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**Pore-scale imaging of hydrogen displacement and trapping in porous media**

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Abstract

Hydrogen can act as an energy store to balance supply and demand in the renewable energy sector. Hydrogen storage in subsurface porous media could deliver high storage capacities but the volume of recoverable hydrogen is unknown. We imaged the displacement and capillary trapping of hydrogen by brine in a Clashach sandstone cylinder at 2-7 MPa pore fluid pressure using X-ray computed microtomography. Hydrogen saturation obtained during drainage at capillary numbers of $<10^{-7}$ was $\sim50\%$ of the pore volume and independent of the injection pressure. Fluid configuration in the pore space was indicative of a water wetting system at all conditions. Capillary trapping of hydrogen via snap-off during secondary imbibition at a capillary number of $2.4\times10^{-6}$ systematically increased with pressure, 20%, 24% and 43% of the initial hydrogen trapped at 2, 5 and 7 MPa, respectively. Injection of brine at increasing capillary numbers up to $9.4\times10^{-6}$ reduced capillary trapping. Based on these results, we recommend more shallow, lower pressure sites for future hydrogen storage operations in porous media.

Keywords: geological hydrogen storage, μCT, porous media, recovery, drainage, imbibition

Highlights:

- Hydrogen injectivity and recovery in rock is imaged with x-ray computed micro-CT
- Hydrogen recovery decreases with increasing reservoir depth
- Hydrogen recovery increases with increasing brine flow rate
- Hydrogen trapping occurs via snap-off processes
- Nitrogen is a poor proxy for hydrogen
1. Introduction

The storage of surplus electrical energy could increase the utility of renewable energy sources thereby reducing the environmental impact of energy generation\(^1\,\,^2\). Storage mediums like batteries, compressed air, capacitors, or flywheels are only applicable for the short-term and small-scale electricity storage\(^3\). The use of hydrogen (H\(_2\)) as an energy vector however could provide long-term storage to balance the intermittent demand and supply challenges affecting renewable methods\(^3\). Considering the low energy density of H\(_2\)\(^4\), storage of H\(_2\) in large storage sites is the only solution for economical, gigawatt to terawatt-scale H\(_2\) storage. Underground storage of H\(_2\) in salt caverns is an established technology\(^5\), yet, only subsurface porous media (saline aquifers and depleted oil and gas fields), can provide TWh storage capacities that could balance seasonal demands\(^4\). Relative to cavern storage, inter-seasonal storage in porous media is poorly understood and introduces a range of other complexities\(^2\), including potential pore-clogging by microbial growth\(^6\), gas loss out of diffuse lateral boundaries, viscous fingering of H\(_2\) into reservoir brines, residual trapping and possible reactions with the primary formation fluid and reservoir minerals\(^7\,\,^10\). Each of these requires consideration of multiphase flow, transport and reaction\(^2\,\,^8\).

Recent years have seen several studies on H\(_2\) geochemistry\(^11\,\,^13\) and the elucidation of many important flow characteristics of H\(_2\) including; Hydrogen relative permeability\(^14\,\,^15\), interfacial tension (IFT)\(^16\,\,^17\), and H\(_2\)/brine/rock contact angles\(^14\,\,^16\,\,^24\). Yet, additional data describing the H\(_2\) fluid flow in different porous formations and under varying conditions are vital to make accurate predictions of the H\(_2\) plume development and to define optimum production strategies\(^8\). Of particular relevance is the degree of capillary trapping, which leads to a reduced volume of recoverable H\(_2\), in this way impacting the economic feasibility of the operation\(^8\). The capillary forces that control capillary trapping also control the relative permeability\(^8\). As such
studies on residual trapping give insight to a range of crucial input parameters for pore-scale and reservoir H₂ storage models.

The effects of the brine pore fluid pressures and of brine flow rate on capillary trapping of H₂ are hitherto unknown. The brine pore fluid pressure is linked to the reservoir depth via the hydrostatic gradient, hence an investigation of the latter could facilitate the definition of an optimal storage depth for gas recovery. The flowrate affects the capillary number, \( N_c \), via equation 1:

\[
N_c = \frac{q \mu}{\sigma}
\]  

where \( q \) is the flow, \( \mu \) is the viscosity and \( \sigma \) is the interfacial tension (IFT). As \( N_c \) increases, viscous forces dominate capillary forces and capillary trapping of the nonwetting phase decreases\(^25\). This capillary desaturation with increasing \( N_c \), depends on the rock type\(^26\) and on the kind of nonwetting phase\(^25\) and is observed around critical capillary numbers of \( 10^{-5} \) to \( 10^{-8} \).\(^25\)

A non-destructive standard technique for visualization and analysis of wetting and non-wetting phase displacement processes in porous media is x-ray micro-computed tomography (\( \mu \)CT)\(^27\). Pore-scale models are directly reliant on \( \mu \)CT images to build up the basic models for appropriate understanding of gas storage operations\(^28\). Previously published \( \mu \)CT studies on two-phase flow in porous media involving gas have largely focused on supercritical carbon dioxide (sCO₂) in sandstones and limestones, e.g.\(^27, 29-34\). Reported saturations of sCO₂ in non-aged (i.e. not wettability altered by exposure to oil or organic acids) water-wet rocks range from 30-60% during drainage and 15-30% during imbibition, at \( N_{Ca} \) between \( 10^{-8} \) to \( 10^{-6} \) and \( 10^{-8} \) to \( 2 \times 10^{-5} \), respectively\(^27, 30, 32-34\). Studies using subcritical, gaseous carbon dioxide (CO₂), which could be more readily compared to H₂, are scarce. Yet, the characteristic trapping curves for sCO₂ and CO₂, which show the residual saturation (\( S_{\text{nnwr}} \)) as a function of initial saturation (\( S_{\text{nwz}} \)), are not significantly different\(^35\). Saturations of nitrogen (N₂) during drainage and...
Imbibition in sandstones with 6-22% porosity is 43-64% and 43%, respectively, at $N_C$ between $1-7\times10^{-8}$ \cite{36,37}. Carbon dioxide trapping increases at lower pressures due to decreasing water contact angles \cite{38}. Unlike in CO$_2$ storage, trapping is not desirable in geological H$_2$ storage as it leads to unrecoverable H$_2$.

