
4. For the drainage experiments all the water from end-piece 1 and the perforated plates is drained before the gas reaches the sample (Fig. 2).
5. During the drainage process all the water remains in pore space of the SIPERM plates, hydrophilic filter and the void space of end-piece 2 (Fig. 2).
6. The compressibility of water is neglected for all pressure conditions.
7. The porosity for all samples used is constant during the drainage and imbibition process.
8. The capillary pressure is defined as the difference in the gas and water bulk phase pressures and measured by the PDT device.

As an illustration we discuss the procedure to obtain the capillary pressure curve for a primary drainage experiment conducted with a constant CO₂ injection rate at a system pressure of \(P = 85 \text{ bar}\) and \(T = 27^\circ\text{C}\). Fig. 3 shows the cumulative water production and gas injection data together with \(P_c\) as a function of time. The drainage process starts at point \(A\), where the capillary entry pressure is reached. A fast increment in differential pressure, from 0 to 5 mbar is observed and the corresponding cumulative water production and gas injection are 12.75 ml and 13.75 ml, respectively. The produced water volume is in agreement with the total void volume of end-piece \(A\). The drainage process ends at point \(B\). At this moment, a steep rise in capillary pressure is observed and the liquid CO₂ attains the SIPERM filter. The cumulative water production and gas injection at this point is 61.67 ml and 63.03 ml, respectively.

The irregularity in the measured \(P_c\) is due to the delay in response of the water pump, which is set to a constant production pressure. The water pump measures the pressure with an accuracy of 10 mbar, and consequently, the data consist of a series of spikes, which are not shown in most of the cases, by plotting only local minima. In some exceptional cases, however, the local minima still show these irregularities. To obtain the \(P_c-S_w\) curve, we compute the water saturation from the water production volume using the following expression:

\[S_w(t) = 1 - \frac{V_{wp}(t) - V_{wp}(t_s)}{\varphi V_{sample}},\]  

where \(V_{wp}\) is the water pump volume and \(\varphi V_{sample}\) is the pore volume of the sample. The corresponding capillary pressure curve (experiment 12) is shown in Fig. 7 and the details of this measurement are further discussed in Section 4.2.

4. Experimental results

In this section, the experimental results are presented for the unconsolidated sand–CO₂–water system. Nitrogen (N₂) experiments are performed to facilitate the interpretation of the CO₂ experiments with the strong dissolution effects. We also describe the repeatability of the experimental method and the effects of different sand packs used. To clarify the correlation between the experiments and the numbering, an overview of the sample and system properties applied during the experiments is given in Table 1.

4.1. Experimental results at atmospheric pressures

To assess the repeatability of the experimental method and of the way we construct the unconsolidated porous medium, we have conducted three primary drainage experiments for three different sand packs, using fine unconsolidated sand with an average particle size of \(160 < D_{50} < 210 \mu\text{m}\). For the intermediate water saturation range \((0.4 < S_w < 0.8)\) the capillary pressure curves are repeatable with a deviation in \(P_c\) of \(±1.5 \text{ mbar}\). The
repeatability slightly decreases near the end point saturations ($P_c \pm 3$ mbar).

The second series of experiments at atmospheric conditions is performed on four different coarse sand packs with an average grain size range of $360 < D_{50} < 410$ μm. This coarse sand is also used for high pressures measurements ($P > P_{atm}$). We apply gas injection rates of $u_{inj} < 0.02 PV/h$, and therefore, we can assume that the $P_c-S_w$ curves are obtained under quasi-static conditions (see assumption 3, Section 3). Two primary drainage curves are measured with $N_2$ (experiments 4 and 5) and two with $CO_2$ (experiments 6 and 7). The results for the primary drainage curves are presented in Fig. 5. The differences in capillary pressures are mainly due to different sand packing and temperature conditions. Indeed, the $P_c-S_w$ curves show the repeatability of the experimental method and the results are within the precision of the experimental method (see Fig. 4). The peak at $S_w = 0.5$ (experiment 6) is attributed to an experimental artifact. A difference in residual water saturation ($S_{wc}$) is observed between the $CO_2$ drainage and $N_2$ drainage experiments. Comparing both the $N_2$ experiments, $S_{wc}$ is 0.16 and 0.11 for experiments 4 and 5, respectively. In the case we use $CO_2$, the difference in residual water saturation is much smaller, $S_{wc} = 0.06$ and $S_{wc} = 0.08$ for experiments 6 and 7, respectively. Finally, from Fig. 5 we observe that the drainage curves of the $N_2$–water system and the $CO_2$–water system are slightly different, but in the same range. This can be explained by the small difference in interfacial tension between $CO_2$ and $N_2$ (see Table 1).

### 4.2. Experimental results at high pressures, $P > 1$ bar

The $P_c-S_w$ relationships for the coarse sand sample are investigated at conditions of practical interests. Applying different pressure and temperature conditions we can compare the capillary pressure behavior for different interfacial tensions of $CO_2$ (Table 1), which will result in a pressure dependent capillary pressure. Moreover, the effect of the dissolution of carbon dioxide into the water phase as function of the fluid pressure can be determined by comparing the $CO_2$ and $N_2$ capillary pressure curves.

