Hydrogen flooding of a coal core: effect on coal swelling

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Key points

- Hydrogen geo-storage in deep coal seams is feasible from a flooding and adsorption perspective
- Hydrogen flooding does not cause any measurable coal swelling under deep coal seam conditions
- Coal permeability is not affected by hydrogen flooding under deep coal seam conditions

Abstract

Hydrogen is a clean fuel which has the potential to drastically decarbonize the energy supply chain. However, hydrogen storage is currently a key challenge; one solution to this problem is hydrogen geo-storage, with which very large quantities of $\text{H}_2$ can be stored economically. Possible target formations are deep coal seams, and coal permeability is a key parameter which determines how fast $\text{H}_2$ can be injected and withdrawn again. However, it is well known that gas injection into coal can lead to coal swelling, which drastically reduces permeability. We thus injected $\text{H}_2$ gas into a coal core and measured dynamic permeability, while imaging the core via x-ray microtomography at reservoir conditions. Importantly, no changes in coal cleat morphology or permeability were observed. We conclude that $\text{H}_2$ geo-storage in deep coal seams is feasible from a fundamental petro-physical perspective; this work thus aids in the large-scale implementation of a hydrogen economy.
1. Introduction

Hydrogen is a clean fuel which has the potential to completely decarbonize the energy supply chain (e.g. compare Hanley et al. 2018; Tarkowski 2019). Hydrogen is currently stored in high-pressure surface tanks or in chemical form (e.g. as ammonium or hydride, Zhang et al. 2016a; Berta et al., 2018); however, these storage options provide only limited storage space. An alternative, underground H$_2$ storage (UHS), can store drastically more H$_2$, and can thus potentially be operated in a much more economical way. One example is H$_2$ storage in underground salt caverns – a method used for at least 30 years now (Tarkowski and Czapowski 2018). Such salt caverns, however, are not abundant or geographically widespread. It is thus of high interest to evaluate additional geologic formations with respect to their H$_2$ storage potential (Pan et al. 2021). One target formation of interest are deep coal seams, which can adsorb and thus store substantial amounts of H$_2$ (Iglauer et al. 2021; Keshavarz et al. 2021). It is, however, vital that H$_2$ can be injected and withdrawn again in a fast, efficient manner. This
essentially means that coal permeability must be sufficiently high so that H$_2$ gas flow is sufficiently rapid. This is for instance not the case for CO$_2$ geo-sequestration projects targeting coal seams, and it is well known that CO$_2$ injection leads to a dramatic loss of coal permeability due to coal swelling (e.g. Pan et al. 2010; Zhang et al. 2016b). It is therefore of fundamental importance to examine coal swelling behaviour when coal is exposed to pressurized H$_2$ gas, and how this is related to coal permeability.

We thus imaged H$_2$ gas injection into a coal core plug via high resolution in-situ 3D x-ray micro-tomography (µCT) at true reservoir conditions, and measured how coal cleat morphology and the associated coal permeability changed due to H$_2$ exposure. This is presented and discussed in detail below.

2. Experimental Procedure

A deep coal seam at a depth of approximately 250 m was simulated in the laboratory. Bituminous coal (from Morgantown, West Virginia, USA; supplied by Wards Scientific US; vitrinite reflectance = 0.86) was selected and small core plugs (5 mm diameter and 10 mm length) were drilled. The coal had a porosity of 3.7% (measured via Helium porosimetry using a CoreLab UltraPoroPerm-910 instrument), and the coal was also thoroughly analysed via XRD (performed with a RAYONS X-Rays instrument equipped with a cobalt K$_\alpha$ radiation source at 40 kV and 40 mA), TGA (using a PerkinElmer-Thermogravimetric Analyzer-TGA 4000), ATR-FTIR (with a PerkinElmer-Spectrometer 100-FT-IR instrument), BET (performed at 77 K; to measure specific surface area, pore volume and average pore size of the coals using a Tristar II
3020 instrument) and ultimate and proximate analysis. Results are shown in Table 1 and in the supplementary file.

<table>
<thead>
<tr>
<th>Proximate analysis (wt %)</th>
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<tbody>
<tr>
<td>Inherent Moisture</td>
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<tr>
<td>--------------------</td>
</tr>
<tr>
<td>Bituminous</td>
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<table>
<thead>
<tr>
<th>Ultimate analysis (wt %)</th>
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<tbody>
<tr>
<td>Carbon</td>
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<tr>
<td>----------------</td>
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<tr>
<td>Bituminous</td>
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<table>
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<tr>
<th>Maceral Composition (volumetric, %)</th>
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<tr>
<td>Vitritine</td>
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<tr>
<td>----------</td>
</tr>
<tr>
<td>Bituminous</td>
</tr>
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</table>

Table 1: Proximate and ultimate analysis results and maceral composition.