Some observational studies have suggested that H$_2$ is less wetting on rocks than CO$_2$ \cite{19,21}. At the time of writing two µCT studies, one micro-model study and one nuclear magnetic resonance (NMR) study on H$_2$ exist: Al-Yaseri et al. (2022)\cite{39} used NMR to find H$_2$ $S_{nwi}$ and $S_{mnw}$ of 4% and <2%, respectively, in a Fontainebleau sandstone at 0.4 MPa and ambient temperature. Higgs et al. (2021)\cite{16} µCT-imaged H$_2$ injection into a 5 mm diameter and 7.6 mm length core of Bentheimer sandstone at pressures of 6.8 to 20.8 MPa and documented decreasing IFT between H$_2$ and water with increasing pressure (72.5 mN/m at 6.9 MPa to 69.4 mN/m at 20.7 MPa). Jha et al. (2021)\cite{40} conducted a single cycle H$_2$-brine displacement sequence in a 5 mm diameter and 15 mm length Gosford sandstone, and used µCT to calculate an $S_{nwi}$ of 65% during drainage and a $S_{mnw}$ of 41% after brine imbibition. Rock samples in Jha et al. (2021)\cite{40} and Higgs et al. (2021)\cite{16} were sufficiently short for capillary end effects to dominate the flow behaviour, where the wetting phase accumulates close to the production face of the core \cite{41}. The experiment by Jha et al. (2021)\cite{40} was performed at ambient pressure and leaves open the question of variations in H$_2$ wetting and flow behaviour at reservoir conditions \cite{19}. Increasing pore fluid pressures have been reported to increase the gas saturation and pore network connectivity for nitrogen (N$_2$) in a brine wet, aged Bashijiqike tight sandstone (0.6% gas saturation at 2 MPa versus 43% at 8 MPa) \cite{36}. The effect of $N_C$ increases from $7.7\times10^{-7}$ to $3.8\times10^{-4}$ on the H$_2$ flow through a sandstone micro-model at 0.5 MPa was investigated by Lysyy et al. (2022)\cite{20} who found that H$_2$ saturation increased correspondingly from 18% to 79% \cite{20}.
In this work, we used µCT to investigate the displacement and capillary trapping of H₂ by brine in 4.7 mm diameter and 54-57 mm length Clashach sandstone cores as a function of gas and brine pore fluid pressure (2-7 MPa) and flow rate (20 to 80 µl min⁻¹, corresponding to H₂ and brine bulk $N_C$ of $1.7-6.8 \times 10^{-8}$ and $1.2-9.4 \times 10^{-6}$, respectively). We show that the H₂ $S_{swi}$ is independent of pore fluid pressure but that higher brine pore fluid pressures during secondary imbibition increase capillary trapping of H₂, indicating increased trapping at elevated reservoir depths. Higher flowrates during secondary imbibition on the other hand decrease capillary trapping. Our work advances the current understanding of H₂ flow in porous media by delivering the first realistic estimates on how much H₂ can be recovered from the subsurface after injection, disregarding any H₂ loss by microbial or geochemical reactions, as a function of reservoir depth and flow rate.

2. Materials and Methods

2.1 Core-flooding experiments

We performed non-steady and steady state, two-phase core flooding experiments with H₂ (purity 99.9995 vol.%, BOC Ltd.) and brine (0.5 M CsCl or 2 M KI, Sigma-Aldrich) in a Clashash sandstone (Permian, Aeolian sandstone from near Elgin in Scotland. Clashach composition: ~96 wt.% quartz, 2% K-feldspar, 1% calcite, 1% ankerite⁴², porosity 11.1-14.4%⁴²-⁴⁴) at ambient temperature (~293 K). The Clashash sandstone, with its low mineralogical variability, yet still comparably big pore space, was chosen in order to facilitate the visualization of the injected H₂ and the interpretation of the results.

Two types of experiments were carried out: The first set of experiments (from now on referred to as UoE (Univeristy of Edinburgh) experiments) was carried out using the µCT instrument at the University of Edinburgh and were aimed at imaging the displacement and capillary...
trapping of H₂ by brine as a function of saturation after drainage and imbibition under different experimental conditions. Three UoE experiments were carried out that investigated the effect of injection pressure (2-7 MPa), whereof each was repeated once (UoE exp. 1-3, Table 1). The standard error on the H₂ saturation in the repeated experiments was calculated as the standard deviation devided by the square root of the number of repeated experiments. One UoE experiment looked at the effect of the H₂/brine injection ratio on the H₂ saturation (UoE exp. 4, Table 1). This experiment was carried out to evaluate the effect of H₂ injection into aquifers with different magnitudes of brine flow (hydrodynamic aquifers), and to simulate the far field situation, where H₂ and brine move together. Another UoE experiment investigated the effect of secondary drainage and imbibition (UoE exp. 5, Table 1). UoE exp. 6 used N₂ instead of H₂. This experiment was undertaken in order to compare the flow behaviour of the two gases, which is of relevance because N₂ is sometimes used as an analogue for H₂, e.g. in permeability measurements. Because rearrangement processes in the pore volume were noted previously for N₂, UoE exp. 7 (Table 1) was undertaken to examine the stability of H₂ in the rock volume over an experimental duration (10 hours): Ten PV of H₂ were injected into a brine-saturated rock and keeping the pressure constant inside the pressure vessel, with imaging undertaken at the start and after 10 hours. The effect of bulk capillary number on drainage and imbibition was deduced by a comparison of the results from UoE exp. 2 and 5 which used flowrates of 20 and 80 µl min⁻¹, respectively, and 5 MPa injection pressure (Table 1).

The second type of experiment (from now on referred to as the ‘dry rock experiment’; Table 1) used synchrotron radiation (Diamond Light Source, I12-JEEP tomography beamline) to capture the time-resolved displacement of H₂ by brine in a dry, H₂-saturated rock. This experiment served as a base of comparison to the displacements of H₂ in wet, brine-saturated rock (UoE experiments).

All experiments used a bespoke x-ray transparent core holder for a 5 mm diameter rock core,
### Table 1: Overview over experiments

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Type of x-ray source</th>
<th>Description</th>
<th>Sample</th>
<th>H₂/brine injection ratio(s)</th>
<th>Flowrate (µl min⁻¹)</th>
<th>Injection Pressure (MPa)</th>
<th>Confining Pressure (MPa)</th>
<th>Pore volumes injected</th>
<th>Repetitions of experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>UoE exp. 1</td>
<td>laboratory</td>
<td>Primary drainage and imbibition in non-steady state displacements of H₂ and brine</td>
<td>1</td>
<td>-</td>
<td>20</td>
<td>7</td>
<td>9</td>
<td>10</td>
<td>1 entire repetition, 1 repetition on drainage only</td>
</tr>
<tr>
<td>UoE exp. 2</td>
<td>laboratory</td>
<td>Primary drainage and imbibition in non-steady state displacements of H₂ and brine</td>
<td>1</td>
<td>-</td>
<td>20</td>
<td>5</td>
<td>9</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>UoE exp. 3</td>
<td>laboratory</td>
<td>Primary drainage and imbibition in non-steady state displacements of H₂ and brine</td>
<td>1</td>
<td>-</td>
<td>20</td>
<td>2</td>
<td>9</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>UoE exp. 4</td>
<td>laboratory</td>
<td>Simultaneous, steady state injections of H₂ and brine</td>
<td>1</td>
<td>1:4, 1:1, 4:1</td>
<td>20</td>
<td>5</td>
<td>9</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>UoE exp. 5</td>
<td>laboratory</td>
<td>Primary and secondary drainage and imbibition in non-steady state displacements of H₂ and brine</td>
<td>1</td>
<td>-</td>
<td>80</td>
<td>5</td>
<td>9</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>UoE exp. 6</td>
<td>laboratory</td>
<td>Non-steady state displacements of N₂ and brine</td>
<td>1</td>
<td>-</td>
<td>20</td>
<td>5</td>
<td>9</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>UoE exp. 7</td>
<td>laboratory</td>
<td>H₂ stability</td>
<td>1</td>
<td>-</td>
<td>80</td>
<td>5</td>
<td>9</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>Dry rock</td>
<td>synchrotron</td>
<td>Non-steady state, brine injection into dry, H₂ saturated rock</td>
<td>2</td>
<td>-</td>
<td>5</td>
<td>5</td>
<td>10</td>
<td>10</td>
<td>-</td>
</tr>
</tbody>
</table>
which was a scaled-up version of the cell described by Fusseis et al. (2014). In UoE experiments a carbon-fibre reinforced PEEK pressure vessel was used to permit good x-ray transparency. The dry rock experiment used an aluminium pressure vessel to comply with the health and safety requirements at Diamond Light Source. The specifications of the pressure vessels of PEEK and aluminium were engineered with safety factors of 2 times or more over and above the maximum applied confining pressure (10 MPa; Table 1).