For the 8 bar conditions we performed three measurements with $CO_2$ and one with $N_2$. The primary drainage and secondary imbibition curves for experiments 8–11 are presented in Fig. 6. In these four measurements the boundary conditions are such that the gas pressure is set to a constant pressure during the total capillary cycle. Consequently, the water pump is set to a refill rate of 0.5 ml/h. Except at low water saturations the reproducibility for both the drainage and imbibition processes appears to be excellent, considering the different sand packs [41]. The small irregularities at high water saturations for the secondary imbibition experiment (experiment 9, Fig. 6) are attributed to summer temperatures in the laboratory, exceeding the upper limit of the temperature control system. For the primary drainage experiment 10 (Fig. 6) there are no data points between 0.85 < $S_w$ < 0.95. For both the secondary imbibition experiments 9 and 10, the residual gas saturation is determined at $S_w = 0.92$. Different sand packing combined with the lower temperature (26°C for 8 and 28°C for 9 and 10) result in a small deviation for the saturation range of 0.15 < $S_w$ < 0.5 and a lower residual gas saturation of $S_{gr} = 0.02$.

From Fig. 6, it is clear that the $N_2$ injection test shows drainage and imbibition capillary pressures similar to the $CO_2$ measurements. However, as a consequence of different dissolution properties between $N_2$ and $CO_2$ the residual gas saturation with $N_2$ is higher than for $CO_2$, where $S_{gr}$ for $N_2$ is 0.21.

In Fig. 7, the results are presented for measurements performed at system pressures above 80 bars. Experiment 12 is conducted with liquid $CO_2$ ($T = 27°C$) and supercrit-

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**Fig. 4.** Primary drainage capillary pressure curves for $CO_2$ injection in fine sand ($160 < D_{50} < 210$ μm) for atmospheric conditions. In each case the $CO_2$ injection rate is 0.5 ml/h. The differences observed are an indication of the repeatability of the experimental method.

**Fig. 5.** Primary drainage capillary pressure curves for $N_2$ and $CO_2$ injection at atmospheric conditions. The capillary pressure for both gasses are in the same range due to similar interfacial tensions. For experiment 4, $S_{wc}$ is higher compared to the other experiments. This is a result of the relatively high injection rate, $u_{inj} = 2$ ml/h, applied for the saturation range between 0.18 and 0.27.
ical conditions are applied for experiment 13 (T = 40 °C). It can be seen that the drainage capillary pressure for liquid CO₂ and supercritical CO₂ is of the same range. For the supercritical situation the primary drainage shows significant irregular behavior as a result of sudden imbibition events, whereas for the liquid CO₂ conditions a smooth Pₚ–Sₜ curve is measured. The secondary imbibition curve shows negative capillary pressure values for Sₜ > 0.5 (Fig. 7).

To show the pressure dependence of the capillary pressure for drainage, we compare in Fig. 8 the primary drainage curves for CO₂ pressures of 1, 8 and 85 bar. The secondary imbibition curves for experiments 8, 10 and 13 are compared in Fig. 9. For both the primary drainage and the secondary imbibition a decrease in capillary pressure is measured for increasing CO₂ pressures. The pressure dependence of the drainage capillary pressure is a result of the interfacial tension[24] (Table 1). Hence, the capillary pressure curves can be scaled according to the interfacial tension, as shown in Fig. 10. Here, Pₚ/σ is plotted as function of Sₜ and small deviations between the three pressure conditions are observed. Contrary to the drainage curves, the secondary imbibition curves cannot be properly scaled by the interfacial tension. In Fig. 11, we show that the values of Pₚ/σ for supercritical conditions are much smaller than for gaseous CO₂ (P = 8 bar), implying that other mechanisms influence the capillary pressure at high pressures and temperatures. This will be further discussed in Section 5.
4.3. Production and injection behavior during primary drainage

In this section, we describe the results obtained for the injection and production behavior of five primary drainage experiments. Figs. 12 and 13 show the cumulative water production and nitrogen injection for experiment 4 (at 23°C, 8 bar, and 27°C) and experiment 11 (at 27°C, 85 bar, and 40°C). For both experiments, the nitrogen injection rate is 0.5 ml/h. At t = 3.4 × 10^5 s, the gas injection rate is changed from 0.5 ml/h to 2 ml/h for experiment 4. During the measurements with nitrogen, the injected and produced cumulative volumes are similar. A discrepancy between the water production and gas injection volumes for the atmospheric condition is observed near S_{wc}, which can be explained by viscous forces. For the high pressure nitrogen case (8 bar), the measured water production shows an irregular behavior, which is attributed to temperature effects.

The production and injection curves for primary drainage experiments with CO2 are presented in Figs 14–16. The differences between the injected and produced volumes for the atmospheric case (Fig. 14) and the 8 bar experiment (Fig. 15) can be explained by the dissolution effects of CO2 in water (Section 5). When liquid CO2 is injected (Fig. 16) these effects are not observed and the cumulative gas volume injected is almost equal to the cumulative water volume produced.

The details of the measured injection and production curves for both nitrogen and CO2 are compared with the numerical results and are further discussed in the next section.
5. Discussion

To get a better understanding of the different processes and mechanisms observed in the experiments, we have developed a one-dimensional, fully implicit flow simulator. The model equations are derived in Appendix A and the model input parameters are presented in Table A.1.