The specific surface area of the coal was 0.34 m²/g, average pore size was 16.38 nm, pore volume was 0.0014 cm³/g and microporoues content was 0.12. The mineral fraction in the coal consisted of 70 wt% quartz and 30 wt% kaolinite; ash composition was 46.5% SiO₂, 33.6% Al₂O₃, 10.9% Fe₂O₃, 2.04% CaO, 0.78 MgO, 1.52% Na₂O, 1.28% K₂O, 1.32% TiO₂, 0.02% Mn₃O₄, 0.17% P₂O₅, 1.09% SO₃, 0.29% Sr, 0.25% BaO, traces of ZnO and 0.05% V₂O₅. Furthermore, CO₂ and H₂ adsorption capacity and diffusion coefficients were measured previously (on separate coal samples) – demonstrating that substantial amounts of H₂ can be adsorbed (~0.1 mole H₂/kg coal at

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3 MPa and 303 K) and that H₂ diffuses relatively quickly through the coal (a H₂ diffusion coefficient of ~1.5 x 10⁻⁸ m²/s was measured for 296 K and 1.3 MPa equilibrium pressure), Iglauer et al. (2021); Keshavarz et al. (2021).

The coal plug was then placed into an x-ray transparent high pressure μCT cell (Iglauer and Lebedev 2018) and vacuumed for 24 hours to remove all air from the system. The temperature was kept constant at 296 K (i.e. isothermal conditions), a pore pressure of 2.758 MPa was applied and overburden stress was raised to 6.205 MPa (i.e. 3.447 MPa effective stress was applied during the whole experiment), and the coal plug was μCT imaged at two high resolutions (1.50 µm and 4.00 µm, using the 3D x-ray microscope VersaXRM500 Xradia-Zeiss). Subsequently, 18000 pore volumes H₂ gas (from BOC, HPG, 99.99 mol% purity) were injected into the plug applying a pressure drop of 0.22 MPa (2.978 MPa inlet pressure and 2.758 MPa outlet pressure). Three high precision syringe pumps (ISCO Teledyne 500D, accuracy 0.1%) were used to apply injection pressure, backpressure and overburden pressure with high accuracy. Dynamic coal permeability was measured during H₂-flooding by measuring the H₂ flow rate through the plug at this constant pressure drop and applying Darcy’s law. H₂ injection was then stopped, and the system was kept at these conditions for 24 hours. The coal core was then μCT imaged again at the same high resolutions in-situ. Note that this μCT resolution is insufficient to resolve the complete pore space in the coal matrix, which can be even of atomic volume, but cleat (= fracture) networks can be reliably imaged (e.g. compare Zhang et al. 2016b,c; Ramandi et al. 2016).

The images were cropped, their image contrast adjusted, and outliers were removed via the application of a median filter, and the subsequent removal of outliers. The removal
of outliers replaces a pixel by the median value of neighbours (radius of 2 pixels here), if the pixels is 50% brighter or darker than the neighbourhood (Schneider et al., 2012). This process was performed for both bright and dark outliers three times, after which the percentage of removed outliers was below 5%. This conservative filtering was performed using Fiji ImageJ (Schindelin et al., 2012). The first and last 100 images were removed from the image stack to avoid the strongest ring artifacts. Darkest pixels were assumed to be void space as H₂ gas has a low x-ray attenuation. 3D void space (cleats) was segmented and counted in 3D using Fiji as well, taking into account integrated density, mean and standard deviation of grey values, minimum, maximum and average grey values, as well as computed centroids and centres of mass within the bounding box (Bolte and Cordelieres, 2006).

3. Results and Discussion

3.1 Coal cleat network morphology evolution

For H₂ geo-storage project assessment it is vital to know how much H₂ can be stored in a reasonable timeframe, and how fast H₂ can be withdrawn again (Pan et al. 2021). Previously, it has been shown that substantial amounts of H₂ can be adsorbed on the coal and storage capacity is thus in principle large (Iglauer et al. 2021). However, it is currently unknown how coal swelling and the associated coal permeability is affected by H₂-exposure; indeed, only very few data are available to assess UHS as a true economic technical option (Zhang et al. 2016a; Pan et al. 2021). Potential changes in the coal cleat network characteristics (before and after H₂ flooding) were thus quantified and compared.
Figure 1. 3D visualizations of the coal phases before (top row) and after (bottom row) H2-exposure. A,D: maceral phase (turquoise); B,E: mineral phase (blue); C,F: cleats (= void space; red).
Figure 2. Cleat size distribution in the coal before and after \( H_2 \)-flooding.

Table 2. Coal cleat network characteristics before and after \( H_2 \) flooding at 296 K, 2.758 MPa pore pressure and 3.447 MPa effective stress.