Rock cores for the experiments were obtained by diamond drill coring with a water-flushed chuck, followed by preparation of the core ends by grinding on a lathe. Experiments used a set of four high-pressure pumps (Cetoni Nemesys™, flowrate range 0.072 nl s⁻¹ to 13.76 ml s⁻¹): One for the injection of H₂, one for the injection of brine, one to hold the backpressure and one for the confining pressure (Fig. 1). A bespoke manifold system composed of high-pressure 1/8” and 1/16” 316 stainless steel and 1/16” PEEK tubing (Swagelok, Top Industrie and Cole Parmer, respectively) connected the pumps to the core-flood cell (Fig. 1). Additional pressure transducers (ESI Technology; accuracy 0.1% full-scale) were coupled to the flow system at the inlet and outlet to allow for higher precision pressure monitoring than was possible using the integral pressure gauges in the syringe pumps. Cyclic H₂ and brine injections used a Clashach outcrop sample without further cleaning of 4.7 mm diameter and a relatively long length of 54-57 mm to avoid the influences of capillary end effects. To prevent leakage of H₂ into the confining fluid, the rocks were jacketed in aluminium foil and poluolefin heatshrink tubing and sealed with silicone adhesive between the conical-ended pistons within the pressure vessel. In UoE experiments, a water-wet rock was first saturated with brine (0.5 M CsCl) at a flow rate of 70 µl min⁻¹. Afterwards, H₂ was injected (drainage) into the brine-saturated rock at flow rates of 20-80 µl min⁻¹, based on desired capillary-regime \( N_C \) of 1.7-6.8×10⁻⁸ (The viscosity of H₂ is 9.01 µPa s at 298K and 4.7 MPa and the IFT between H₂ and water is 72.6 mN m⁻¹ at 298K and 5 MPa). Subsequently, the brine was reinjected (imbibition) at flow rates of 20-
Figure 1: Experimental setup showing the manifold system that connected the X-ray transparent pressure vessel to a set of four high-pressure Cetoni Nemesys™ pumps: one to inject H\textsubscript{2}, one inject brine, one to maintain backpressure and one to maintain confining pressure. The materials for the connections were 316 stainless steel (black), HPLC (green) and PEEK or carbon fibre reinforced PEEK (blue). The pressure vessel consisted of carbon fibre reinforced PEEK in UoE experiments and of aluminium in the dry rock experiment (see text).

Pressure and flow rate control was achieved with the Q-mix software.

80 µl min\textsuperscript{-1}, resulting in $N_C$ of $2.35\text{-}9.45\times10^{-6}$ (using the same IFT between H\textsubscript{2} and water of 72.6 mN m\textsuperscript{-1} at 5 MPa and 298 K\textsuperscript{49,50} and a viscosity of 1.247 Pa s at 5 MPa that was estimated from the reported 1.2503 Pa s and 1.233\times10^{-3} Pa s at 0.1 MPa and 25 MPa, respectively, and 298 K\textsuperscript{51}). The $N_C$ the N\textsubscript{2} experiment was $3.5\times10^{-8}$ (using an IFT of 73 mN m\textsuperscript{-1} between N\textsubscript{2} and water 1t 298K and 10 MPa\textsuperscript{35} and a viscosity of $1.89\times10^{-5}$Pa s at 5 MPa and 295K\textsuperscript{48}). Each injection used ten pore volumes to ensure completely flushing of the sample cores with the injected fluid.

In the dry rock experiment, H\textsubscript{2} was directly injected into a dry rock at a flow rate of 70 µl min\textsuperscript{-1}. Subsequently, the brine (2 M KI) was injected at a flow rate of 5 µl min\textsuperscript{-1}, resulting in $N_C$ of $5\times10^{-7}$ (using the same IFT between H\textsubscript{2} and water of 72.6 mN m\textsuperscript{-1} at 5 MPa and 298 K\textsuperscript{49,50} and a viscosity of $1.07\times10^{-3}$Pa s for 0.6 M KI and 293 K\textsuperscript{42}).
The combined application of an x-ray transparent core holder and µCT allowed the visualization of the fluid saturation distributions at pore scale at each injection step. The difference in the x-ray attenuation coefficient of the fluids (H₂ and 0.5 M CsCl/2 M KI) provided an excellent contrast between the two fluid phases and the rock on the acquired µCT images, combined with the respective radiation energy in the two different laboratories. 3D volumes were acquired from the lower central portion of the sample to avoid the impact of capillary end effects on fluid saturation. For the UoE experiments, image acquisition used a µCT instrument built in-house at the University of Edinburgh, comprising a Feinfocus 10-160 kV reflection source, a Micos UPR-160-air rotary table and a Perkin-Elmer XRD 0822 1 MP amorphous silicon flat panel detector with a terbium doped gadolinium oxysulfide scintillator. Data acquisition software was developed in-house. The following settings were used for UoE experiments: 120 keV, 16 W, 2 seconds exposure time, 1200 projections and 2 frames per stop. The voxel size was 5.4 μm³. In the dry rock experiment, time-resolved imaging of the H₂ and brine displacement processes was achieved by means of a 65 keV monochromatic beam detected by a high-resolution imaging camera with optical module 2 (PCO.edge 5.5, 7.91 x 7.9 μm/pixel with FoV 20 mm x 12 mm) using 17-25 milliseconds exposure time and 900 projections. The voxel size was 7.9 μm³.

