

# Storing CO<sub>2</sub> as solid hydrate in shallow aquifers: Electrical resistivity measurements in hydrate-bearing sandstone

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**Abstract.** A recent proposed carbon dioxide (CO<sub>2</sub>) storage scheme suggests solid CO<sub>2</sub> hydrate formation at the base of the hydrate stability zone to facilitate safe, long-term storage of anthropogenic CO<sub>2</sub>. These high-density hydrate structures consist of individual CO<sub>2</sub> molecules confined in cages of hydrogen-bonded water molecules. Solid-state storage of CO<sub>2</sub> in shallow aquifers can improve the storage capacity greatly compared to supercritical CO<sub>2</sub> stored at greater depths. Moreover, impermeable hydrate layers directly above a liquid CO<sub>2</sub> plume will significantly retain unwanted migration of CO<sub>2</sub> toward the seabed. Thus, a structural trap accompanied by hydrate layers in a zone of favorable kinetics are likely to mitigate the overall risk of CO<sub>2</sub> leakage from the storage site. Geophysical monitoring of the CO<sub>2</sub> storage site includes electrical resistivity measurements that relies on empirical data to obtain saturation values. We have estimated the saturation exponent in Archie's equation,  $n \approx 2.1$  (harmonic mean) for CO<sub>2</sub> and brine saturated pore network, and for hydrate-bearing seal ( $S_H < 0.4$ ), during the process of storing liquid CO<sub>2</sub> in Bentheimer sandstone core samples. Our findings support efficient trapping of CO<sub>2</sub> by sedimentary hydrate formation and show a robust agreement between saturation values derived from PVT data and from modifying Archie's equation.

## 1 Introduction

Carbon capture and storage (CCS) technologies are expected to play a substantial role in the transformation of the energy sector toward reduced emissions of anthropogenic greenhouse gases [1]. Captured CO<sub>2</sub> is typically injected and stored in a supercritical state [2] in aquifers and depleted reservoirs at great depths. Once injected, CO<sub>2</sub> is retained in the sediments by physicochemical processes including structural trapping, capillary trapping, fluid dissolution, and mineral reactions. The contribution from each trapping process varies greatly with time [3]. Structural and capillary trapping are highly relevant from the onset of injection, while fluid dissolution and mineral reaction are believed to have a significant impact at a later stage.

More recently, an additional trapping mechanism suggests liquid CO<sub>2</sub> stored and contained by an upper CO<sub>2</sub> hydrate layer located at the base of the gas hydrate stability zone (GHSZ). This self-sealing hydrate layer makes an artificial cap rock that can prevent upward migration of CO<sub>2</sub> [4,5]. Cooler storage conditions enhances the CO<sub>2</sub> storage capacity due to increased CO<sub>2</sub> density, increased mobility control (important if long inter-well distance), and increased CO<sub>2</sub> solubility in water compared to storage of supercritical CO<sub>2</sub>.

Experimental work has verified that CO<sub>2</sub> hydrate can form at the base of the GHSZ and reduce the CO<sub>2</sub> diffusion rate significantly in unconsolidated media [6]. Furthermore, high-density storage of CO<sub>2</sub> hydrate in silica sand has been demonstrated [7], as well as CO<sub>2</sub> hydrate

acting as permeability barriers and successfully sealing off the pore space [8,9]. CO<sub>2</sub> immobilization by hydrate formation was directly visualized using MRI and micromodels [10]. A substantial GHSZ is ideal to make sure escaped liquid CO<sub>2</sub> is immobilized and converted to solid hydrate before reaching the seabed, and thus extending the hydrate sealing layer. Predicted thickness of the GHSZ for offshore Western Europe is nearly 0.5 km of the upper sediments [11], showing great potential for liquid CO<sub>2</sub> storage at shallow depths.

Resistivity measurements are routinely used to determine presence of sedimentary hydrates both in the field and in the laboratory. However, relevant empirical data are needed for saturation quantifications. These can be obtained and calibrated based on controlled laboratorial experiments. For a medium with uniform cross-section transmitting a uniform flow of electric current, resistivity is found from:

$$R_t = Z \frac{A}{L} \cos(\theta) \quad (1)$$

where  $R_t$  is the bulk resistivity,  $Z$  is the measured impedance,  $A$  is the cross-sectional area of the sample,  $L$  is the length of the sample, and  $\theta$  is the phase angle. The Formation Factor ( $F$ ) relates empirically to porosity through [12]:

$$F = \frac{R_0}{R_w} = a\phi^{-m} \quad (2)$$

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where  $R_0$  is the resistivity of a fully brine-saturated sample,  $R_w$  is the resistivity of the brine,  $\phi$  is the porosity of the sample,  $m$  is the cementation exponent and  $a$  is the tortuosity factor.  $R_w$  is calculated using a standard conversion [13]:

$$R_w = 0.0123 + \frac{3647.5}{[C]^{0.955}} \quad (3)$$

where  $C$  is the ion content of brine. The  $R_w$  value is corrected for temperature variations by [14]:

$$R_w(2) = R_w(1) * \frac{(T_1 + 21.5)}{(T_2 + 21.5)} \quad (4)$$

where  $T_1$  is ambient temperature and  $T_2$  is sample temperature. The Resistivity Index ( $RI$ ) that applies to sediments partially saturated with a non-conductive material such as oil, gas, or hydrate, is defined as:

$$RI = \frac{R_t}{R_0} = S_w^{-n} \quad (5)$$

where  $R_t$  is the measured bulk resistivity,  $S_w$  is the brine saturation and  $n$  is the saturation exponent.

