Hydrogen wettability and capillary pressure in Clashach sandstone for underground hydrogen storage

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ABSTRACT

To meet global commitments to reach net-zero carbon (C) emissions by 2050, the energy mix must be adjusted to reduce emissions from fossil fuels and transition to low or zero C energy sources. Hydrogen (H\textsubscript{2}) can support this transition by facilitating increased renewable (zero C) energy use by acting as an energy store to balance supply and demand. Underground H\textsubscript{2} storage in porous media is investigated due to its high capacity and economical price. An important unknown in underground porous media H\textsubscript{2} storage is the volume of recoverable H\textsubscript{2} which is partly controlled by the H\textsubscript{2} wettability.

We computed receding and advancing contact angles for the H\textsubscript{2}-brine-Clashach sandstone system at pore fluid pressures of 2-7 MPa and for nitrogen (N\textsubscript{2})-brine-Clashach sandstone at 5 MPa, based on X-ray microtomography images of gas displacement and trapping in Clashach sandstone. A centrifuge analysis of the capillary pressure ($P_c$) at varying water saturations was conducted for N\textsubscript{2}. The H\textsubscript{2} $P_c$ curve was derived from the N\textsubscript{2} $P_c$, the N\textsubscript{2} wettability measurements, and existing information on the density differential and the interfacial tensions between brine and H\textsubscript{2} and N\textsubscript{2}, respectively.

The results show no change of the H\textsubscript{2}-brine-Clashach sandstone contact angles within the examined pressure range, with mean receding (drainage) and advancing (imbibition) contact angles of 61°± 24-26° and 58°± 20-22°, respectively, at all pore fluid pressures, indicating a water-wet rock and that increased hydrogen residual trapping at higher pressure was not controlled by wettability. N\textsubscript{2}-brine-Clashach sandstone receding and advancing contact angles were 66°± 21° and 62°± 24°, respectively. We found H\textsubscript{2} $P_c$ of 0.43 MPa at irreducible water saturations of 12.6-14.0%. Our results provide detailed insights into the controls on H\textsubscript{2}
displacement and capillary trapping as well as crucial input parameters for the modelling and design of H₂ storage operations in porous media.

KEYWORDS Hydrogen, underground storage, µCT, wetting state, capillary pressure, flow experiments, nitrogen

GRAPHICAL ABSTRACT
1. INTRODUCTION

Climate change is a major problem of increasing global relevance that will have wide ranging adverse implications for all life on Earth [1, 2]. In order to mitigate climate change we must reduce our reliance on fossil fuels, which currently account for over 75% of our greenhouse gas emissions, reduce atmospheric carbon dioxide (CO$_2$) concentrations and transition to a low carbon (C) society [1]. This requires the implementation of passive and active CO$_2$ sequestration technologies (e.g., [3-5]), and an increase in the proportion of renewable energy such as wind and solar energy into the near future. A major challenge for renewable energy is the imbalance between supply and demand [6]. A way of overcoming this imbalance is the generation of H$_2$ via electrolysis of water during periods of renewable energy oversupply with subsequent underground H$_2$ storage [7, 8] that allows for recovery and use of H$_2$ as an energy source during periods of renewable energy shortage. Electricity generation from stored H$_2$ could balance seasonal electricity demands, yet the low energy density of H$_2$ requires large-scale storage capacities that are only available in geological media [9]. While underground storage of H$_2$ in salt caverns plays an important part in the daily and weekly reduction of energy imbalances, seasonal balancing may only be achieved with H$_2$ storage in underground porous media including depleted gas fields and saline aquifers that have TWh storage capacities [9, 10].

Emerging evidence suggests there are no important showstoppers for the implementation of porous media H$_2$ storage [11-19]. Yet, certain knowledge gaps remain to be addressed, amongst them the H$_2$ fluid flow behavior in the porous medium, which, along with the injected cushion gas, governs gas injectivity and recovery from the reservoir [9, 20]. Of particular importance for describing the H$_2$ fluid flow in the porous medium is the determinations of capillary pressure and relative permeability [21] as well as quantification of H$_2$ saturation and trapping inside rocks, which can be achieved through pore-scale visualization studies [22]. These factors
directly relate to the fluids present inside the porous medium and inform simulation models to predict H₂ displacement and trapping and upscaling to the reservoir scale.

The key parameter for controlling multiphase fluid flow in porous media is wettability [23]. Wettability is characterized as the spatial distribution of the contact angle at the contact line between two fluids and the solid matrix. It is measured through the densest fluid, with a contact angle of 0 reflecting a perfectly wetting fluid [24, 25]. Wettability influences flow dynamics such as relative permeability, $P_c$ and irreducible water saturation, all of which in turn are influenced by the pore network morphology, connectivity and tortuosity. Accurate knowledge of wettability over geological conditions (e.g. rock mineralogy, brine composition, pressure, temperature) is key for the design and optimization of H₂ storage projects [26].