2.2 Image analysis

Tomographic reconstructions were undertaken by filtered back projection using Octopus 8.9 on a GPU accelerated workstation. All subsequent image processing and analysis of tomographic data was performed using Avizo Version 9.1.1 (FEI, Oregon, USA). Data from UoE experiments were processed using a non-local means filter. Processing of the dry rock experiment used a combination of median filter and unsharp mask to reduce image noise. Segmentation of UoE experiment data used a global threshold on the 2D greyscale image histogram, and encompassed two phases. In the water-saturated scans, water and rock were
treated as two discrete phases. In scans after brine and H$_2$ injections, the H$_2$ was treated as one
phase and the brine and rock as a single separate phase, following protocols of Andrew et al. (2014)$^{32}$. Holes and spots which were at the resolution limit of the data were removed from all
datasets (applied thresholds corresponded to 3$^3$ and 5$^3$ voxels, respectively). Based on the
segmented image of the water-saturated scan in UoE experiments, a pore size distribution was
calculated. The 3D image was separated into individual pores and throats using Avizo’s
‘s’separate objects’ module, which calculates a chamfer distance map of the pore-space and then
applies a marker based watershed algorithm to the distance map to define discrete pore bodies
as catchment basins separated by the watershed which marks the location of pore throats (SI
Figure S1d). Supporting information Figure S1 shows the work flow for the water-saturated
scan.

In scans following brine and H$_2$ injections in UoE experiments, the segmented image was
analysed in 3D using the ‘labeling’ and ‘label analysis’ modules to identify, label and measure
the volume of each H$_2$ cluster. Hydrogen cluster size distributions were compared to the pore
size distribution to evaluate the H$_2$ connectivity and identify trapping mechanisms during brine
imbibition.

2.3 Capillary pressure

Recovered Clashach cores were submerged in 25% w/v NaOH solution (Fisher Scientific) for
2 hours to remove the aluminium foil from the core surface, and rinsed in successive milli-Q
water, acetone and ethanol ultrasonic baths. Subsequently, the cores were cut and squared to
the dimensions of 25 mm, overlapping the µCT visualized rock volumes, and cleaned
ultrasonically with milli-Q water to remove grinding products. Mercury injection capillary
pressure (MICP) was performed on the cleaned cores, using a micromeritics automated
mercury injection equipment (Autopore IV 9500) to estimate the capillary pressure-saturation
relationship and pore size distribution. The pressure range tested was from vacuum to 379 MPa.
3. Results

3.1 Characterization of the pore space

The µCT-evaluated porosity of the Clashach sandstone from the segmented volume of the water-saturated rock was 12.5% to 13.5%, depending on the imaged region of the rock core. The MICP-evaluated pore throat size distribution showed a large number of very small pore throats with <5 µm radius and a small number of small to intermediate size pore throats (>5 to 90 µm) (Fig. 2). The largest pore throat had a radius of 195 µm (Fig. 2). The µCT-evaluated size distribution of the pores evidenced a narrow pore size distribution with comparably small pores with radii <50 µm (Fig. 2, 4a).

3.2 Hydrogen wetting behaviour and stability in UoE experiments

Hydrogen sat in the centre of the pore bodies. Residual brine sat in corners, pore throats (Fig. 3b and c) and, as a subtraction of the water saturated scan from the H₂-and brine filled rock revealed, in thin films around the grains (Fig. 3d). The injected H₂ remained stable within the pore volume under no-flow conditions and at constant pore fluid pressure over a time period of 10 hours which was the maximum experimental duration (SI Fig. S2).

3.2 Effect of pore fluid pressure on hydrogen connectivity, saturation and recovery

Hydrogen saturation during drainage was independent of the pore fluid pressure with 49.8%, 51.7% and 39.7%-52.6% saturation at pore fluid pressures of 2, 5 and 7 MPa, respectively (Fig. 4a-c, f, SI Fig. S3). Hydrogen connectivity during drainage generally showed one large,
Fig. 3: (a) Water-saturated Clashach sandstone with the water shown in black and the rock in different shades of grey. (b) and (c) Brine-saturated Clashash sandstone after injection of $\text{H}_2$. $\text{H}_2$ (black) fills the centre of the pores while the brine (dark grey) remains in corners and small pore throats around grains. (d) and (e) Subtraction of the water-wet scan from the brine-saturated scan after $\text{H}_2$ injection, following registration of the brine-saturated scan after $\text{H}_2$ injection to the water-saturated scan, revealing discontinuous brine thin films around grains. The rim around the Al foil in (d) is caused by continued shrinkage of the Al foil onto the rock during the experiments.
Fig. 4: 3D rendering of $\text{H}_2$ and $\text{N}_2$ clusters with saturation percentages in UoE experiments. Discrete clusters were rendered in colours, where mainly one color marks one large, connected cluster and different colors indicate several, not connected clusters. (a-c) Effect of pore fluid pressure on $\text{H}_2$ clusters and saturation after drainage and after primary imbibition. (a) 2 MPa, (b) 5 MPa and (c, f) 7 MPa, all at a constant flow rate of 20 µl min$^{-1}$ corresponding to capillary numbers of $1.7 \times 10^{-8}$ and $2.4 \times 10^{-6}$, respectively. Large, connected clusters that existed after drainage were broken down to numerous smaller clusters after imbibition, with apparently no clear relationship between $\text{H}_2$ saturation and pore fluid pressure. Experiments were repeated once at 2 and MPa, and at 7 MPa twice for drainage runs and once for imbibition. For experiments at 2 MPa and 5 MPa averages and standard errors for the $\text{H}_2$ saturation are reported. For experiments at 7 MPa, due to the discrepancy in the results, both of the full primary drainage and imbibition experiments are visualized in (e) and (f). (d) Effect of cyclic injections on $\text{H}_2$ clusters and saturation: Averages and standard errors of the $\text{H}_2$ saturation after primary and secondary drainage, and after primary and secondary imbibition, all at 5 MPa pore fluid pressure and a flow rate of 80 µl min$^{-1}$ corresponding to a capillary number of $9.4 \times 10^{-6}$. (e) Nitrogen clusters and saturations during drainage and imbibition at 5 MPa pore fluid pressure and a flow rate of 20 µl min$^{-1}$. For the full display of the results see SI Fig. S3 and SI Fig S4.
connected cluster at all pore fluid pressures except for one out of three images at 7 MPa which showed three large disconnected clusters (Fig. 5, SI Fig. S3). During drainage, the largest H$_2$ cluster had a volume of 1x10$^8$ μm$^3$ at all pore fluid pressures except for the one run at 7 MPa with the disconnected clusters were the largest volume was 7x10$^7$ μm$^3$ (Fig. 5e).