Hydrate growth is accompanied by an effective reduction of the pore space as well as a salinity increase of the remaining brine that is not converted to solid hydrate. Both of these processes results in a continuous change in  $R_0$  as hydrate grows, and a dynamic  $R_0^*$  needs to be implemented in eq. 5. This  $R_0^*$  is calculated from eq. 2 by adjusting  $R_w$  and  $\phi$  as hydrate grows.  $R_w$  is found from eq. 3-4 by keeping track of the salinity increase during hydrate growth from PVT data. PVT data is also used to monitor the hydrate saturation during hydrate growth, and  $\phi_{eff}$  is then found from the following relation:

$$\phi_{eff} = \phi(1 - S_H) \quad (6)$$

where  $S_H$  is the hydrate saturation. The cementation exponent  $m$  is calculated by eq. 2 when the sample (with known porosity) is completely filled with brine. This  $m$  is then assumed constant as hydrate grows in the pore space [15]. The tortuosity factor  $a$  is set to 1 to ensure that  $R_w = R_0$  in the limiting case where  $\phi \rightarrow 1$ .

Finally, the saturation exponent  $n$  is derived during hydrate growth by a modified version of eq. 5:

$$\log\left(\frac{R_t}{R_0^*}\right) = -n \log S_w \quad (7)$$

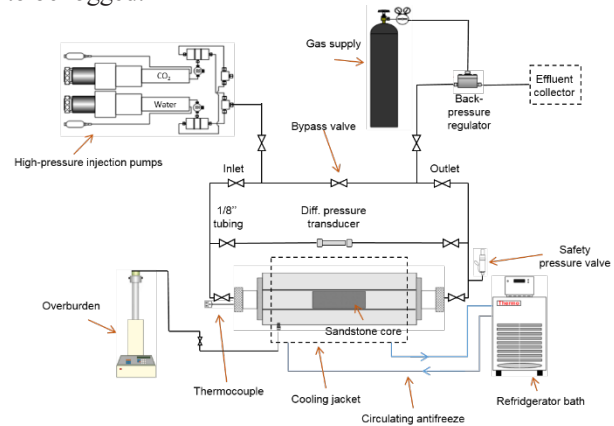
The  $n$  is found as the slope when plotting the left side of eq. 7 as a function of  $-\log S_w$ .

The majority of hydrate resistivity studies presented are related to CH<sub>4</sub> hydrate in the context of mapping and production of natural gas through various dissociation processes [15-18]. To the best of the authors' knowledge, this paper presents the first reported resistivity measurements on sedimentary CO<sub>2</sub> hydrate. We provide

the saturation exponent  $n$  during CO<sub>2</sub> injection into brine-filled cores and subsequent CO<sub>2</sub> hydrate formation. Saturation values derived from resistivity measurements are compared with PVT derived saturations to investigate the applicability of using resistivity measurements to monitor the evolving CO<sub>2</sub> hydrate seal in subsurface carbon storage.

## 2 Materials and methods

Homogenous and quartz-dominated Bentheimer sandstone (95.5% quartz, 2.0% kaolinite, 1.7% K-feldspar, 0.8% other [19]) was used in this study. Average porosity and absolute permeability were measured to 0.22 and 1.1 D, respectively. Twin samples, all with diameter of 5 cm and length 15 cm, were cleaned, dried at 70 °C for 24 hours, and fully saturated with brine (3.5 or 5.0 weight% NaCl) under vacuum. The brine-saturated cores were positioned in a core holder containing a rubber sleeve, fixed upstream end-piece, and floating downstream end-piece (see Fig. 1). A nitrogen-supported back-pressure regulator was connected downstream and an effluent sample collector measured brine production. A refrigerated circulator supplied the system with cooling fluid. Precise high-pressure pumps regulated overburden and pore pressure. The laboratory setup allowed pressure differences and bulk resistivity (Hewlett-Packard LCR-meter; 1 kHz, two-electrode setup) across the core sample to be logged.



**Fig. 1.** Coreflooding laboratory setup including sandstone core sample, core holder, cooling system, pressure and temperature measurements, back-pressure regulator, and high-pressure pumps to regulate pore pressure and overburden. Modified from [20].

The pore space was pressurized with brine to 7.0 MPa, while the confinement pressure was set to 10.0 MPa. The core was then flooded with brine ( $\mu=1.07$  cP) over a range of injection rates and absolute permeability was calculated. The waterflood was followed by liquid CO<sub>2</sub> ( $\mu=0.07$  cP) injection at constant volumetric flow rate (0.5, 5 or 10 cm<sup>3</sup>/min) to achieve a mixture of water and CO<sub>2</sub> in the pore space mirroring CO<sub>2</sub> invasion into an aquifer.