Recent investigations of H₂ contact angles in quartz or sandstone report ranges of 5° to 60° [16, 22, 27-32], depending on the measurement methodology, the experimental conditions and whether hysteresis was studied. Notably, there is an apparent discrepancy in the published studies on H₂ contact angles. While Hashemi et al. [28] and Higgs et al. [27] reported contact angles of 25-45° in Bentheimer and Berea sandstones without meaningful pressure or temperature correlations of the contact angle (captive-bubble method, 0.7-10 MPa and 20-50 °C), Iglauer et al. [31] reported an increase of H₂/brine/quartz contact angles of 10-15° with a pressure increase from 10 to 15 MPa using the tilted plate method.

Similar discrepancies are also found in H₂ relative permeabilities studies. Rezaei et al. [17] showed that shallower i.e. lower pressure sites are recommended for future H₂ storage operations in porous media due to a reduced relative permeability at higher H₂ saturations and high pressures of 10.7-20.7 MPa (unsteady state method, vertical core). This contrasts with previous findings by Yekta et al. [29] who documented little change of the H₂ relative permeability at pressure increases from 5.5 MPa to 10 MPa using the steady state technique. In addition, Rezaei et al. [17] showed good similarity between H₂ and N₂ relative permeability
curves, while Lysyy et al. [33], Al-Yaseri et al. [34] and Zhang et al. [32] report divergent displacement behavior of H$_2$ and N$_2$. Thaysen et al. [11] reported similar displacement behavior of H$_2$ and N$_2$ during drainage but the residual saturation after imbibition, $S_{nwr}$, was much higher for N$_2$.

In this work, we used previously acquired X-ray microtomography (µCT) images of H$_2$ and brine core-flood experiments in a Clashach sandstone at 2-7 MPa pore fluid pressure and ambient temperature (293 K) [11] to determine *in-situ* macroscopic H$_2$/brine/Clashach sandstone contact angles after drainage, $\theta_{\text{receding}}$, and imbibition, $\theta_{\text{advancing}}$, and hence, to identify a possible control of wettability on the H$_2$ injectivity and recovery. We hypothesized that $\theta_{\text{advancing}}$ would decrease with increasing pore fluid pressure, corresponding to previous observations of increased trapping at higher pressure [11]. Using µCT-images of N$_2$ and brine core-flood experiments in a Clashach sandstone at 5 MPa, we further quantified N$_2$/brine/Clashach sandstone contact angles. Measurements of the $P_c$ at varying brine saturation for N$_2$ were conducted and results were combined with the N$_2$ wettability during drainage, as well as with existing information on the density differential and the interfacial tensions between brine and H$_2$ and N$_2$, to calculate the H$_2$ $P_c$. We show that, for the same rock sample, the $\theta_{\text{advancing}}$ did not change with pore fluid pressure, indicating that, based on the wettability alone, no change in H$_2$ trapping with increasing pressure is expected. This work pioneers a high-precision H$_2$ capillary pressure curve for Clashach sandstone with H$_2$ $P_c$ of 0.43 MPa at irreducible water saturations of 12.6-14.0%. The aim of this study is to provide detailed insights into the controls on H$_2$ movement, displacement and capillary trapping. Our results may serve to inform the basic models for appropriate understanding of gas storage operations, as well as to influence their designs and predictions.

2. MATERIALS AND METHODS
2.1 Core Flood Experiments

Two-phase non-steady core flooding experiments at 2-7 MPa pore fluid pressure and ambient temperature (∼293 K) by Thaysen et al. [11] were used as input data for this wettability study. In short, the H₂ (purity 99.9995 vol.%, BOC Ltd.) and brine (0.5 M CsCl, Sigma-Aldrich) injections used the same untreated Clashach sandstone outcrop sample of 4.7 mm diameter and a length of 57 mm (Clashach composition: ∼96 wt.% quartz, 2% K-feldspar, 1% calcite, 1% ankerite [35], porosity 11.1-14.4% [35-37]). For all experiments, the same water-wet Clashach sandstone plug was first saturated with brine at a flow rate of 70 µl min⁻¹. Afterwards, H₂ was injected (drainage) into the brine-saturated Clashach sandstone plug at a flow rates of 20 µl min⁻¹, based on desired capillary-regime capillary numbers, \( N_C \), of \( 1.7 \times 10^{-8} \) (The viscosity of H₂ is 9.01 µPa s at 298 K and 4.7 MPa [38] and the IFT between H₂ and water is 72.6 mN m⁻¹ at 298 K and 5 MPa [39, 40]). Subsequently, brine was reinjected (imbibition) at a flow rates of 20 µl min⁻¹, resulting in \( N_C \) of \( 2.4 \times 10^{-6} \) (using the same IFT between H₂ and water of 72.6 mN m⁻¹ at 5 MPa and 298 K [39, 40] and a viscosity of \( 1.07 \times 10^{-3} \) Pa s for 0.6 M KI and 293 K [35]). One experiment at 5 MPa and 298 K used N₂ instead of H₂. The \( N_C \) of the N₂ experiment was \( 3.5 \times 10^{-8} \) (using an IFT of 73 mN m⁻¹ between N₂ and water at 298 K and 10 MPa [41] and a viscosity of \( 1.89 \times 10^{-5} \) Pa s at 5 MPa and 295 K [38]). At the end of each experiment (one drainage and imbibition cycle), the Clashach sandstone sample was depressurized, following reinjection of brine to ensure that all H₂ was removed from the core to prepare for subsequent experiments. 3D volumes were acquired with µCT from the lower central portion of the sample at the end of each injection step (ten pore volumes). Images were processed as described in Thaysen et al. [11].