Fig. 5: (a) Pore size distribution as derived from the micro-CT image of the water-wet rock. Hydrogen cluster size distributions after drainage and imbibition in experiments at 20 μl min$^{-1}$ flowrate and pore fluid pressures of 2 MPa (b), 5 MPa (c) and 7 MPa (d), and cumulative pore size and H$_2$ cluster size (CS) distributions at different pore fluid pressures (e), where squares, triangles and rhombi mark the distinct repeat experiments. (f) Hydrogen cluster size distribution after drainage for all experiments and (g) Hydrogen cluster size distribution after imbibition for all experiments. Note the large H$_2$ clusters of ~10$^8$ μm$^3$ that exist after drainage in (b)-(d). A decrease in the biggest cluster volume after imbibition in (b)-(d) along with an increase in the number of small clusters marks the change in H$_2$ structure during the drainage and imbibition processes. Histogram plots in (a)-(d), (f) and (g) used a bin size of 10.
Hydrogen clusters during drainage were at all pore fluid pressures much larger than discrete pores with a maximum volume of $1.3 \times 10^6 \ \mu m^3$ (Fig. 5e, a). Comparing all H$_2$ cluster size distributions during drainage (Figure 5f) reveals that all drainage curves, including two of the distributions at 7 MPa (squares and rhombi), have largely the same distribution, however one of the three distributions at 7 MPa (triangles) is distinct. This outlier experiment corresponds to the experiment showing a lower $S_{nwi}$ (Fig. 4c).

Capillary trapping of H$_2$ during imbibition seemed independent of the pore fluid pressure with 10%, 12% and 4-21% of trapped H$_2$ at 2, 5 and 7 MPa, respectively (Fig. 4a-c,f, SI Fig. S3), corresponding to 20%, 22% and 11-43% of the initially injected H$_2$. During imbibition, large H$_2$ clusters were broken down into smaller clusters (Fig. 5a-d), in line with the visual changes of the H$_2$ clusters (Fig. 4a-c and f). The largest H$_2$ clusters after imbibition remained above the maximum pore size during all experiments except for one experiment at 7 MPa (triangles in Fig. 5g, Fig. 5a), showing that not only was H$_2$ trapped in discrete pore bodies but also as larger H$_2$ ganglia. The break-down of the largest H$_2$ clusters during imbibition caused the number of clusters in the size range log 4 to log 6 $\mu m^3$ to increase while the number of very small clusters of log 2-4 $\mu m^3$ typically decreased (Figs. 5b-d). Comparing all H$_2$ cluster size distributions during imbibition (Figure 5g) shows that the distributions at 2 and 5 MPa are largely the same while the imbibition distributions at 7 MPa are distinct.

Injections of H$_2$ and brine into the same rock volume and at the same flow rates and pore fluid pressures of 2-5 MPa were repeatable with small standard errors between 0.01-0.66% (Fig. 4a and b, Fig. 5b and c). At 7 MPa very distinct $S_{nwi}$ and $S_{nwr}$ were measured (Fig. 4c and f); During drainage the standard error was 4.8% at an average H$_2$ saturation of 47.4%. The standard error during imbibition was 8.5% at an average saturation of 12.9%. The pressure differences between inlet and outlet during these experiments were within the error of the pressure sensors.
of 0.1% full-scale.

3.3 Effect of hydrogen/brine injection ratio on hydrogen connectivity and saturation

We studied the effect of the H$_2$/brine injection ratio on the H$_2$ saturation in order to evaluate the effect of H$_2$ injection into hydrodynamic aquifers, and to evaluate what happens in the far field, where fluids will be moving together.

The results showed that the H$_2$ saturation and H$_2$ interconnected pore volume increased with increasing H$_2$/brine injection ratio from 32.6% at 4 µl min$^{-1}$ H$_2$ plus 16 µl min$^{-1}$ brine to 43.2% at 16 µl min$^{-1}$ H$_2$ plus 4 µl min$^{-1}$ brine (Fig. 6).

The H$_2$ clusters in simultaneous injection experiments occupied many of the same pore spaces as the clusters after H$_2$ in the non-steady state experiments at the same pressure and total flowrate (Fig. 4b, Fig. 6, SI Fig. S5), and even at the lowest H$_2$ brine injection ratio of 4 µl min$^{-1}$ H$_2$ plus 16 µl min$^{-1}$ brine, the H$_2$ clusters were large, and spanning multiple pores. The percolation threshold, i.e. one connected path from inlet to outlet, was apparently only reached at 100% H$_2$ injection (Fig. 4b vs. Fig. 6, SI Fig. S5). The pressure...
differences between inlet and outlet during the simultaneous injection experiments were up to 0.05 MPa.

The H₂ cluster volume distributions were similar at different H₂:brine injection ratios (Fig. 7a). However, with increasing ratio the smallest H₂ clusters of volume ~log 2 μm³ decreased in number while the number of intermediate size (log 2.5 to log 6.25 μm³) H₂ clusters and the volume of the biggest cluster increased (Fig. 7a), confirming observations of increasing H₂ saturation and connectivity with increasing injection ratio (Fig. 6).

3.4 Effect of flowrate on hydrogen saturation and recovery

At constant pore fluid pressure of 5 MPa, increases in the flowrate during drainage from 20 µl min⁻¹ to 80 µl min⁻¹, corresponding to bulk $N_C$ of 1.7 x 10⁻⁸ to 6.8x10⁻⁸, respectively, decreased the H₂ saturation from to 51.7% to 47.7% (Figure 4b and d). Correspondingly, increases in the brine flowrate during imbibition from 20 µl min⁻¹ to 80 µl min⁻¹, corresponding to bulk $N_C$ of 2.4x10⁻⁶ and 9.4x10⁻⁶, respectively, reduced the $S_{nwt}$ from 11.5% to 7.2% (Fig. 4b and d).

In line with this, the H₂ cluster size distributions at the two flowrates showed that larger clusters were mobilized at 80 µl min⁻¹ (maximum cluster sizes of log 6.25 μm³ at 80 µl min⁻¹ vs. log 6.75 μm³ at 20 µl min⁻¹; Fig. 7b). At both flowrates the largest H₂ clusters were still bigger than...
the largest pore of $<\log 6 \mu m^3$ (Fig. 7b vs. Fig 6a), indicating that H$_2$ was trapped also as larger ganglia.

3.5 Secondary drainage and imbibition

Secondary drainage and imbibition did not significantly change the H$_2$ saturation (47.9% and 7.0%) compared to primary drainage and imbibition (47.6% and 7.3%), based on results at 5 MPa and 80 $\mu l$ min$^{-1}$ flowrate (SI Fig. S4, Fig. 4d-e).

3.6 Dry rock experiment

In the dry-rock experiment, the brine entered the H$_2$-filled dry rock via piston-like displacement, (Fig. 8b), eventually recovering the H$_2$ entirely (Fig. 8d). Before all H$_2$ was recovered, there was an intermediate stage where previously brine-filled pores (Fig. 8b) showed several very small H$_2$ bubbles (Fig. 8d).