Fig. 17 plots the experimentally and the numerically obtained $P_c$–$S_w$ curves for the CO$_2$–water system at atmospheric conditions (experiment 6). It is clear that the measured capillary pressure curve shows good agreement with the predicted capillary pressure curve, based on the bulk gas and water pressure (see Eq. (A.18)). This indicates that the experimental method is validated by the numerical model and that the assumptions, listed in Section 3 are justified. Small discrepancies between the measured and predicted curves near the end point saturations are a result of the input capillary pressure curve, based on the Leverett-J function (see Eq. (A.8), Appendix A.3). Moreover, the numerical simulations show that the SPERM plates at the bottom have no effect on the measured $P_c$–$S_w$ curve for the flow conditions applied. Indeed, it can be expected that for viscous dominated displacement, i.e., higher injection rates, the effects of the SPERM plates on $P_c$ are observed [43].

The small values for $S_w$ measured for low and high pressure primary drainage experiments with CO$_2$ can be
explained by the quasi-static conditions. For the small injection rates, the displacement is capillarily dominated \((Ca \sim 10^{-7})\) and entrainment of water plays a minor role [38]. For the drainage process with \(N_2\), experiment 4 in Fig. 5, we conclude that the exceptional high gas injection rate applied near \(S_{wc}\) (2 ml/h) causes more hydraulic isolation of water filled pores [38]. Hence the water phase becomes more disconnected and viscous forces start to dominate for higher saturations [40]. An increase in \(S_{wc}\) compared to the other experiments is than observed. This behavior is also predicted by the model, where near \(S_{wc}\) the production of water tends to zero and a fast increment in \(P_c\) is computed (e.g., Fig. 12).

Differences in \(S_{gr}\) between \(CO_2\) and \(N_2\) imbibition experiments (Fig. 6) are a result of the dissolution behavior of \(CO_2\). This effect is observed in experiment 10 where water breakthrough occurs for almost one day and a reasonable amount of water is produced (12.4 ml). After we start the secondary drainage experiment (not shown here), the volumetric water balance is derived, and only 9 ml of water is produced before the increment of \(P_c\) is observed (similar to event \(A\) in Fig. 3). Under the assumptions that no water remains in the stainless steel filters and the gas tubing (see Fig. 2) and \(\frac{\omega_w}{\omega_g} \approx 1\) (Eq. (A.13)), the water saturation at the start of the secondary drainage process approximates \(S_w = 1\). This indicates that the total amount of residual \(CO_2\) present at the moment of water breakthrough after imbibition, has been dissolved in the water. Therefore, we assume that the water phase is not fully saturated with \(CO_2\) at the end of the imbibition process.

One of the objectives of this work is to provide experimental data for the capillary pressure, measured for the rock–water–\(CO_2\) systems in the relevant temperature and pressure range, e.g., experiments 12 and 13 (Fig. 7). The only reference with data on capillary pressures with which we can compare our results are the measurements reported by Bennion and Bachu [16]. They reported on positive drainage capillary pressures for the supercritical \(CO_2\)-brine systems, ranging from 0.1 \((S_w = 1)\) to 1000 bar \((S_w = S_{wc})\). However, these capillary pressures were obtained from indirect measurements (relative permeability) and for low permeable cores \((2.1 \times 10^{-14} \text{ m}^2)\).

The complex behavior of the \(CO_2\)-water system is observed during supercritical displacement (experiment 13, Fig. 7) and is explained by phase instabilities in the vicinity of the critical point. Small system perturbations, like temperature variations and corresponding thermal expansion effects, will cause density and viscosity changes. This results in occasional water imbibition during continuous \(CO_2\) injection (observed as fast drops in \(P_c\)). In addition, temporary \(CO_2\)-wet conditions are considered. Because the \(CO_2\) trapped in the crevices of the sand will not instantaneously dissolve in the water, the water will ‘see’ a surface consisting of sand and gas patches.

The negative secondary imbibition capillary pressures, measured for \(S_w > 0.5\) (Fig. 9), indicates that the \(CO_2\)-water–sand system becomes intermediate wet. Chiquet et al. [11] already concluded that the wettability of minerals, such as quartz, can be significantly altered in the presence of \(CO_2\) under typical sequestration conditions. For these high pressures and temperatures, the solvent properties of \(CO_2\) improve and together with the decrease of pH of water, the surface charges become less negative. This will reduce the electrostatic interfacial forces that favor positive capillary pressures. In addition to this, the contact angle increases for supercritical conditions. This is shown in Fig. 11, from which it is clear that imbibition capillary pressure does not scale with the interfacial tension.

To obtain a correct interpretation of the diffusion and dissolution mechanisms, and their impact on the capillary pressure, the experimental results for the water production and the gas injection behavior are compared to the model predictions. From the numerical simulations it appears that the results in cumulative volumes are independent of the discretization (Fig. 18). The injection and production characteristics for the primary drainage experiments with \(N_2\) and \(CO_2\) are presented in Figs. 12–16. Good agreement between the predicted and measured volumes is found for both the low and high pressure conditions. For the 8 bar \(N_2\) experiment (Fig. 13), the measured water production curve is on average a straight line, which is also predicted by the model. Due to the low solubility of \(N_2\) in water \((K_H \approx 8 \times 10^9 \text{ Pa})\), the mass transfer rate, defined by the right hand side of Eq. (A.2), does not have a significant effect on the water production curves.