2.2 Wettability Analysis
The wettability was characterized for one of each duplicate H$_2$ experiment carried out at 2, 5 and 7 MPa (see asterisks in Fig. 1) and for the N$_2$ experiment (Fig. 1g) by measuring the gas/brine/Clashach sandstone contact angles on each voxel at the three-phase contact line on a sub-volume of 500 µm$^3$ using a highly accurate, widely-applied algorithm for automatic contact angle measurement of µCT-images [42]. The algorithm identifies and meshes the interfaces throughout the segmented stack of images and then reduces noise and imposes a constant curvature by smoothing the data. Subsequently, two normal vectors are placed at each contact point and the dot product of these vectors (where they meet at the contact line) is used to determine the contact angle at each contact point along the contact line [42]. Data dispersion in contact angle measurements was calculated as the standard deviations of the mean.

2.3 Hydrogen Capillary Pressure ($P_{c,H_2}$)

The capillary pressure with air displacing brine, using N$_2$ as a proxy, was determined using the high-speed centrifuge method [43] on two Clashach core plugs that were drilled from the same outcrop rock as the one sample used for the core flood experiments (see Supporting Information (SI) for method details). A comprehensive description of the $P_c$ measurement for air is provided in the SI Text S1. To compute the $P_{c,H_2}$ from the air $P_c$, we employed the recently published conversion factor, $\psi_{N_2/H_2}$ (Eq. 1) [44]:

$$\psi_{N_2/H_2} = \frac{\Delta \rho_{N_2/water} \gamma_{H_2/water} \cos \theta_{H_2/water}}{\Delta \rho_{H_2/water} \gamma_{N_2/water} \cos \theta_{N_2/water}}$$  

(1)

where $\Delta \rho_{N_2/water}$ and $\Delta \rho_{H_2/water}$, represent the density differential between the gases and saline water under reservoir conditions. Brine density was deduced using the Danesh method [45]. The terms $\gamma_{N_2/water}$ and $\gamma_{H_2/water}$, denote the interfacial tension (IFT) between the gases and water.
Figure 1. 3D renderings of gas clusters with gas saturation percentages in the pore space after drainage and primary imbibition at 2-7 MPa. Discrete clusters were rendered in colors, where mainly one color marks one large, connected cluster and different colors indicate several, not connected clusters. (a-b) H\textsubscript{2} at 2 MPa, (c-d) H\textsubscript{2} at 5 MPa and (e-f) H\textsubscript{2} at 7 MPa, (g) N\textsubscript{2} at 5 MPa, all at a constant flow rate of 20 µl min\textsuperscript{-1}. Asterisks mark data utilized for the contact angle analysis. Adapted from Thaysen et al. [11].
and made use of the methodology for calculation of the IFT by Meybodi et al. [46], as previously detailed [44]. The last terms, $\cos \theta_{N_2/water}$ and $\cos \theta_{H_2/water}$, represent the wettability of the Clashach sandstone samples. With this conversion factor in place, the $P_{cH_2}$ at varying water saturations is ascertained by Eq. 2

$$P_{cH_2} = \Psi_{N_2/H_2} \times P_{cN_2}$$  \hspace{1cm} (2)

All parameters used to calculate the $\Psi_{N_2/H_2}$ and $P_{cH_2}$ are provided in SI Table 2.

### 3 RESULTS

#### 3.1 H$_2$-brine-Clashach sandstone contact angles relative to H$_2$ pore space saturations

Hydrogen-brine-Clashach sandstone contact angles were normally distributed and showed $\theta_{receding}$ of 61.09°, 61.01° and 60.82° at 2, 5 and 7 MPa pore fluid pressure, with standard deviations of 24°, 26° and 24°, respectively (Fig. 2a). $\theta_{advancing}$ were 57.8 ± 21°, 58.1 ± 22° and 57.8 ± 20° at 2, 5 and 7 MPa pore fluid pressure, respectively (Fig. 2b). Initial H$_2$ saturation was~50% at all pore fluid pressures (Fig. 1). Trapped H$_2$ in the pore space after imbibition increased from 10-12% at 2-5 MPa to 21% at 7 MPa (Fig. 1), with a significant cluster build-up at 7 MPa (Fig. 1e). The total mass of trapped H$_2$ at 2, 5 and 7 MPa, considering saturation and density differences with pressure, was 0.022 mg, 56.3-67.6 mg and 165.6 mg, respectively.