3.7 Comparison to nitrogen

The N$_2$ saturation was similar to the H$_2$ saturation during drainage (48.7% vs. 51.7 ± 0.66%, respectively) but N$_2$ saturation after brine imbibition was much higher (33.9% vs. 11.5 ± 0.64%, respectively; Fig. 4e, SI Fig. S6). The $N_e$ of H$_2$ and N$_2$ during drainage were $1.7x10^{-8}$ and $3.5x10^{-8}$, respectively.

4. Discussion

4.1 Pore space

The $\mu$CT-evaluated porosity of the Clashach sandstone from the segmented volume of the water-saturated rock of 12.5-13.6% was within the range of the published porosities of 11.1-14.4% for Clashach sandstone$^{42-44}$. The distributions of pore size and pore throat size as evaluated by $\mu$CT and MICP, respectively, suggested that mostly small pores of $<50 \mu m$ radii were joined by very small throats of $<5 \mu m$ radii with a few small to intermediate size throats.
Fig. 8. The dry-rock experiment summarized. (a) H₂-saturated, dry rock, (b) scan during brine imbibition shortly after appearance of the first brine in the rock, (c) scan during brine imbibition after 115 minutes, with several small, isolated H₂ bubbles inside pore bodies (d), and (e) brine-saturated rock after two hours of imbibition showing 100% recoverability of H₂.

of >5 to 90 µm radii in between (Fig. 2). The largest pore throat of 195 µm radius was probably measured at the surface of the rock core where the drilling process affected the pore space. The pore throat distribution for our Clashach sandstone sample was very similar to the pore throat distribution for Berea sandstone. Compared to the pore throat distributions for Bentheimer
sandstone and Doddington sandstone\textsuperscript{54}, our Clashach sandstone sample showed smaller pore throat sizes. Limestones generally show a wider pore throat size distributions than sandstones\textsuperscript{54}.

4.2 \textit{H}_2 flow behaviour and trapping mechanisms

Hydrogen behaved as a non-wetting phase, filling the centre of the pores, with residual brine in the pore corners and throats (Fig. 3b and c), indicating a water wetting system. The largest \textit{H}_2 cluster was much larger than discrete pores at any pore fluid pressure during drainage (Fig. 5), indicating a good connectivity of the \textit{H}_2\textsuperscript{55}. Hydrogen trapping occurred via snap-off of \textit{H}_2 ganglia (Fig. 9). Snap-off competes with piston-like, i.e. pore-filling, displacement during the displacement of a non-wetting fluid by a wetting fluid in porous media\textsuperscript{21}, and is known as the swelling of water in the corner layers of a pore throat during water invasion in water-wet porous rocks until the threshold capillary pressure is exceeded, resulting in spontaneous filling of the throat with water and disconnection of the non-wetting phase which can lead to trapping\textsuperscript{21}. Brine films around grains were not directly visible in the tomographic images (Fig. 3b and c).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig9.png}
\caption{Example of a snap-off event. (a) Labelled \textit{H}_2-filled volume after drainage (orange), spanning over several pores, and total pore space (transparent blue) showing one large interconnected \textit{H}_2-filled pore volume. (b) Labelled \textit{H}_2-filled volume after brine imbibition (different coloured shades) and the total pore space (transparent blue) showing several, not connected \textit{H}_2 ganglia and the snapped-off \textit{H}_2 droplet (cobalt blue) in the centre, left hand side. (c) Pore body visualisation of the same volume.}
\end{figure}
but were revealed by subtraction of the water-saturated scan from the brine-saturated scan after H$_2$ injection, following the registration of the brine-saturated scan after H$_2$ injection to the water-wet scan (Fig. 3d and e). Figures 3d and 3e suggest that brine films were discontinuous and very thin. When H$_2$ was injected into a dry rock, 100% of the injected H$_2$ could be recovered (Fig. 8e) which substantiated the theory that sub-resolution brine films around grains and snap-off of H$_2$ ganglia caused decreased H$_2$ recovery in experiments using an initially brine saturated rock (UoE experiments). The occurrence of several very small H$_2$ bubbles in the dry-rock experiment (Fig. 8d) indicated Roof snap-off$^{56}$ of H$_2$ ganglia.

4.3 Effect of pore fluid pressure and hydrogen/brine injection ratio

We observed no dependence of the H$_2$ saturation during drainage on pore fluid pressure, considering that 2 out of 3 experiments at 7 MPa showed the same the same H$_2$ saturation of $\sim$50 % as at 2 and 5 MPa (Fig. 4a-c,f, and SI Fig. S3). The one experiment at 7 MPa which had only 39.7% H$_2$ saturation (Fig. 4c, SI Fig. S3 and blue triangles in Fig. 5f) did also not have the same H$_2$ cluster size distribution as the remaining experiments (Fig. 5f), despite using the same experimental settings as for all other experiments at 7 MPa, and the log archives of the pore fluid pressures and injected volumes revealed no abnormalities. A shift in the distribution of cluster sizes can indicate a change in wettability, regardless of the measured H$_2$ saturation. Yet, as two of the results at 7 MPa showed a similar distribution as at the other pressures, it seems likely that this experiment is an outlier. The experiment was acquired after a filament change on the µCT apparatus, which implied that a slightly different part of the same rock core was imaged (13.6% vs. 12.5% porosity). Yet, in principle this should not have affected the results significantly, and subsequent experiments did return to show $\sim$50% H$_2$ saturation, e.g. the H$_2$ stability experiment (SI Fig. S2).

The observed constant drainage H$_2$ saturations with increasing pore fluid pressures from 2 to 7 MPa are in line with a lack of a dependence of the H$_2$ wettability on pressure increases from 2-
10 MPa in Berea and Bentheimer sandstone\(^{18}\), with only very small increases of \(\sim 3\text{-}6^\circ\) in the H\(_2\) contact angles at pressure increases from 2 to 7 MPa in Basalt\(^{21}\) and clay\(^{24}\) and quartz\(^{19}\), and with a previous findings of no change in the characteristic trapping curves for CO\(_2\) and N\(_2\) at a wide range of pressure and temperature conditions\(^{35}\). The general anticipation of an increase in gas saturation with injection pressure\(^{57,58}\) may still be valid over pressure ranges larger than the one investigated here. At unchanged wettability, the \(S_{\text{nwi}}\) is controlled by the capillary pressure which in turn is controlled either by the fractional flow (during simultaneous injection) or by the viscous force pressure drop (during single fluid phase injection). Thus, the independence of the \(S_{\text{nwi}}\) from the pore fluid pressure indicates that the viscous pressure drop is not being significantly altered by the changing pressure, e.g., the H\(_2\) viscosity change is not having a major impact on the force required to drive flow. Significant loss of H\(_2\) from the gas phase at higher pressures by dissolution into the brine is precluded by the low solubility of H\(_2\) of \(\sim 0.02\) mol kg\(^{-1}\) at 2.5 MPa\(^{59}\). The H\(_2\) stability experiments showed that H\(_2\) saturation at 5 MPa did not change over a time period of ten hours (49.55\% at time zero vs. 49.53\% ten hours after; SI Fig. S2), evidencing a stable result and no H\(_2\) loss by dissolution.