Two different hydrate growth conditions were designed in the laboratory: i) hydrate formation at constant pressure (CO<sub>2</sub> pressurized from both core ends,

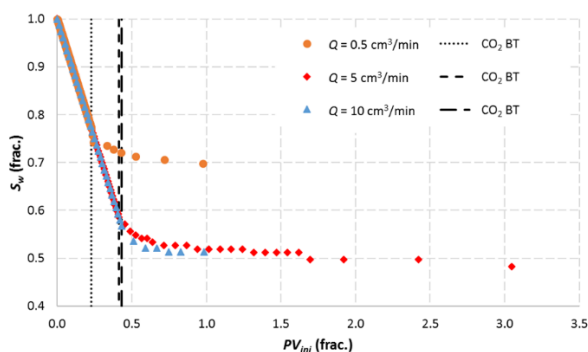
bypass valve open) and ii) flow-induced hydrate formation during CO<sub>2</sub> injection with constant volumetric flow rate. Onset of hydrate formation within the pore space was determined from the increase in resistivity, temperature, and differential pressure.

### 3 Results and discussion

#### 3.1 CO<sub>2</sub> – brine system (outside GHSZ)

The CO<sub>2</sub> injection rate into a porous media affects the displacement efficiency and fluid saturations within the pore network. Achieving substantial CO<sub>2</sub> storage capacity in a multiple well scenario relies on an efficient displacement process from injector to producer(s). Though supercritical CO<sub>2</sub> can recover about the same amount of water at core-scale, the more optimum mobility ratio between liquid CO<sub>2</sub> and water is likely to be important at long interwell distances.

Fig 2 shows the rate dependency on macroscopic sweep efficiency, which govern the initial fluid distribution before hydrate formation. Three experiments with CO<sub>2</sub> injection rate of 0.5 cm<sup>3</sup>/min (circles), 5 cm<sup>3</sup>/min (diamonds) and 10 cm<sup>3</sup>/min (triangles) were conducted outside of the GHSZ (20 °C) at 7.0 MPa. Injection rate (capillary number) affects both overall  $S_w$  and pore-level fluid distribution. A linear production profile is valid before CO<sub>2</sub> breakthrough (BT), supplemented with water production measurements. Delayed CO<sub>2</sub> BT (indicated with broken vertical lines) for 5 and 10 cm<sup>3</sup>/min implies improved sweep compared to the low injection rate (0.5 cm<sup>3</sup>/min). However, doubling the injection rate from 5 to 10 cm<sup>3</sup>/min had insignificant effect on the displacement process, reaching a plateau where approximately 50% of the brine remained after injecting several pore volumes (PV) of liquid CO<sub>2</sub>. Though the experiments were designed to minimize capillary end effects by increasing the core length and using relatively high flow rates, the lowest rate (0.5 cm<sup>3</sup>/min) experiment is prone to a more heterogeneous saturation profile due to reduced displacement efficiency. At breakthrough, saturation fractions in the pore space were  $S_w = 0.77$  and  $S_{CO_2} = 0.23$  (0.5 cm<sup>3</sup>/min),  $S_w = 0.59$  and  $S_{CO_2} = 0.41$  (5 cm<sup>3</sup>/min), and  $S_w = 0.57$  and  $S_{CO_2} = 0.43$  (10 cm<sup>3</sup>/min).



**Fig 2.** Drainage of initial water by liquid CO<sub>2</sub> in Bentheimer core samples at different injection rates; 0.5 cm<sup>3</sup>/min, 5 cm<sup>3</sup>/min, and 10 cm<sup>3</sup>/min.

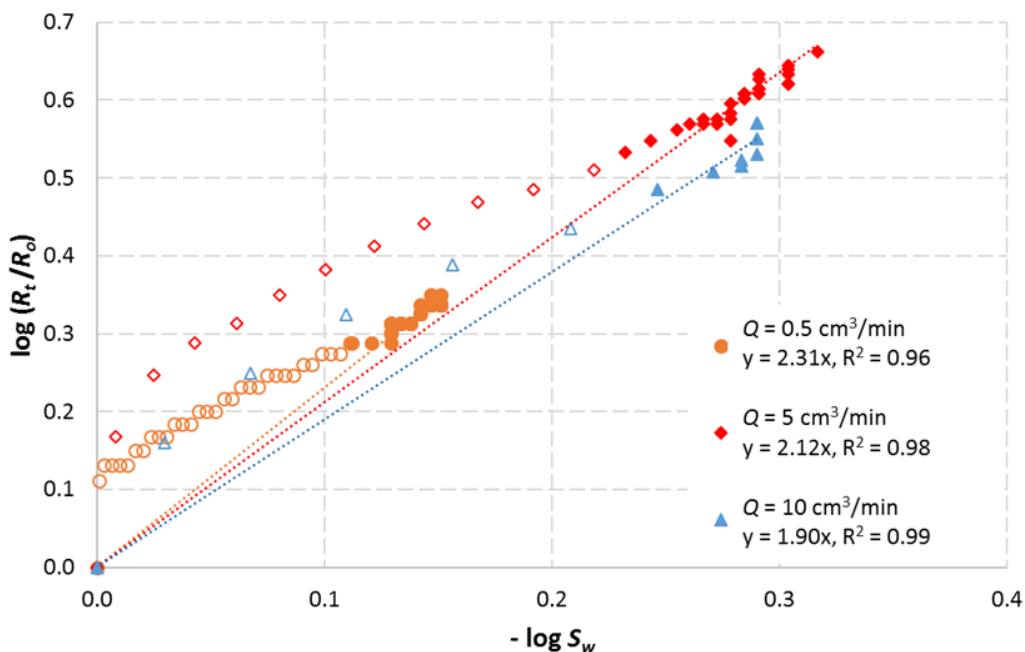
The bulk resistivity increased with increasing CO<sub>2</sub> saturation because electrically conductive brine was replaced by insulating CO<sub>2</sub> in the pore space. Fig 3 presents a logarithmic cross plot of water saturation ( $S_w$ ) and resistivity index ( $RI$ ) during CO<sub>2</sub> injection into the cores. The saturation exponent  $n$  was found as the slope of the curves, with emphasis on the first saturation point ( $S_w = 1$ ) and the last saturation points (after CO<sub>2</sub> BT in the cores) when determining the slope of the curves (solid filled markers). The use of Archie's equation is not applicable until CO<sub>2</sub> has reached the end of the core, achieving a predominantly uniform two-phase saturation profile throughout the entire core length. This is illustrated by the data points (no fill) obtained before CO<sub>2</sub> BT, which deviate from the linear trend lines in Fig. 3.