Contrary to the experiments with \(N_2\), the dissolution rate and the diffusion of \(CO_2\) in water influence the water production profiles for \(P = P_{atm}\) and \(P = 8\) bar (see Figs. 14 and 15). The water production during \(CO_2\) injection at atmospheric conditions (Fig. 14) is initiated very slowly (stage 1) because the \(CO_2\) dissolves into the water and the process is dominated by diffusion. The duration of stage 1 corresponds to the characteristic diffusion time, defined by

![Fig. 18. Numerical computations for CO2 injection at atmospheric conditions for three different discretizations. As input parameters we use: \(V_{inj} = 0.5 \text{ ml/h}, D_L = 1 \times 10^{-2} \text{ m}, T = 28^\circ\text{C}\) and the capillary pressure data from experiment 6 (see Table A.1). No effect of the grid size on the water production behavior is computed.](image-url)
\( t_c = H^2/D_g \). Because the water saturation does not decrease significantly, we assume \( H \) (the water column in the sample) to be constant during stage 1. For constant \( H \) and \( D_g = 2 \times 10^{-3} \mathrm{m}^2/\mathrm{s} \) \([44]\), \( t_c \approx 3 \) days. For \( t > t_c \), the gas pressure starts to build up and the water production increases (stage 2). Subsequently, the production curve becomes parallel to the gas injection profile, until \( S_w \) has reached (stage 3). From this moment the water production is almost horizontal (stage 4).

For the 8 bar CO₂ experiment, (Fig. 15), different boundary conditions were applied (\( P_{g,z=0} = \text{constant}, u_{w,z=-L} = \text{constant} \)). The constant water production is indicated by the constant slope. Similar to the atmospheric case (experiment 6) the gas injection curve is subject to the CO₂ dissolution rate in the first stage of the experiment, \( t < 1.2 \times 10^5 \) s. As a result of the constant water production, the water column in the sample decreases, which results in a smaller \( t_c \). The model predicts similar behavior as observed during the measurement. However, a discrepancy in cumulative gas production is found between the simulated and measured data after \( t \approx 1.5 \times 10^5 \) s. This results in an underestimation of the predicted cumulative CO₂ volume at the end of 12.2 ml.

For the liquid CO₂ case (Fig. 16) the dissolution and diffusion effects do not influence the water production behavior, and both the experimental and numerical results show an incompressible-like displacement. Because \( c_{egg} \gg c_{wg}^{eq} \) (Eq. (A.2) and Eq. (A.13)), the influence of the mass transfer on the CO₂ pressure, is negligible. Here, \( c_{egg} \) is the concentration of CO₂ in the liquid CO₂ phase. Comparison of experiment 12 with experiments 6 and 10, shows that the solubility of gaseous CO₂ is relatively smaller than for liquid CO₂ \([21]\). A small deviation in cumulative production and injection of approximately 1 ml is found over the period \( t < 4 \times 10^5 \) s. Different mass transfer rates are investigated for the liquid CO₂ conditions, and indeed, no effect on the water production profiles is predicted.

The comparison between the gaseous CO₂ and N₂ experiments shows the large effect of the dissolution of CO₂ on the injection/production behavior. However, the capillary pressure is not influenced by dissolution effects, because the capillary pressure curves obtained for the CO₂–water and N₂–water system (Figs. 5 and 6) are all in the same range.

6. Conclusions

(1) A capillary pressure set-up has been developed and validated that can be used to measure the capillary pressure behavior for CO₂ sequestration applications.

(2) For the small injection rates applied, the viscous forces are negligible and the capillary pressure curves are considered as static.

(3) The numerical results show that the SIPERM filters do not influence the measured \( P_c - S_w \) curves for the applied flow conditions.

(4) Increasing CO₂ pressures result in decreasing primary drainage capillary pressures for all samples used. This can be explained by the decrease in interfacial tension \([24]\).

(5) From the comparison between the N₂ and CO₂ experiments, we conclude that the capillary pressure is not influenced by the dissolution of CO₂ in water.

(6) Measurements close to the critical point of CO₂ show alternate drainage and imbibition events during CO₂ injection. This is a result of small perturbations that change the density and viscosity of CO₂ and temporary CO₂-wet behavior.

(7) The wettability of the quartz sand is altered to intermediate wet in the presence of CO₂ under supercritical conditions. This is a result of improving solvent properties of CO₂ and the decreasing pH of water \([11]\).

(8) Good agreement is found between the experimental results and the model prediction for both the CO₂ and N₂ injection drainage experiments.

(9) The model shows that the water production and gas injection behavior depends largely on mass transfer rate and diffusion of CO₂ in water. These effects become negligible for the injection of liquid CO₂.

(10) The capillary pressure behavior must be considered in CO₂ sequestration application, e.g., the caprock integrity \([11]\) and drainage and imbibition events in heterogeneous rocks \([9]\). Our measurements show that wetting alteration and the abrupt phase changes and accompanying density and viscosity changes may effect the success of CO₂ sequestration.