#### 3.2 N$_2$-brine-Clashach sandstone contact angles relative to N$_2$ pore space saturations

Nitrogen-brine-Clashach sandstone contact angles were normally distributed and were 66.5° ± 21° and 62.1° ± 24° after drainage and imbibition, respectively, at 5 MPa pore fluid pressure
Figure 2. Drainage (a) and imbibition (b) contact angle distributions measured at the H₂/brine/Clashach sandstone interface at 2, 5 and 7 MPa pore fluid pressure. Note the different y-axes scales. The number of contact angles in these graphs is proportional to the H₂ saturation in the pore space. During drainage, a mean contact angle of 61° was observed at all pressures and H₂ saturation in the pore space was similar. During imbibition, the mean contact angle was 58° at all pore fluid pressures and a larger volume of H₂ was trapped at 7 MPa relative to at lower pressures.

(Fig. 3). Initial and residual saturations of N₂ were 49% and 34%, respectively (Fig. 1g).

3.3 $P_c$ and irreducible water saturation

Figure 4 shows the drainage $P_c$ curve for H₂ for two Clashach sandstone plugs with permeabilities of 139 mD and 178 mD, respectively. Under ambient conditions, $P_{cH2}$ is approximately 1.3 to 1.36 times greater than that of N₂ (SI Table S2). The most pronounced impact on $P_c$ stems from differences in wettability, contributing to approximately 19% of the effect (SI Table S2). The IFT and density differential between H₂ and N₂ relative to brine
contribute less to the differences in $P_c$, as IFT for both $H_2$ and $N_2$ exhibit a variation of less than 8% and the density differential is less than 3% (SI Table S2). The irreducible water saturation of Clashach sandstone is 12.6-14% and is reached at 0.43 MPa and 0.35 MPa for $H_2$ and $N_2$, respectively (Fig. 4, SI Table S2).

4. DISCUSSION

4.1 $H_2$-brine-Clashach sandstone contact angles

We observed normal distributions of $\theta_{\text{receding}}$ and $\theta_{\text{advancing}}$ (Fig. 2). If the solid surface was truly smooth and mineralogically homogeneous, all contact angles would be identical. The pore walls of naturally occurring rocks however are characterized by a certain surface roughness and mineralogical heterogeneity; hence, contact angles in real rock samples show some scatter, creating a distribution of contact angles [24]. In addition, the voxel size of 5.4 µm$^3$ of the µCT images implies an inability to completely resolve the three-phase contact line which could cause segmentation errors and contact angle measurement errors, contributing to the scatter in contact angles. The mean contact angle for drainage is 66.4° and for imbibition is 62.1°. Figure 3. Contact angle distributions at the $N_2$/brine/Clashach sandstone interface after drainage and imbibition at 5 MPa pore fluid pressure showing average contact angles of 66° and 62°, respectively.
observed large range of contact angles. Resolution limitations on contact angle measurements manifest in particular during drainage when the saturation of the nonwetting phase increases and the fluid-fluid interfaces move into the pore throats where the voxel count is limited [47].

Considering standard deviations of 20-26% in the H₂ contact angle measurements, the mean drainage and imbibition contact angles of 61° and 58°, respectively, were not significantly different. Standard deviations are within the upper range of the standard deviations reported in the literature for the here applied 3D local method [16, 42]. Contact angles are generally expected to be larger for imbibition than for drainage [21]. The here observed a higher drainage contact angle may be an artefact caused by resolution limitation to our measurements.

Hydrogen/brine/Clashach sandstone contact angles after imbibition were 58° at all pore fluid pressures (Fig. 2b), indicating a water-wet rock and, despite the significant cluster build-up at 7 MPa (Fig. 1e, 2b), wettability does not change with pore fluid pressure. These combined findings are in line with H₂ cluster size distributions for the same experimental data [11], which
show an increase in the number of intermediate size clusters at 7 MPa, without shifting the cluster distribution horizontally, suggesting no wettability change.

The amount of \( \text{H}_2 \) residual trapping is a function of 1) the contact angle, 2) the rock porosity and rock pore morphology, 3) the initial \( \text{H}_2 \) saturation and connectivity, and 4) the \( \text{H}_2 \)-brine IFT. The IFT of \( \text{H}_2 \)-brine decreases by 1% with pressure increases from 2 to 7 MPa (from 73.982 to 73.293 mN m\(^{-1}\))\(^{[27]} \) and is hence unlikely to impact residual trapping significantly. Hence, with no changes in the IFT and in the contact angle (Fig. 2b), and no change in the rock porosity and rock pore morphology due to the deployment of the same Clashach sandstone sample in all experiments, increased trapping at 7 MPa can only be attributed to the decreased \( \text{H}_2 \) connectivity during drainage. Noteworthily, a poorer initial connectivity of hydrogen was not confirmed by the repetition of primary drainage at 7 MPa (Fig. 1f). It is possible, that some salt precipitated during the experiments and blocked a pore throat which could have altered the \( \text{H}_2 \) flow path, thereby leading to decreased initial connectivity and/or increased \( \text{H}_2 \) trapping during imbibition. Salt precipitation is more pronounced at higher pressures as higher pressures lead to increased drying of the brine by the injected gas \(^{[12]} \). The increased \( \text{H}_2 \) \( S_{\text{wtr}} \) at 7 MPa is subject to further investigations. Future work should target conducting repeated cyclic \( \text{H}_2 \) and brine injection experiments at 7 MPa pore fluid pressure and higher, as well as experiments with \( \text{H}_2 \)-saturated brine, to elucidate the reproducibility and any potential effect of gas dissolution on our results.