The saturation exponent  $n$  increased with decreasing CO<sub>2</sub> flow rate, and was 1.9 for 10 cm<sup>3</sup>/min, 2.1 for 5 cm<sup>3</sup>/min, and 2.3 for 0.5 cm<sup>3</sup>/min. This again reflects the different macroscopic sweep efficiencies that were achieved for the different flow rates, and highlights that  $n$  is sensitive to the displacement history. The  $n$  values identified in our CO<sub>2</sub>-brine systems corroborate with  $n$  values reported for similar conditions [21,22]. CO<sub>2</sub> is a highly reactive fluid that can influence resistivity measurements through i) dissolution and dissociation where new ions are provided to the solution, and ii) contribution of surface conductivity – even in clay free rocks [21,23]. Both processes lead to increased electrolytic conductivity and may thus overestimate the water saturation if not accounted for. These effects are negligible if the water is highly saline [24]. In the next section, we will compare the water saturation derived from Archie's using the estimated  $n$  values with measured PVT data, to find if these effects are relevant to our systems with seawater salinity or higher.

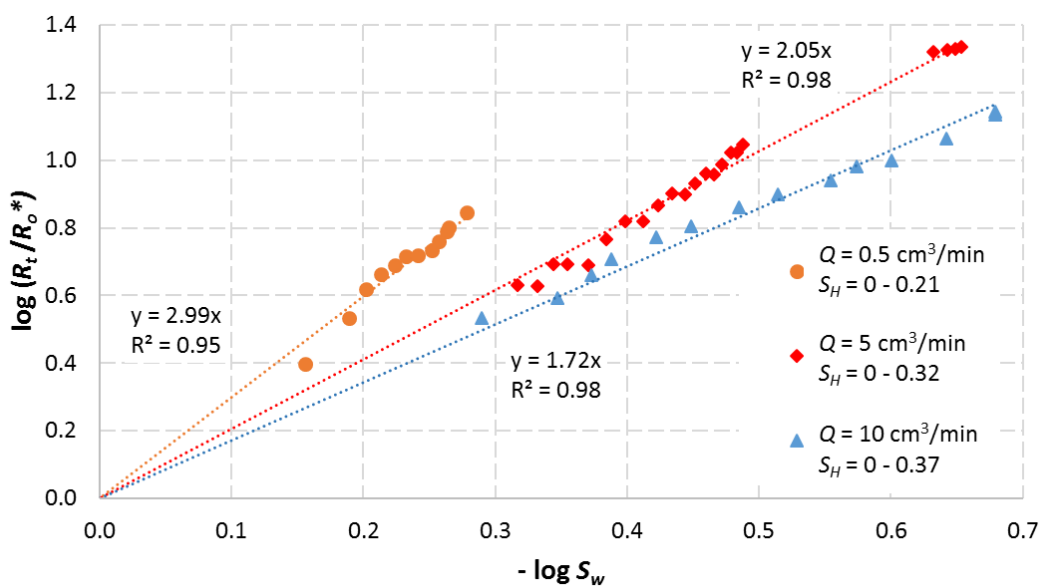
#### 3.2 CO<sub>2</sub> hydrate – brine system (within GHSZ)

To simulate the conditions of shallow CO<sub>2</sub> storage sites in offshore Western Europe, a temperature and pressure regime of 4 °C and 7.0 MPa pore pressure were chosen. This puts the system well within the GHSZ for CO<sub>2</sub> hydrate. Two hydrate growth scenarios were tested; i) static hydrate formation at constant pressure and ii) flow-induced hydrate formation under continuous CO<sub>2</sub> injection. Both approaches resulted in formation of CO<sub>2</sub> hydrate and subsequently immobilization of the injected CO<sub>2</sub> over a range of thermodynamic conditions.