Looking at the \(S_{\text{nwr}}\) data only (Fig. 4a-c,f), there was no clear dependency on pore fluid pressure during imbibition. Any change may, however, have been masked by the high variation between the two results at 7 MPa (4-21\% Fig. 4c and f). Considering that the experiment at 7 MPa with the low \(S_{\text{nwi}}\) of 40\% could be identified as an outlier (see the discussion in the beginning of section 4.3, and Fig. 5f, blue triangles) and that the \(S_{\text{nwr}}\) is a function of the \(S_{\text{nwi}}\) where a lower \(S_{\text{nwi}}\) will tend to overestimate recovery\(^{54,60}\), we may disregard the \(S_{\text{nwr}}\) of 4\%. The large increase in trapped H\(_2\) in the second full primary drainage and secondary imbibition experiment at 7 MPa (Fig. 4f) was probably due to the poorer intial H\(_2\) connectivity\(^{60}\). The H\(_2\) cluster size distribution for this experiment showed an increase in the number of intermediate size clusters compared to the other experiments (Fig. 5g, darkyellow squares), without however shifting the
cluster distribution, suggesting no wettability change. This indicates that variation in one or more of the other thermophysical properties – density, viscosity, or IFT – have resulted in the impact on the pore scale fluid configuration (Figure 10). Meanwhile, a poorer initial H$_2$ connectivity was not confirmed by the third repetition of primary drainage at 7 MPa (SI Fig. S3g). More experiments at 7 MPa are needed to confirm the result of increased trapping at higher pore fluid pressures.

![Graph showing density, viscosity, and interfacial tension of hydrogen versus depth](image)

**Fig. 10:** Density (green line), viscosity (red line), and interfacial tension (blue line) of hydrogen versus depth (Hassanpouryouzband et al. 2021).  

Given a hydrostatic gradient of ~10 MPa/km an increase of the $S_{swr}$ with increasing pore fluid pressure, as suggested by the second experiment at 7 MPa (Fig. 4f), would indicate that deeper aquifers are less favourable for H$_2$ storage operations. However, unlike our non-steady state experiments which showed barely any pressure difference between inlet and outlet, in a real H$_2$ storage operation, the well pressure is significantly higher than the reservoir pressure and the brine is not injected, but naturally flowing into previously H$_2$-saturated rock when the H$_2$
is recovered—again due to a pressure difference. Our displacement study results are hence applicable to the fringe of the H$_2$-saturated zone, only, where pressure differences are very small. A decreased H$_2$ recovery with depth would not align well with other criteria for an economical and safe H$_2$ storage operation, such as a lower cushion gas requirement with elevated depth and reduced risks for H$_2$-linked microbial activity at higher depths due to higher temperatures.

The pressure/depth effect on our results can be further related to the variation of key pore-scale displacement parameters for H$_2$ with depth (Fig. 10): The IFT of H$_2$ reduces with depth whereas the H$_2$ viscosity increases, both of which in theory should augment the displacement of H$_2$ with water and reduce the $S_{nwr}$.$^{62, 63}$ However, increased $S_{nwr}$ with decreasing IFT and increasing viscosity has also been demonstrated$^{64}$ which may be due to a simultaneously increased likelihood of unstable displacement/non-uniform fronts$^{10, 65}$ during both drainage and imbibition processes at decreasing IFT and increasing viscosity, based on the augmenting effect of both parameters on $N_C$ (Eq. 1). Such unstable displacement processes at higher pore fluid pressures, addition to a variation in the thickness of the brine thin films with pressure, may explain the decrease in interconnected H$_2$-filled pore volume from one large cluster at 2-5 MPa to three clusters at 7 MPa and have lead to increased snap-off and trapping during imbibition (Fig. 4f).

The $S_{nwr}$ of 10-21% was significantly less than the previously reported H$_2$ $S_{nwr}$ of 41% for a sandstone under ambient conditions.$^{40}$ As mentioned previously, the short length rock sample in Jha et al. (2021)$^{40}$ suggests that their results were affected by capillary end effects.$^{46}$ However, the applied the relatively high bulk brine $N_C$ of 2.4x10$^{-6}$ may have mobilised more residual H$_2$ than under strict capillary regime conditions.

During simultaneous injection of H$_2$ and brine, which may be representative of H$_2$ injection into hydrodynamic aquifers or simulate the far field conditions, H$_2$ saturation and H$_2$
interconnected pore volume increased with increasing H$_2$/brine injection ratio (Fig. 6). This indicated that a lower brine flow is favoured over high flow environments in terms of optimising the H$_2$ storage operation. The structure was apparently not percolating in any of the simultaneous injection experiments as opposed to during 100% H$_2$ injection (Fig. 6 vs. Fig. 4b), yet considering significant pressure differences of up to 0.05 MPa between inlet and outlet in simultaneous injection experiments which were not observed in experiments injecting 100% H$_2$, the connections between the H$_2$ clusters may have been broken when the injection (and thereby the pressure gradient) was stopped for the scan.

4.4 Effect of capillary number on initial and residual saturation

Classical pore-scale displacement theory predicts little change in residual phase saturation in response to increases in flow rate until $N_C$ exceeds $10^{-6}$-$10^{-5}$. However, for most subsurface reservoirs there will be rapid decreases at $N_C$ of $10^{-4}$ or more, when viscous forces become dominant$^{54}$. The bulk brine $N_C$ applied in this study ($2.4$-$9.4 \times 10^{-6}$) was within the range of little saturation change but exceeded the threshold of $N_C < 10^{-6}$ for which the flow generally is said to be capillary dominated$^{54}$. This may indicate that viscous forces caused a significant effect of $N_C$ on the $S_{nwi}$ in our experiments (Fig. 4b and d), and these forces are likely to be even greater at local scale than at bulk$^{54}$. The H$_2$ cluster size distribution after imbibition at $N_C = 9.4 \times 10^{-6}$ was shifted with respect to the distribution at $N_C = 2.4 \times 10^{-6}$ (Fig. 7b), indicating a change in the wetting behaviour and supporting previous findings of preferential desaturation of larger clusters at higher $N_C$$^{66}$.

We observed a 4% decrease in $S_{nwi}$ in our experiments when bulk $N_C$ was increased from $1.7 \times 10^{-8}$ to $6.8 \times 10^{-8}$ (Fig. 4b and d). Critical nonwetting phase $N_C$ of $2 \times 10^{-8}$ and $10^{-5}$ during imbibition have been reported for water–gas systems and water-oil systems, respectively$^{67}$, indicating that the threshold of $N_C < 10^{-6}$ for capillary dominated flow$^{54}$ is not rigid. However, considering reported increases in the H$_2$ saturation after drainage with increasing $N_C$ from
7.7×10⁻⁷ to 7.7×10⁻⁵, and acknowledging the small observed difference in $S_{nwi}$, we cannot exclude that the effect of flow rate was down to experimental variability.