Acknowledgements

The research presented in this work was carried out as part of the CATO program: CO₂ Capture, Transport and Storage in the Netherlands (http://www.CO2-cato.nl/). The financial support is gratefully acknowledged. We thank A. Hoving, L. Vogt, P.S.A. de Vreede and H.G. van Asten for technical support.

Appendix A. Numerical model for the unconsolidated sand–water–CO₂ system

We consider the injection of CO₂ and N₂ in a cylindric unconsolidated sample, originally filled with water. The sample consists of unconsolidated sand with constant porosity, \( \varphi \) and permeability, \( k \). The sample is vertical, with a height \( H \) and a diameter \( D_{\text{inner}} = 84 \) mm. The gas inlet is at the top of the sample at \( z = 0 \) and the water outlet is positioned at \( z = -L \) and gravity is taken into account.

In Table A.1, the model input parameters are presented which are used in the simulations. Furthermore, the summaries of physical input parameters and variables are given in Tables A.2 and A.3.
A.1. Model equations of the mathematical model

The conservation of mass of each component in each phase is given by the following equations, which express the liquid water mass balance (Eq. (A.1)), the gas mass balance in the gaseous phase (Eq. (A.2)) and the combined gas mass balance in the liquid water and the water vapor in the gaseous phase (Eq. (A.3))

\[
\frac{\partial}{\partial t}(S_w c_{wg}) + \frac{\partial u_w c_{wg}}{\partial z} - D_g \frac{\partial^2 c_{wg}}{\partial z^2} = -q_{g-w,w}, \quad (A.1)
\]

\[
\frac{\partial}{\partial t}(S_g c_{gg}) + \frac{\partial u_g c_{gg}}{\partial z} = q_{g-w,g}, \quad (A.2)
\]

\[
\frac{\partial}{\partial t}(S_g c_{gw}) + \frac{\partial u_g c_{gw}}{\partial z} + \frac{\partial u_g c_{gw}}{\partial z} = 0. \quad (A.3)
\]

In these equations \( S_w \) is the water saturation and \( S_g \) is the gas saturation. Furthermore, \( u_w \) and \( u_g \) is the Darcy velocity of the water and the gas respectively and \( q_{g-w,w} \) is the mass transfer between the gas phase and the liquid water (Eq. (A.9)). The component concentration is denoted by \( c_j \), where \( j \) denotes the phase \( (j = w,g) \) and \( j \) is the component \( (j = w,g) \). This system of equations is solved for \( S_w, P_g \) and \( c_{gw} \) using the relationships described in Appendix A.3.

A.2. Model assumptions

The following model assumptions for the quasi-1D model are made:

(1) The temperature is constant over the experimental time.
(2) For the initial condition, an equilibrium water saturation is present such that the gas and water velocities are zero.
(3) Only vertical flow is considered.
(4) For the drainage process gas is injected as pure gas.
(5) Two components are present in the sample: the water (w), and gas (g) component.
(6) For \( \text{N}_2 \) the ideal gas law is used and for \( \text{CO}_2 \) the Span and Wagner EOS [20] is used.
(7) Thermodynamic equilibrium between the water component in the water and gas phase is considered.
(8) The volume of water and gas are additive, i.e., there is no volume contraction upon mixing.
(9) Mass transfer for the gas component in the gas and water phase is considered.
(10) No interaction between the solid and mobile phases is taken into account.
(11) The water and the rock are incompressible.

A.3. Constitutive relationships

The volumetric flux of phase \( z \) is given by Darcy’s law, which reads

\[
u_z = -\frac{k_{z-w} \partial P_z}{\mu_z} \left( \frac{\partial c_{wg}}{\partial z} - \rho_{z-g} \right). \quad (A.4)
\]

In Eq. (A.4), the viscosity of the gas component, \( \mu_z \) is a function of \( P \) and \( T \) (Table A.3) and the water viscosity, \( \mu_w \) is a function of \( T \) (Eq. (A.20)). The phase pressures and densities are denoted by \( P_z \) and \( \rho_z \) (Table A.3), respectively. The absolute permeability, \( k \), is obtained from the Carman–Kozeny relation, given by

\[
k = \frac{1}{150 (D_{50})^2} \frac{\varphi^3}{(1 - \varphi)^2}, \quad (A.5)
\]

where \( \varphi \) and \( D_{50} \) (Table A.1) are respectively the sample porosity and the average grain size. The relative permeability functions \( k_{rw} \) and \( k_{rg} \) are given by the Brooks–Corey functions:

\[
k_{rw} = k_{rw}^{*} \left( S_w \right)^{2+3}, \quad k_{rg} = k_{rg}^{*} \left( 1 - S_w \right)^{2} \left( 1 - \left( S_w \right)^{2+3} \right). \quad (A.6)
\]

Here the effective water saturation, \( S_{we} \), is defined as

\[
S_{we} = \frac{S_w - S_{wc}}{1 - S_{wc}}. \quad (A.7)
\]

The capillary pressure is defined as \( P_c = P_g - P_w \), and derived from the Leverett-J function,

\[
P_c(S_w) = \frac{\sigma \sqrt{\varphi}}{k} \frac{1}{\left( \frac{1 - S_{wc}}{1 - S_{wc}} \right)^{\frac{1}{2}} \left( \frac{S_w - S_{wc}}{1 - S_{wc}} \right)^{\frac{1}{2}}}, \quad (A.8)
\]

where the interfacial tension and the residual water saturation are respectively denoted by \( \sigma \) and \( S_{wc} \) (Table A.1). For \( \text{N}_2 \) it is assumed that \( \sigma \) does not vary for the pressure range from 1 to 10 bar and for \( \text{CO}_2 \) the interfacial tension changes as function of pressure and temperature. During the simulation, \( \sigma \) for \( \text{N}_2 \) and \( \text{CO}_2 \) remains constant.