Fig 4 shows a logarithmic cross plot of water saturation ( $S_w$ ) and resistivity index ( $RI$ ) during CO<sub>2</sub> hydrate formation in the pore space. The saturation exponent  $n$  is derived from the slope of the best-fit linear model to all measured data points during CO<sub>2</sub> hydrate formation. Final hydrate saturation depended on initial displacement of water by CO<sub>2</sub>, and the more efficient displacement, the more hydrates were formed. Improved CO<sub>2</sub> sweep led to higher number of interfaces that acted as potential nucleation sites, and reduced water shielding in the samples. Increasing the initial CO<sub>2</sub> flow rate from 0.5 cm<sup>3</sup>/min to 10 cm<sup>3</sup>/min, increased the final hydrate saturation by almost a factor of 2.



**Fig 3.** Logarithmic cross plot of RI and  $S_w$  during  $\text{CO}_2$  injection in brine-filled Bentheimer core samples at injection rates: 0.5, 5 and  $10 \text{ cm}^3/\text{min}$  at experimental conditions of 7.0 MPa and  $20 \text{ }^\circ\text{C}$ . Data point markers with no fill (non-uniform saturation profile) were excluded from the linear trend lines. The saturation exponent  $n$  ranged between 1.9 – 2.3.

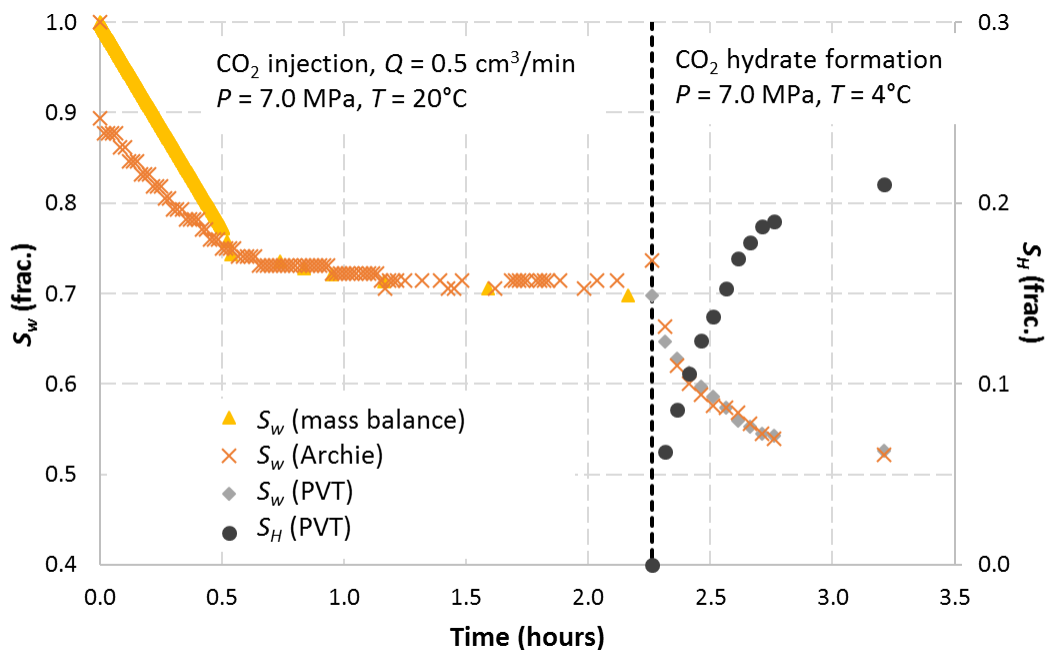


**Fig 4.** Logarithmic cross plot of RI and  $S_w$  during  $\text{CO}_2$  hydrate formation in Bentheimer core samples from a range of initial brine saturations caused by varying  $\text{CO}_2$  injection rates: 0.5, 5 and  $10 \text{ cm}^3/\text{min}$  at 7.0 MPa and  $4 \text{ }^\circ\text{C}$ . Depending on the saturation profiles, the saturation exponent  $n$  ranged from 1.7 to 3.0.

When hydrates, water and  $\text{CO}_2$  were present simultaneously in the pore space,  $n$  corresponded to 1.7 for  $S_H = 0.37$  ( $S_w = 0.21$ ), 2.1 for  $S_H = 0.32$  ( $S_w = 0.22$ ), and 3.0 for  $S_H = 0.21$  ( $S_w = 0.53$ ). Compared to the  $\text{CO}_2$ -brine system, hydrate formation changed the  $n$  value for the  $0.5 \text{ cm}^3/\text{min}$  drainage experiment (least uniform saturation distribution) from 2.3 to 3.0, for  $10 \text{ cm}^3/\text{min}$  from 1.9 to 1.7, while for  $5 \text{ cm}^3/\text{min}$   $n$  remained unchanged (2.1). In the case of very limited hydrate

formation ( $S_H = 0.21$ ), low bulk resistivity measurements can be ascribed to substantial connectivity and increased ion content of the remaining free water. The obtained  $n$  values are nonetheless in good agreement with recent studies for natural gas hydrate in coarse-grained reservoirs [15], and for glass bead specimen [25].

The next three figures show a direct comparison of saturation values derived from Archie's and from measured PVT data.



**Fig 5.** Comparison of saturation calculations from Archie and measured PVT data for injection rate  $0.5 \text{ cm}^3/\text{min}$  during initial displacement of water by  $\text{CO}_2$  ( $7.0 \text{ MPa}$  and  $20 \text{ }^\circ\text{C}$ ) and the following  $\text{CO}_2$  hydrate formation ( $7.0 \text{ MPa}$  and  $4 \text{ }^\circ\text{C}$ ). Obtained saturation values correlates very well after  $\text{CO}_2$  breakthrough as a uniform saturation profile is established, and throughout  $\text{CO}_2$  hydrate formation.