### 4.5 Comparison to nitrogen

The N₂ saturation was comparable to the H₂ saturation during drainage at similar $N_c$ of 1-3×10⁻⁸ but the $S_{nwr}$ after imbibition was ~20% higher for N₂ than for H₂ (Fig. 4b and e). Using N₂ as a proxy for H₂ in experimental drainage and imbibition studies is hence not advisable. Considering the high degree of N₂ trapping, the use of N₂ as a cushion gas for H₂ storage operations which could reduce operational costs seems favourable. Our results are lower than a reported 64% initial N₂ saturation during drainage and 43% residual N₂ saturation during brine (200 g/L NaI +15 g/L CaCl₂) imbibition in a Berea sandstone (20-22% porosity) at 5.5 MPa and 20°C, and higher than 43% N₂ saturation during drainage in a Bashijiqike tight sandstone (5.6% porosity) at 8 MPa and ambient temperature. The trend in the differences of the N₂ saturation in the above studies follows the same trend as the differences in the porosities of the studied sandstones, with the Clashach sandstone (14% porosity) being intermediate between the two other rocks. This indicates that porosity differences between the different rock types applied in the above experiments defined the observed N₂ saturations, yet differences in the pore throats dimensions may equally have contributed or caused this. Hence $S_{nwi}$ and $S_{nwr}$ depend strongly on (the local conditions within) each rock, and these rock type/local effects may mask any effect of injection conditions. However, trends in the rock-specific behaviour will be controlled by pressure and flow conditions. It follows from this that any rock selected for H₂ storage operations has to be very well characterized, in particular with respect to porosity, tortuosity and capillary pressure curves.

### 4.6 Suitability of the Clashach sandstone for hydrogen storage
It has been postulated that the low viscosity of H$_2$ will cause the gas to travel swiftly, making it little suitable for displacing brine$^{10}$ and causing low H$_2$ injectivity. In this work, we showed that from an injectivity and recovery perspective, untreated Clashach sandstone is suitable for underground H$_2$ storage. However, sandstones aged by exposure to humic acids may be more suitable analogue rocks for experimental investigations of H$_2$ storage in porous media$^{19}$. Considering that aging has previously been shown to alter the wettability of H$_2$ brine-quartz systems from highly water-wet toward intermediate-wet$^{19}$ the stated H$_2$ saturations for our untreated outcrop Clashach sandstone are expected to increase during drainage and decrease during imbibition, further the increasing suitability for H$_2$ storage.

5. Conclusion

In this work, a prima facie examination of H$_2$ flow and displacement processes in porous rock was carried out as a function of capillary numbers of 1.2-6.8x10$^{-8}$ for H$_2$ and 2.4-9.5x10$^{-6}$ for brine, and of pore fluid pressures between 2-7 MPa. Results showed no clear relation between pore fluid pressure and H$_2$ saturation with ~50% of the pore space saturated with H$_2$ during drainage at all pressures, and 20%, 24% and 43% of the initial H$_2$ trapped at 2, 5 and 7 MPa, respectively, during imbibition at a capillary number of 2.4x10$^{-6}$, indicating that higher pressure, i.e. deeper reservoirs are less favourable for H$_2$ storage. Injection of brine at higher capillary numbers reduced capillary trapping and increased H$_2$ recovery. Hydrogen recovery was distinct from N$_2$ recovery, suggesting that N$_2$ is a poor proxy for H$_2$. Based on these results, we recommend more shallow, lower pressure sites for future H$_2$ storage operations in porous media. Future work should aim to measure the influence of pressures above 7 MPa, elevated temperatures and rock aging on H$_2$ and brine displacement processes at a range of different capillary numbers. Dynamic experiments using synchrotron light sources are recommended to examine displacement mechanisms closely.
Author Contributions

The experimental kit was built by Butler and Thaysen. Experiments were carried out by Thaysen, Butler, Hassanpouryouzband, Freitas. Alvarez-Borges, Atwood and Humphreys were the supporting beamline scientists during the experiments at Diamond Light Source. Image reconstruction and tomographic analysis was carried out by Thaysen. Interpretation of the results was by Thaysen, Butler, Hassanpouryouzband, Krevor and Heinemann. The manuscript was written by Thaysen with review by Butler, Krevor Heinemann, Hassanpouryouzband, Freitas and Edlmann. 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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Supplementary Information

Pore-scale imaging of hydrogen displacement and trapping in porous media

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SI Figure S1: Image processing workflow for UoE experiments. (a) The image after reconstruction and filtering. (b) The image after segmenting using a global threshold. (c) The outer part of the rock core touching the Al foil was removed through application of a mask, and a chamfer distance map of the pore space was calculated by assigning each voxel the distance from it to the nearest pore wall. (d) This was then used to separate the pore space into individual pores by calculating the water-shed basins of the distance map.
SI Figure S2: H₂ stability at 7 MPa injection pressure and a flow rate of 20 µl min⁻¹ (capillary number 2*10⁻⁸) at time zero (a) and after ten hours (b). Red circles indicate subtle differences in the hydrogen filled pore volume after ten hours. The difference in the hydrogen saturation for the total scanned rock volume was within error at 49.55% and 49.53% for time 0 and after ten hours, respectively.
SI Figure S3: Enlarged view of 3D renderings of H\textsubscript{2} with saturation percentages in UoE experiments. Discrete clusters were rendered in colours, where mainly one colour marks one large, connected cluster and different colours indicate several, not connected clusters. (a-d) Effect of pore fluid pressure on H\textsubscript{2} clusters and saturation after drainage and after primary imbibition. (a) 2 MPa, (b) 5 MPa and (c-e) 7 MPa, all at a constant flow rate of 20 µl min\textsuperscript{-1} corresponding to capillary numbers of 1.7\times10\textsuperscript{-8} and 2.4\times10\textsuperscript{-6}, respectively. Experiments were repeated once. For experiments at 2 MPa and 5 MPa averages and standard errors for the H\textsubscript{2} saturation are reported. For experiments at 7 MPa, due to the discrepancy in the results, both results are visualized (c-d).
SI Figure S4: Cyclic H₂ injection into Clashach sandstone at 5 MPa and 80 µl min⁻¹ corresponding to a capillary number of 9.4x10⁻⁶, showing no significant differences in H₂ saturation and H₂ connectivity after primary drainage and imbibition as compared to after secondary drainage and imbibition.
SI Figure S5: Comparison of the distribution of the H₂ clusters in the pore space between simultaneous H₂ and brine injection experiments (a-c) and the two repetitions of the non-steady state H₂ injection (d) and (e), all at 5 MPa and a total flow rate of 20 µl min⁻¹.
SI Figure S6: Nitrogen clusters and saturations during drainage and imbibition at 5 MPa pore fluid pressure and a flowrate of 20 µl min$^{-1}$