The dissolution rate of gas in water, \( q_{g-w,w} \) (Eqs. (A.1) and (A.2)), is a function of the gas saturation, \( S_g \), the actual gas concentration in the water, \( c_{gw} \), and the equilibrium gas concentration in the water, \( c_{gw}^0 \), and is defined by

\[
q_{g-w,w} = k_L S_g (c_{gw} - c_{gw}^0), \quad (A.9)
\]

where \( k_L \) is the mass transfer for the dissolution of gas in the water defined by Bird et al. [45]

\[
k_L = D_g \frac{12 \varphi}{(D_L)^2}. \quad (A.10)
\]

Here \( D_g \) is the diffusion coefficient of the gas in liquid water as function of \( T \) [44] and \( D_L \) is the characteristic length of the bubble size. We determine the equilibrium concentration of the gas in the liquid water, \( c_{gw}^0 \), from Henry’s law, given by

\[
P_g = K_{Henry} x_{CO_2}. \quad (A.11)
\]

The Henry’s constant is denoted by \( K_{Henry} \) and \( x_{CO_2} \) is the molar fraction, defined as
\[
\frac{c_{\text{eq}}}{c_{\text{ww}}} + \frac{c_{\text{eq}}}{c_{\text{wg}}} = 1, \quad \frac{c_{\text{ww}}}{c_{\text{wW}}} + \frac{c_{\text{wg}}}{c_{\text{wG}}} = 1, \quad \frac{c_{\text{ww}}}{c_{\text{G}}} + \frac{c_{\text{wg}}}{c_{\text{G}}} = 1,
\]

where subscripts W and G indicate the concentrations of the pure components. Both \( \text{N}_2 \) and vapor water are assumed to behave as an ideal gas, whereas for \( \text{CO}_2 \) non-ideal behavior is assumed (Eq. (A.16)). The ideal gas law is given by

\[
P V = nRT
\]

and the pure concentrations of water and \( \text{N}_2 \) can therefore be written as

\[
c_{\text{gw}} = \frac{P_{\text{w, sat}}}{RT}, \quad c_{\text{gG}} = \frac{P_{\text{g}}}{RT},
\]

where \( P_{\text{g}} \) is the total gas pressure and \( R \) is the universal gas constant. For \( \text{CO}_2 \) we use the Span and Wagner equation of state \([20]\) and the pure \( \text{CO}_2 \) component can be written as

\[
c_{\text{gG}} = \frac{P}{z(P,T)RT},
\]

where \( z(P,T) \) is the gas compressibility of \( \text{CO}_2 \). From Eq. (A.13), \( c_{\text{gw}} \) is determined from

\[
c_{\text{gw}} = \frac{P_{\text{w, sat}}}{RT},
\]

where the water vapor pressure, \( P_{\text{w, sat}} \), is only a function of temperature, \( T \) (Eq. (A.21)).

### Table A.1

Overview of the experimental and numerical model parameters

<table>
<thead>
<tr>
<th>Exp. nr.</th>
<th>Gas</th>
<th>( T ) (°C)</th>
<th>( P ) (bar)</th>
<th>( k_{\text{w,a}} )</th>
<th>( k_{\text{g,a}} )</th>
<th>( \varphi )</th>
<th>( \sigma ) (mN/m)</th>
<th>( \rho ) (g/cm³)</th>
<th>( \gamma )</th>
<th>( S_{\text{w}} )</th>
<th>( \kappa ) (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>( \text{N}_2 )</td>
<td>24</td>
<td>1</td>
<td>0.5</td>
<td>1</td>
<td>3.84</td>
<td>71</td>
<td>0.37</td>
<td>0.51</td>
<td>0.1</td>
<td>400</td>
</tr>
<tr>
<td>6</td>
<td>( \text{CO}_2 )</td>
<td>24</td>
<td>1</td>
<td>0.5</td>
<td>1</td>
<td>3.56</td>
<td>71</td>
<td>0.37</td>
<td>0.45</td>
<td>0.01</td>
<td>400</td>
</tr>
<tr>
<td>10</td>
<td>( \text{CO}_2 )</td>
<td>28</td>
<td>8</td>
<td>0.5</td>
<td>1</td>
<td>7.32</td>
<td>67</td>
<td>0.38</td>
<td>0.49</td>
<td>0.075</td>
<td>400</td>
</tr>
<tr>
<td>11</td>
<td>( \text{N}_2 )</td>
<td>27</td>
<td>8</td>
<td>0.5</td>
<td>1</td>
<td>6.18</td>
<td>71</td>
<td>0.37</td>
<td>0.46</td>
<td>0.075</td>
<td>400</td>
</tr>
<tr>
<td>12</td>
<td>( \text{CO}_2 )</td>
<td>27</td>
<td>85</td>
<td>0.5</td>
<td>1</td>
<td>5.87</td>
<td>30</td>
<td>0.37</td>
<td>0.65</td>
<td>0.03</td>
<td>400</td>
</tr>
</tbody>
</table>