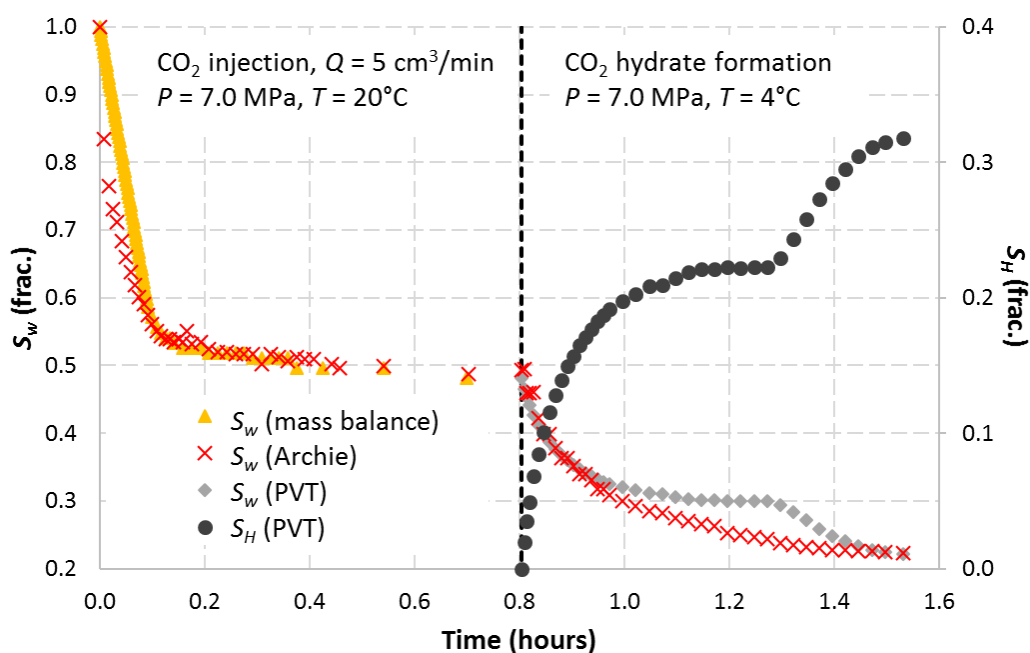
In Fig 5, saturation profiles during the initial displacement and the following hydrate nucleation and growth are displayed for flow rate  $0.5 \text{ cm}^3/\text{min}$ . The aforementioned unsteady-state regime occurring before  $\text{CO}_2$  breakthrough, leads to severe deviation between the Archie saturation and correct linear displacement (mass balance) due to temporarily non-uniform saturation profiles. Once  $\text{CO}_2$  breaks through at the outlet end of the sample, the saturation values from Archie’s match actual PVT values very well at the plateau ( $S_w \approx 0.7$ ). The onset of hydrate formation is indicated with a vertical line (broken). At this point, Archie’s overestimate the water saturation somewhat compared to actual measurements. This apparent increase in water saturation is likely due to a short drop in resistivity linked to hydrate nucleation as reported in the literature [8,16,26]. Another possibility is the aforementioned  $\text{CO}_2$  effects that may overestimate the water saturation, although the effects are most likely inhibited by the saline brine present. For the following hydrate growth process there is a very good agreement between the two water saturation profiles.

In Fig 6, drainage of water by  $\text{CO}_2$  at injection rate of  $5 \text{ cm}^3/\text{min}$  and subsequent hydrate formation is displayed. Again, we observed a deviation in saturation profiles before  $\text{CO}_2$  BT, and a good agreement after the  $\text{CO}_2$  front reached the outlet end of the sample. The consistency continues from the onset of hydrate formation until hydrates occupy approximately 15% of the pore space. At this point the hydrate formation rate decreased substantially and the saturation profiles temporarily plateaued (for 0.2 hours). This period of hampered hydrate growth is not captured using Archie’s saturation calculations, thus underestimating the water saturation