\[ \text{4.2 N}_2\text{-brine-Clashach sandstone contact angles} \]

Considering standard deviations of \(-20\%\) in our experiments, the \( \text{N}_2 \) contact angles for drainage and imbibition were not significantly different. Further, \( \text{N}_2 \) contact angles were not significantly different from \( \text{H}_2 \) contact angles (Figs. 2 and 3). In view of similar \( S_{\text{wtr}} \) for \( \text{H}_2 \) and \( \text{N}_2 \) (Fig. 1c,d, g), the similar \( \theta_{\text{receding}} \) were expected. However, the \( \text{N}_2 \) \( S_{\text{wtr}} \) was \(-20\%\) greater
than for H$_2$ (Fig. 1c,d, g), so a lower gas wettability, i.e. lower N$_2$ $\theta_{\text{advancing}}$, was anticipated.

Because N$_2$ and H$_2$ experiments used the same rock sample, only differences in the contact angle and/or differences in the IFT could have caused the higher $S_{\text{nwr}}$ for N$_2$. For any given pressure, the IFT of N$_2$ is lower than for H$_2$ (SI Table 2), hence, according to theory, at similar $\theta_{\text{advancing}}$, N$_2$ residual trapping should decrease relatively to H$_2$ residual trapping. The higher $S_{\text{nwr}}$ of N$_2$ over H$_2$ is subject to further investigations.

Higher capillary trapping of N$_2$ over H$_2$ has been shown previously in connection to an almost doubled $S_{\text{nwi}}$ of N$_2$ over H$_2$ ($\mu$CT method, Bentheimer sandstone, 1 MPa pressure and ambient temperature) [32]. Here, the lower $S_{\text{nwi}}$ of H$_2$ over N$_2$ was suspected not to be caused by differences in $\theta_{\text{receding}}$ but to arise from H$_2$ dissolution as well as channeling, driven by the lower viscosity of H$_2$ compared to N$_2$ [32]. Our data do not confirm the observations of H$_2$ channeling during drainage (Fig. 1, [11]). Residual H$_2$ was distributed mainly over one side of the rock sample (Fig. 1a, b, c) which could indicate some preferentiality in the H$_2$ fluid flow during imbibition.

4.3 Relation to other work

4.3.1 Hydrogen

To date, ten studies either measured or derived H$_2$/brine/sandstone or pure quartz contact angles. While there is general consensus in the literature that unaged H$_2$/brine/quartz or sandstone systems are water-wet, contact angles vary with rock type, sample preparation and measurement methodology as well as experimental condition. Because the in-situ contact angle method captures the effects of local pore geometry and surface roughness it provides a more accurate representation of the fluid interaction in porous media than contact angle data from the tilted plate method or the captive bubble method [27]. Four studies, all conducted on Bentheimer sandstone, applied the same in-situ contact angle measurement methodology as in
this work: Higgs et al. measured $\theta_{\text{advancing}}$ of 59.8° and 57° at ambient temperature and 0.4 MPa and 2.1 MPa, respectively [27, 48]. Jangda et al. [16] reported $\theta_{\text{advancing}}$ between 52.7° - 53.7° at 10 MPa and 323 K. Zhang et al. [32] reported $\theta_{\text{advancing}}$ of ~57° at ambient temperature and 1 MPa. All results are very close to our $\theta_{\text{advancing}}$ of 58° at 2-7 MPa and ambient temperature. The Bentheimer sandstone is more porous than Clashach (23% porosity vs. 12.5-13.6% porosity, respectively [11, 16, 48]) and has ~4 % less quartz than Clashach, with correspondingly increased clay and feldspar fractions [49].

Previous reports of $\theta_{\text{receding}}$ in Bentheimer sandstone range from 44° to ~75° (1- 2.1 MPa, ambient temperature) [32, 48], a range that brackets the here measured 61°.

The captive bubble method, applied to Bentheimer and Berea sandstones, yielded lower H$_2$/brine contact angles (25°-45°) [27, 28] than the in-situ method but coincided with this study in that there was no correlation between contact angle and pressure (measured over a range of 6.9-20.7 MPa). The captive bubble method was also recently used to measure H$_2$/brine/carbonate rock contact angles, again with no effect of increasing pressure and temperature on the contact angle [50]. However, when applied to quartz samples aged in organic acids, increasing contact angles with increasing pressure and temperature were reported [51].

Using the tilted-plate method on pure quartz, advancing contact angles of 40.8° have been reported (temp: 323 K, pressure: 25 MPa) [52] and increases in contact angles from 0° to a maximum of ~50° were observed at increases from 296 K and 0.1 MPa to 343 K and 25 MPa [31]. The authors argued that the reported trend in contact angles is caused by the increasing intermolecular quartz–gas interactions with increasing molecular gas density at increased pressure [31].