### Table A.2

Summary of physical input parameters and variables used in the numerical model (roman characters)

<table>
<thead>
<tr>
<th>Physical quantity</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample area</td>
<td>( A )</td>
<td>( \frac{1}{2}(0.084)^2 )</td>
<td>m²</td>
</tr>
<tr>
<td>Capillary number</td>
<td>( Ca )</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Water vapor conc.</td>
<td>( c_{\text{gw}} )</td>
<td>Eq. (A.17)</td>
<td>mol/m³</td>
</tr>
<tr>
<td>Gas conc.</td>
<td>( c_{\text{gG}} )</td>
<td>Eq. (A.13)</td>
<td>mol/m³</td>
</tr>
<tr>
<td>Diff. coeff. gas in water</td>
<td>( c_{\text{wg}} )</td>
<td>Independent variable</td>
<td>mol/m³</td>
</tr>
<tr>
<td>Characteristic length</td>
<td>( D_L )</td>
<td>From Gmelin [44]</td>
<td>m³/s</td>
</tr>
<tr>
<td>Average grain size</td>
<td>( D_{50} )</td>
<td>See Table A.1</td>
<td>m</td>
</tr>
<tr>
<td>Gravity constant</td>
<td>( g )</td>
<td>9.81</td>
<td>m/s²</td>
</tr>
<tr>
<td>Sample height</td>
<td>( h )</td>
<td>25 (steel)/27 (PEEK)</td>
<td>mm</td>
</tr>
<tr>
<td>Henry’s constant for ( \text{CO}_2 )</td>
<td>( k_{\text{Henry,CO}_2} )</td>
<td>From Duan and Sun [21]</td>
<td>Pa</td>
</tr>
<tr>
<td>Henry’s constant for ( \text{N}_2 )</td>
<td>( k_{\text{Henry,N}_2} )</td>
<td>From <a href="http://www.henrys-law.org">www.henrys-law.org</a></td>
<td>Pa</td>
</tr>
<tr>
<td>Water, gas rel. perm.</td>
<td>( k_{\text{rw,a}, k_{\text{rg,a}}} )</td>
<td>Eq. (A.6)</td>
<td>m²/m³</td>
</tr>
<tr>
<td>Atmospheric pressure</td>
<td>( P_{\text{atm}} )</td>
<td>1.0135 x 10⁵</td>
<td>Pa</td>
</tr>
<tr>
<td>Gas pressure</td>
<td>( P_{\text{g}} )</td>
<td>Independent variable</td>
<td>Pa</td>
</tr>
<tr>
<td>Water pressure</td>
<td>( P_{\text{w}} )</td>
<td>( P_{\text{w}} = P_{\text{g}} - P_{\text{c}} )</td>
<td>Pa</td>
</tr>
<tr>
<td>Universal gas constant</td>
<td>( R )</td>
<td>8.3165</td>
<td>m³·Pa/m³</td>
</tr>
<tr>
<td>Water saturation</td>
<td>( S_w )</td>
<td>Independent variable</td>
<td>m³/m³</td>
</tr>
<tr>
<td>Gas saturation</td>
<td>( S_g )</td>
<td>( S_g = 1 - S_w )</td>
<td>–</td>
</tr>
<tr>
<td>Residual gas saturation</td>
<td>( S_{\text{gr}} )</td>
<td>0 (used in the simulations)</td>
<td>m³/m³</td>
</tr>
<tr>
<td>Residual water saturation</td>
<td>( S_{\text{wc}} )</td>
<td>See Table A.1</td>
<td>m³/m³</td>
</tr>
<tr>
<td>Temperature</td>
<td>( T )</td>
<td>From experimental data</td>
<td>K</td>
</tr>
<tr>
<td>Gas injection rate</td>
<td>( u_{\text{inj}}^{(i)} )</td>
<td>From experimental data</td>
<td>m³/s</td>
</tr>
<tr>
<td>Darcy gas/water velocity</td>
<td>( u_{\text{D}} )</td>
<td>Darcy’s law, Eq. (A.4)</td>
<td>m³/s</td>
</tr>
<tr>
<td>Molar fraction gas in water</td>
<td>( x_{\text{gw}} )</td>
<td>Eq. (A.12)</td>
<td>–</td>
</tr>
<tr>
<td>Gas compressibility ( \text{CO}_2 )</td>
<td>( z_{\text{g}} )</td>
<td>From Span and Wagner [20]</td>
<td>–</td>
</tr>
</tbody>
</table>
Table A.3
Summary of physical input parameters and variables used in the numerical model (greek characters)