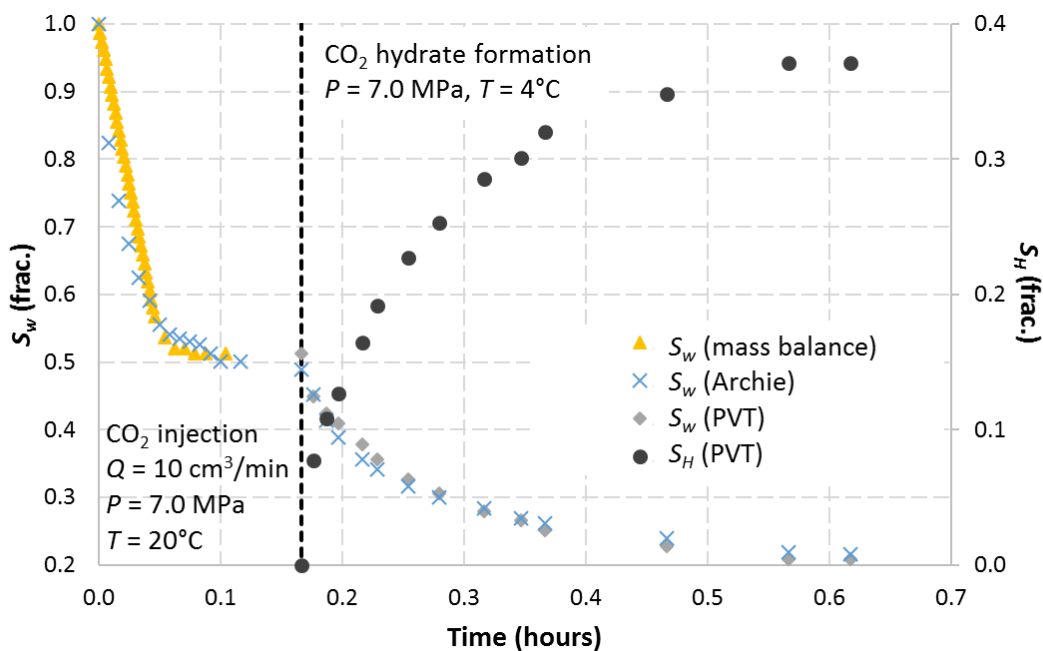
here. Accelerated hydrate formation followed next and this “normalization” caused the end-point saturation values from PVT data and resistivity measurements to match once again.

Fig 7 shows saturation profiles during the initial displacement, and the following hydrate nucleation and growth for flow rate of  $10 \text{ cm}^3/\text{min}$ . The remaining water saturation in the core after  $\text{CO}_2$  breakthrough was almost identical to the  $5 \text{ cm}^3/\text{min}$  experiment. There is a good agreement between the water saturation profiles after this point including the whole hydrate formation period in Fig 7.

$\text{CO}_2$  dissociation effects are highly sensitive to salinity. The 3.5 weight% NaCl solution used in Fig 5-7, belongs in a “high-salinity regime” where the conductivity was actually reduced by up to 15% due to reduced ion mobility [27]. This  $\text{CO}_2$  dissolution effect, if not accounted for, will underestimate the water saturation derived from resistivity measurements. At the time-scale investigated in our study, no consistent impact of  $\text{CO}_2$  dissociation on resistivity measurements was observed. Modifying Archie’s equation by accounting for reduced effective porosity and increased salinity of the remaining water for each time step [16], resulted in resistivity saturation values agreeing very well with obtained PVT measurements.

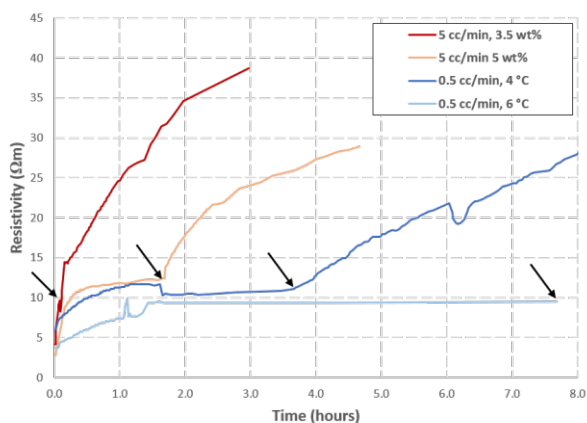


**Fig 6.** Comparison of saturation values obtained from Archie and measured PVT data for injection rate 5 cm<sup>3</sup>/min during drainage (7.0 MPa and 20 °C) and during the following CO<sub>2</sub> hydrate formation (7.0 MPa and 4 °C).



**Fig 7.** Comparison of saturation calculations from Archie and measured PVT data for injection rate 10 cm<sup>3</sup>/min during initial displacement of water by CO<sub>2</sub> (7.0 MPa and 20 °C) and the subsequent CO<sub>2</sub> hydrate formation (7.0 MPa and 4 °C).

In addition to the constant pressure experiments, a series of flow-induced CO<sub>2</sub> hydrate formation experiments were tested for various thermodynamic conditions (within the GHSZ). CO<sub>2</sub> was injected into fully brine-saturated core samples at 7.0 MPa pore pressure and aquifer temperature of 4 °C or 6 °C. In Fig 8, resistivity profiles for different CO<sub>2</sub> flow rates, and salinity and temperature regimes are compared as a function of time. Here, increased flow rate (from 0.5 to 5 cm<sup>3</sup>/min) accelerated hydrate formation and subsequent CO<sub>2</sub> trapping and immobilization. However, in terms of pore volumes (PV) CO<sub>2</sub> injected, we observed no effect of injection rate on hydrate induction time. The initial displacement of brine by liquid CO<sub>2</sub> increased the bulk resistivity from approximately 5 Ωm to 10 Ωm in all four corefloods. Two experiments were flooded with CO<sub>2</sub> at a constant rate of 5 cm<sup>3</sup>/min at 7.0 MPa and 4 °C, where one core contained 3.5 weight% NaCl (red curve) and the other 5 weight% NaCl (yellow) – to demonstrate the effect of salinity increase on hydrate formation. Furthermore, two experiments were flooded with CO<sub>2</sub> at a constant rate of 0.5 cm<sup>3</sup>/min at 7.0 MPa and salinity of 3.5 weight% NaCl, one experiment at 4 °C (blue) and the other at 6 °C (light blue) - to demonstrate the effect of temperature increase.