Calculations of H$_2$/brine contact angles from $P_c$ curves for Berea and Vosges sandstone yielded 45° [30] and 21.6° to 34.9° [29], respectively, depending on the experimental condition.
The $P_{cH2}$ curve for Clashach was similar to the Vosges sandstone $P_c$ curve from Yekta et al. [53] (derived using the results from both of the tested pressure and temperature conditions; Fig. 4), despite the significantly lower relative permeability of the Vosges sandstone. The $P_c$ for Berea sandstone from Boon & Hajibeygi [30] was higher than for Clashach and Vosges sandstone (Fig. 4). The saturations for the $P_c$ measurements in Yekta et al. [53] and Boon & Hajibeygi [30] cover a small range, resulting in a higher uncertainty in the fit of the mercury injection capillary pressure data.

4.3.2 Nitrogen

Studies on N$_2$/brine/rock contact angles are scarce. Reported effective N$_2$ contact angles range from 30° on quartz (captive bubble method, 5 MPa and 313 K) [54] to 25-47° in illite and kaolinite (tilted plate method, 5-10 MPa and 60°C) [55, 56], with 3-6° higher $\theta_{\text{receding}}$ than $\theta_{\text{advancing}}$ [56], and are larger than H$_2$ contact angles of ~10-20° on the same minerals [55]. A stronger gas-wetting behavior of N$_2$ relative to H$_2$ [55] was indicated by our experiments but not statistically significant. Higher wettability of N$_2$ over H$_2$ would be favorable for gas separation during production if N$_2$ is used as a cushion gas.

Our results are close to mean in-situ N$_2$ contact angles of ~71° at 1 MPa and 298 K in Bentheimer sandstone [32] and to ~69° on smooth silicon in water at 5 MPa and 296 K [57]. The observed differences between $\theta_{\text{advancing}}$ and $\theta_{\text{receding}}$ correspond well with previous reports from air-water systems [58]. Our results are significantly higher than 40-60 manually measured in-situ N$_2$ $\theta_{\text{receding}}$ and $\theta_{\text{advancing}}$ of 34°±6° and 46°±6°, respectively, in Berea sandstone at 5.5 MPa and ambient temperature [24]. Considering 2800 times more contact angles measured in this study as well as the use of an automated approach to remove potential selection bias that
might exist in manual methods, one may suspect that our study resulted in more representative answer.

4. CONCLUSION

In this work, in-situ contact angles for the H$_2$/brine/Clashach sandstone system were quantified at 2-7 MPa pore fluid pressure to identify any control of wettability on $S_{nwr}$. Measurements of N$_2$/brine/Clashach sandstone contact angles at 5 MPa and N$_2$ $P_c$ with varying brine saturations, enabled the novel calculation of the $P_{cH2}$ curve.

Contrary to our hypothesis, the average receding contact angles did not decrease with increasing pore fluid pressure but showed a mean of 58° at all pressures, suggesting that observed higher $S_{nwr}$ at 7 MPa were not caused by wettability changes. Instead, the elevated $S_{nwr}$ at increased pressure was likely instigated by a decreased connectivity after drainage, however decreased connectivity was not confirmed by a repetition experiment. More experiments at 7 MPa and higher pressure will need to be undertaken to confirm the trend in $S_{nwr}$ with pressure. Comparison with other studies showed good alignment with other in-situ H$_2$ contact angle measurements in sandstone but revealed that measurements in artificial systems significantly underestimate the H$_2$/brine/sandstone contact angle. Overall, this study and other emerging research suggests that for contact angles around 58°-70°, wettability may not always be the main control for the H$_2$ saturation in the pore space but that H$_2$ dissolution and channeling events may significantly affect those parameters.

Average N$_2$/brine/Clashach sandstone contact angles at 5 MPa were 66° and 62° during drainage and imbibition, respectively, and not significantly different from H$_2$ contact angles. This matched a similar $S_{nwi}$ for N$_2$ and H$_2$, yet could not explain a 20% higher $S_{nwr}$ relative to H$_2$. 
The $P_{cH2}$ plays a noteworthy role in understanding how $H_2$ interacts within porous media. When $H_2$ encounters a rock's pore spaces, this parameter helps quantify the onset of its movement and displacement of the resident fluid, like brine. The novel $P_{cH2}$ for Clashach sandstone in our experiments was determined with a previously unseen precision. At an irreducible water saturation of 13.6-14.0% the $P_{cH2}$ was 0.43 MPa. The relevance of such data extends to areas such as underground $H_2$ storage, where understanding these interactions can influence storage designs and predictions.

ASSOCIATED CONTENT
Supporting information: TEXT S1 ‘Measurements required for the calculation of the Hydrogen capillary pressure’ which comprises the base results used to create Figure 4 (SI Table 2).

AUTHOR INFORMATION

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Author Contributions
The experimental kit was built by Butler and Thaysen. Hydrogen and brine displacement experiments were carried out by Thaysen and Butler. Image reconstruction and tomographic analysis was carried out by Thaysen, Jangda, Menke and Singh. The calculation of the hydrogen capillary pressure with varying brine saturations was by Hassanpouryouzband. Interpretation of the results was by Thaysen, Butler, Heinemann and Hassanpouryouzband. The manuscript was written by Thaysen, with contributions and review from Butler, Hassanpouryouzband, Edlmann, Heinemann, Jangda, Menke and Singh. All authors have given approval to the final version of the manuscript.
Declaration of interest

The authors declare no competing interest.