<table>
<thead>
<tr>
<th>Physical quantity</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sorting factor</td>
<td>$\lambda_s$</td>
<td>Fitting parameter for Eq. (A.8)</td>
<td>–</td>
</tr>
<tr>
<td>CO$_2$ viscosity</td>
<td>$\mu_{CO_2}$</td>
<td>Fenghour et al. [22]</td>
<td>Pa s</td>
</tr>
<tr>
<td>N$_2$ viscosity</td>
<td>$\mu_{N_2}$</td>
<td>$1.8 \times 10^{-5}$</td>
<td>Pa s</td>
</tr>
<tr>
<td>Water viscosity</td>
<td>$\mu_w$</td>
<td>Eq. (A.20)</td>
<td>Pa s</td>
</tr>
<tr>
<td>Water density</td>
<td>$\rho_w$</td>
<td>Eq. (A.19)</td>
<td>kg/m$^3$</td>
</tr>
<tr>
<td>CO$_2$ density</td>
<td>$\rho_{CO_2}$</td>
<td>Span and Wagner EOS [20]</td>
<td>kg/m$^3$</td>
</tr>
<tr>
<td>N$_2$ density</td>
<td>$\rho_{N_2}$</td>
<td>Ideal gas law, Eq. (A.14)</td>
<td>kg/m$^3$</td>
</tr>
<tr>
<td>Sample density</td>
<td>$\rho_s$</td>
<td>From experimental data</td>
<td>kg/m$^3$</td>
</tr>
<tr>
<td>Interfacial tension</td>
<td>$\sigma_{CO_2,w}$, $\sigma_{N_2,w}$</td>
<td>For CO$_2$: Chun and Wilkinson [24]; For N$_2$: 0.072</td>
<td>N/m</td>
</tr>
<tr>
<td>Rock porosity</td>
<td>$\varphi$</td>
<td>From helium measurements, see Table 1</td>
<td>m$^3$/m$^3$</td>
</tr>
</tbody>
</table>

The input parameters used for the numerical simulations are summarized in Table A.1. In each simulation the sand column is discretized into 10 layers. The characteristic length used for the mass transfer coefficient, $k_L$, is chosen as $D_h = 0.01$ m (Eq. (A.10)). The input capillary pressure curves are obtained from a least square curve fitting procedure, from which we estimate the coefficients, $S_{wrc}$, $\gamma$, and $\lambda_s$ of the Leverett-J function, given by Eq. (A.8), using the experimental $P_c$-$S_w$ curves (see Table A.1). The values for $S_{wrc}$, $\lambda_s$, and $\gamma$ are adjustable model parameters and vary because different sand packing are used for each experiment. The capillary pressure, comparable to the measured capillary pressure, is derived from the pressure difference of the bulk phases and represented by

$$P_c = \left( P_{g,z=0} + \frac{\rho_g gH}{2} \right) - \left( P_{w,z=-L} + \frac{\mu_{w}}{\rho_w} \right).$$  \hspace{1cm} (A.18)

The hydrostatic pressure correction for $P_{g,z=0}$ and $P_{w,z=-L}$ is due to placement of the PDT device in the experimental set-up (see Section 2.1 and Fig. 1).

A.4. Temperature and pressure dependent properties of N$_2$, CO$_2$ and water

The liquid water density, $\rho_w(T)$, viscosity, $\mu_w(T)$ and the water vapor pressure, $P_{w,sat}(T)$ are obtained from Tortike and Farouq Ali [47] (see also [46]), and are respectively given by

$$\rho_w(T) = 3786.31 - 37.24877 T + 0.196246T^2$$
$$- 5.04708 \times 10^{-4} T^3 + 6.29368 \times 10^{-7} T^4$$
$$- 3.08480 \times 10^{-10} T^5,$$  \hspace{1cm} (A.19)

$$\mu_w(T) = -0.0123274 + \frac{27.1038}{T} - 23527.5 \frac{1}{T^2} + 1.01425e7 \frac{1}{T^3}$$
$$- 2.1734e9 \frac{1}{T^4} + 1.8693e11 \frac{1}{T^5},$$  \hspace{1cm} (A.20)

and

$$P_{w,sat}(T) = 103(-175.776 + 2.29272T - 0.0113953T^2$$
$$+ 2.6278 \times 10^{-5} T^3 + 2.73726 \times 10^{-8} T^4$$
$$+ 1.13816 \times 10^{-11} T^5),$$  \hspace{1cm} (A.21)

A.5. Boundary conditions

Two sets of boundary conditions are considered for the drainage process:

1. We consider a constant gas injection rate at $z = 0$ and a constant water pressure at $z = -L$.

2. We consider a constant gas pressure at $z = 0$ and a constant water extraction rate at $z = -L$.

The volume change of the gas injection pump is incorporated using the expression:

$$\frac{1}{M} \frac{\partial \rho_{G,p} V_p}{\partial t} + A \frac{c_{GG} \rho_{G,p}}{L} = 0,$$  \hspace{1cm} (A.22)

where $\rho_{G,p}$ is the density of the gas phase in the pump, $V_p$ is the gas volume and $A$ the sample area. Dependent on the boundary conditions, constant CO$_2$ injection or constant CO$_2$ pressure, we solve Eq. (A.22) for $P_{g,p}$ or $\mu_{p}$, respectively. Moreover, $u_w = 0$ at $z = 0$ and $u_g = 0$ at $z = -L$.

References