**Fig 8.** Resistivity profiles for various temperature and salinity conditions. Arrows indicate hydrate nucleation detected by a combination of pressure, resistivity, and temperature readings. Increase in salinity/temp caused a delayed CO<sub>2</sub> hydrate seal formation during continuous flow experiments.

The 5 cm<sup>3</sup>/min constant rate experiment at lowest salinity (Fig 8 – red curve) started forming solid hydrates in the pore space shortly after CO<sub>2</sub> breakthrough (nucleation indicated with black arrows). By increasing the brine salinity from 3.5 to 5 weight% (yellow curve), we observed a prolonged induction time of approx. 1.5 hours (factor 9 increase) from flow-induced hydrate formation. When injecting CO<sub>2</sub> at 0.5 cm<sup>3</sup>/min at 3.5 weight%, the effect of increasing the sandstone temperature from 4 °C to 6 °C was a factor 2 increase in induction time from 3.8 hours (blue) to 7.6 hours (light blue – resistivity data beyond this point is missing, however point of hydrate nucleation was identified from pressure and temperature logs).

The flow-induced hydrate induction time was evidently sensitive to salinity and temperature variations, and must be taken into consideration when screening for potential carbon storage sites. All four experiments led to solid CO<sub>2</sub> hydrate formation eventually. The steady increasing resistivity profiles after nucleation demonstrated hydrate growth in the pore network and decreased effective porosity and permeability. All corefloods experienced significant differential pressure build-up across the samples after hydrate formation, effectively stopping the CO<sub>2</sub> production at the outlet. These observations suggest that the injected CO<sub>2</sub> phase is made discontinuous by pore-spanning hydrate layers acting as permeability barriers, and thus successfully obstruct viscous CO<sub>2</sub> flow in the core sample for the time investigated.

## Conclusions

Electrical resistivity measurements providing fluid saturations relevant for CO<sub>2</sub> hydrate storage, resulted in the following key experimental observations:

For two-phase CO<sub>2</sub>-brine systems, the saturation exponent  $n$  ranged from 1.9 – 2.3 (harmonic mean  $n \approx 2.1$ ) depending on the CO<sub>2</sub> injection rate used during the drainage process. Because the saturation exponent is sensitive to the saturation profile along the core length, it is not recommended to rely on saturation values derived from resistivity measurements using a 2-electrode setup in non-uniform fluid distribution processes.

During CO<sub>2</sub> hydrate formation, the saturation exponent  $n$  ranged from 1.7 – 3.0 (harmonic mean  $n \approx 2.1$ ) depending on the initial distribution of brine, which resulted in different final CO<sub>2</sub> hydrate saturations. The estimated values of  $n$  may be used to map the brine saturation  $S_w$  and the CO<sub>2</sub> hydrate saturation ( $S_H = 1 - S_w$ ) in excess water conditions, and are in good agreement with previously measured  $n$  values during methane hydrate growth. Resistivity measurements are increasingly important for  $S_H < 0.4$ , as acoustic methods currently cannot obtain sufficient velocity contrasts in zones of low hydrate saturation.

CO<sub>2</sub> hydrates effectively blocked the CO<sub>2</sub> flow path and sealed off the sandstone pore network during flow-induced hydrate formation for different injection rates and thermodynamic conditions. Moderate increase in brine salinity or aquifer temperature resulted in significantly prolonged induction time before CO<sub>2</sub> hydrate formed under constant flow rate. Once stored, unwanted CO<sub>2</sub> remobilization/migration was obstructed by formation of sedimentary hydrate layers. This observed mechanism could act as an additional safety factor against leakage from geological stored CO<sub>2</sub> located below the gas hydrate stability zone.

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## Nomenclature

$a$  = tortuosity constant  
 $A$  = area, L<sup>2</sup>, m<sup>2</sup>  
 $C$  = ion content of brine, ppm  
 $F$  = formation factor  
 $L$  = length, L, m  
 $m$  = cementation exponent  
 $n$  = Archie's saturation exponent  
 $RI$  = resistivity index  
 $R_o$  = resistivity of fully water saturated sample, (mL<sup>3</sup>)/(tq<sup>2</sup>), Ωm  
 $R_t$  = resistivity of sample, (mL<sup>3</sup>)/(tq<sup>2</sup>), Ωm  
 $R_w$  = resistivity of brine, (mL<sup>3</sup>)/(tq<sup>2</sup>), Ωm  
 $S_{CO_2}$  = saturation of CO<sub>2</sub>, fraction  
 $S_H$  = saturation of hydrate, fraction  
 $S_w$  = saturation of water, fraction  
 $S_w^*$  = initial saturation of water, fraction  
 $T$  = temperature, T, °C  
 $Z$  = impedance, (mL<sup>2</sup>)/(tq<sup>2</sup>), Ω  
 $\Delta P$  = differential pressure, m/(Lt<sup>2</sup>), bar  
 $\theta$  = phase angle, °  
 $\phi$  = porosity, fraction  
 $\phi_{eff}$  = effective porosity, fraction  
 $\mu$  = viscosity, cP

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