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ABBREVIATIONS

H₂ = hydrogen, N₂ = nitrogen, Nc = capillary number, Pc = capillary pressure, Pch₂ = hydrogen capillary pressure, Smwi = initial saturation, Smwr = residual saturation, θadvancing = imbibition contact angle, θreceding = drainage contact angle.

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1. IPCC, IPCC report Global Warming of 1.5 C: Summary for Policymakers. 2018


TEXT S1 Measurements required for the calculation of the Hydrogen capillary pressure

Permeability to nitrogen

Two fully dried Clashach sandstone plugs (length: 5.0 cm, diameter: 3.8 cm) were each placed in a Hassler core holder (Standard Core Holder- HCH Series, Core Laboratories, UK), maintaining a sleeve pressure of 2.76 MPa. Dry nitrogen was channeled through the core plug at a consistent flow rate until the pressure readings were stable, and both the upstream and downstream pressures were documented. The steady-state permeability to nitrogen at a low mean pore pressure was determined using equation 1:

\[
 k_{air} = \frac{1000 \times Pa \times \mu_N \times q_N \times L}{(P_i - P_0)(P_i + P_0)/2 \times A} \quad (1)
\]

where \( k_{air} \) is the permeability (mD), \( q_N \) is the flow rate of nitrogen at atmospheric pressure (cm\(^3\)/s), \( \mu_N \) is the viscosity of nitrogen (cP), \( L \) is the length of core plug (cm), \( A \) is the cross-sectional area of core plug (cm\(^2\)), and \( P_i, P_0 \) and \( P_a \) are the upstream pressure, the downstream pressure and the atmospheric pressure, respectively (all in atm).

Helium Porosity and Grain Density

The clean and dry plug samples were first weighed. Subsequently, their grain volumes were determined using a Pycnometer System (UltraPore\textsuperscript{TM}300, Anton-Paar ,USA). This automated gas displacement pycnometer computes density and grain volume by assessing the pressure variation of helium within a pre-calibrated volume that expands into a matrix cup housing the plug sample. The system relies on computer-based processing for all pressure readings and calculations, effectively minimizing potential transcription errors.
Each of the clean, dry samples was placed into a designated matrix cup connected to the system. Helium, with a predetermined pressure sourced from a reference cell of known volume, was expanded into the matrix cup, and the resultant pressure was recorded. Using Boyle’s Law, grain volumes were computed based on a modified version of the standard equations:

Boyle’s Law calculation \[ P_1V_1 = P_2V_2 \] (2)

Grain volume calculation \[ P_1V_{\text{ref}} = P_2(V_{\text{ref}} + V_{\text{matrix}} - V_g - V_{\text{disk}}) \] (3)

Therefore:

\[ V_g = ((V_{\text{matrix}} + V_{\text{ref}}) - (P_1/P_2 \cdot V_{\text{ref}})) - V_{\text{disk}} \] (4)

where \( P_1 \) and \( P_2 \) are the pressure of helium in the reference cell and after expansion into matrix cup, respectively, \( V_{\text{ref}} \) is the volume of the reference cell, \( V_{\text{matrix}} \) is the volume of the matrix cup, \( V_g \) is the grain volume of the plug sample, and \( V_{\text{disk}} \) is the disk volume added to cup to reduce dead space. To determine the true grain volume, the volume of any mounting material was accounted for and subtracted.

The system is equipped with a precision 0-1.37 MPa transducer. Its linearity and hysteresis have an impressive accuracy, registering less than +/- 0.11% of full scale. To ensure its precision, the system undergoes calibration twice daily using steel disks with known volumes. These disks receive their calibration externally. The calibration correlation factor must consistently fall within the range of 1.0000 +/- 0.0001 for validity. For enhanced accuracy, beyond the regular calibrations, check plugs are measured roughly after every ten samples. At the conclusion of each worksheet, at least one sample undergoes a double-check to ensure consistency.

Grain density was derived from the grain volume and the dry weight of the sample. Adjustments were made for the weight of any mounting material when necessary. Bulk volume
(\(V_b\)) was ascertained using mercury displacement. Subsequently, pore volume (\(V_p\)) and porosity (\(\phi\)) were computed according to equations 5 and 6:

\[
V_p = V_b - V_g
\]  
\[
\phi = V_p / V_b
\]

Table S1 shows the results of the \(N_2\) permeability, the porosity and the grain density measurements.

SI Table 1. Permeability and Porosity of Clashach core samples

<table>
<thead>
<tr>
<th>Plug</th>
<th>(K_{N2}), millidarcies</th>
<th>Porosity, frac</th>
<th>Grain density, g/cc</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>139</td>
<td>0.130</td>
<td>2.64</td>
</tr>
<tr>
<td>2</td>
<td>178</td>
<td>0.131</td>
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</tbody>
</table>

Core Sample Saturation with 0.5 M Caesium Chloride

The clean and dry Clashach sandstone plugs were first weighed. Subsequently, they were placed inside a sealed container and subjected to evacuation for a period of 24 hours. After the evacuation, the container was filled with the same brine that was utilized for the \(H_2\) and brine core-flood experiments (0.5 M \(CsCl\)). The brine was then pressurized to 13.8 MPa, and this pressure was sustained for an additional 24 hours.

After the stipulated time, the brine pressure was gently released. The samples, now saturated with brine, were extracted from the container and weighed. The difference in weight between
the dry and saturated samples serves as an indicator of the brine volume within each sample.

This value was collated with the pore volume deduced from helium injection.

In addition, every brine-saturated sample was weighed when submerged in the saturating brine. Utilizing Archimedes' principle, a bulk volume was computed. Saturation porosity was then determined using the derived saturation pore volume and the calculated Archimedes bulk volume. This saturation porosity was subsequently compared to the porosity determined through helium injection.

**Capillary Pressure Determination**

The Clashach sandstone plugs were pressure-saturated with 0.5 M CsCl, as detailed in section 2.3.3. Each plug was positioned in a rotor bucket equipped with a graduated receiving tube and mounted onto the body of a high-speed centrifuge. The centrifuge employed was an ACES200—an automated, camera-enabled system that incorporated a modified Beckman L100 Optima centrifuge with its associated control software.

The receiving tube and the void around each sample were filled with the displacing phase, which in this context, is air. The rotor can accommodate up to three 1.5-inch diameter plugs simultaneously. In scenarios where brine saturation diminishes (like in drainage, which is the case here), the receiving tubes are strategically positioned farther from the rotation's center than the plugs, ensuring efficient brine collection.

The rotor, loaded with the plugs, was subjected to varied rotation speeds, ranging between 800 to 7500 rpm. These speeds were chosen to generate equivalent capillary pressures ($P_c$) within a spectrum of approximately 0.02 MPa to around 2.07 MPa, especially for an air-displacing-brine mechanism. While the rotor was spinning, a stroboscopic light illuminated the receiving tube to determine the volume of brine displaced from each plug. Readings can be
taken either manually or captured with a camera. In this case, we recorded the readings manually. Every core plug was retained at each specific capillary pressure until it reached equilibration for the given pressure. After a span ranging from 24 to 48 hours, equilibration was confirmed if the fluid volume displaced from each core plug remained unaltered for a consecutive 4-hour period. The rotor bucket assemblies' weights were recorded before and post-test to identify any potential evaporative losses. The volumes of brine displaced, plug pore volumes, and the respective capillary pressures derived from test parameters were utilized to deduce capillary pressure and saturation data. Further details about the method can be found elsewhere [43].

Calculation of Centrifuge Air-Brine Capillary Pressure from Brine Displacement Data

Average brine saturations were adjusted for capillary end effects, and the end-face brine saturations were derived using Pierre Forbes' methodology [59]. Capillary Pressure ($P_c$) was deduced from the rotation rates via equation 7:

$$P_c = 1.578 \times 10^{-7} \times (\rho_b - \rho_{air}) \times (R - L/2) \times L \times \text{RPM}^2$$

(7)

where $\rho_b$ is density of brine (1.06 g/cm$^3$), $\rho_{air}$ is the density of air (0.0012 g/cm$^3$), $R$ is the distance from centre of rotation to outer face of the core plug in cm, $L$ is the length of core plug in cm, and RPM are revolutions per minute. From the above relationship it can be seen that the capillary pressure generated for each sample at each spin speed can be different due any differences in plug length.

The average brine saturation, $S_{w_{avg}}$, is determined using equation 8:
where $V_p$ is the pore volume in cm$^3$ and $V_{\text{displaced}}$ is the volume of displaced fluid in cm$^3$.

Capillary pressure curves for each sample were derived using Forbes' equations [59]. The results, presented in both tabular and graphical formats, include inlet end-face brine saturations.
Table 2. Parameters required for calculation of the H₂ capillary pressure using the N₂ capillary pressure data. $P_c$ = capillary pressure, $\psi$ = conversion factor.

<table>
<thead>
<tr>
<th>$N_2$ $P_c$ (MPa)</th>
<th>Brine Sat. Sample 1</th>
<th>Brine Sat. Sample 2</th>
<th>Density $N_2$ (kg/m$^3$)</th>
<th>Density $H_2$ (kg/m$^3$)</th>
<th>Density 0.5 M CsCl (kg/m$^3$)</th>
<th>IFT $N_2$ (mN/m)</th>
<th>IFT $H_2$ (mN/m)</th>
<th>Wettability $N_2$ (Cos(0))</th>
<th>Wettability $H_2$ (Cos(0))</th>
<th>$N_2$/Brine density difference</th>
<th>$H_2$/Brine density difference</th>
<th>Density Difference Ratio</th>
<th>IFT Ratio</th>
<th>Wettability ratio</th>
<th>$\psi$</th>
<th>$H_2$ $P_c$ (MPa)</th>
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