<table>
<thead>
<tr>
<th>Saturation state</th>
<th>Cleat porosity [%]*</th>
<th>Median cleat volume ([\text{mm}^3])*</th>
<th>Average cleat volume ([\text{mm}^3])</th>
<th>Permeability [mD]</th>
</tr>
</thead>
<tbody>
<tr>
<td>before ( H_2 ) flooding</td>
<td>1.1</td>
<td>(8.79 \times 10^{-8})</td>
<td>(18.8 \times 10^{-8})</td>
<td>0.39</td>
</tr>
<tr>
<td>after ( H_2 ) flooding</td>
<td>1.1</td>
<td>(5.07 \times 10^{-8})</td>
<td>(16.7 \times 10^{-8})</td>
<td>0.39</td>
</tr>
</tbody>
</table>

*measured on the \( \mu \)CT images
Importantly, H$_2$ exposure led to no measurable change in the coal cleat porosity, cleat network morphology or cleat size distribution (compare Figures 1 and 2 and Table 2 where the pore space morphology and the cleat network statistics before and after H$_2$ flooding are summarized). All phase fractions (mineral phase, maceral phase and the cleat system (void space)) remained constant during and after H$_2$-flooding, and fracture nucleation or propagation was not observed. Note that the small changes in Figures 1 and 2 and Table 2 were caused by the natural variation in coal (as the imaged volumes did not exactly overlap). We conclude that H$_2$ gas does not lead to swelling of the maceral phase; in contrast, CO$_2$ injection clearly leads to dramatic swelling of the maceral phase, even to the extent that the swelling stress is so high that it can fracture the mineral phase inside the coal (Zhang et al. 2016b,c). Compare these effects also with CH$_4$ and N$_2$ gas exposure; CH$_4$ exposure leads to significant maceral swelling, while N$_2$ exposure leads to minor maceral swelling (Zhou et al. 2013). Indeed, coal swelling follows the order CO$_2$ > CH$_4$ > N$_2$ > H$_2$. This is related to the polarizability of these molecules (and thus the Van der Waals interaction forces between the gas molecules and the maceral phase; CO$_2$ polarizability is 29.1 × 10$^{-25}$ cm$^3$, that of CH$_4$ is 25.9 × 10$^{-25}$ cm$^3$, that of N$_2$ is 17.4 × 10$^{-25}$ cm$^3$ and that of H$_2$ is 8 × 10$^{-25}$ cm$^3$; Rallapalli et al. 2011; Ahmed and Rothenberger 2015), which directly determines maceral-gas interaction affinity, this is also for instance expressed in a much higher adsorption capacity of coal for CO$_2$ when compared to H$_2$ (Iglauer et al. 2021, Keshavarz et al. 2021). Note that CO$_2$ also forms hydrogen bonds with carbonyl and alcohol groups present in the coal, further increasing CO$_2$-coal affinity (Fuji et al. 2002).
3.1 Dynamic coal permeability

Above observations are consistent with the measured dynamic coal permeability, which remained constant throughout H₂-flooding, Fig. 3. The fluctuations were within the error margin of the experiment, and as can be seen permeability did not change even after flooding the core with 18000 pore volumes of H₂. We conclude that injection of H₂ and subsequent withdrawal of H₂ from the storage reservoir is feasible from a fundamental fluid dynamical perspective. As high amounts of H₂ can be adsorbed, H₂ geo-storage in coal seams is a promising novel technique to store very large amounts of H₂ in a cost-effective manner.

**Figure 3.** Dynamic coal permeability measured during H₂ flooding. PVI = pore volumes of H₂ injected.
4. Conclusions

H₂ geo-storage provides an alternative option for H₂ storage, at a giant scale (e.g. Zhang et al. 2016a; Tarkowski 2019). One key target formation are deep coal seams, which can adsorb large amounts of H₂ (Iglauer et al. 2021; Keshavarz et al. 2021, Pan et al. 2021). However, a sufficiently large coal permeability is required for efficient H₂ injection (for storage) and H₂ withdrawal (when the fuel is needed). In this context it is well known that CO₂ injection leads to dramatic swelling of the maceral (organic) phase, e.g. Zhou et al. (2013); Zhang et al. (2016b), which drastically reduces coal permeability. It is therefore of vital importance to assess how H₂-exposure influences the cleat network in the coal and the associated coal seam permeability. As this is unknown for H₂, we performed coal coreflooding tests and injected H₂ into a bituminous coal at UHS conditions (296 K, 2.758 MPa pore pressure, 3.447 MPa effective stress – which approximates the geothermal conditions prevailing at a depth of 250 m). The coal plug was imaged at high resolution with an x-ray tomograph, and coal permeability was measured in parallel. Importantly, no change in cleat morphology or permeability was observed.

We conclude that H₂-injection into deep coal seams does not induce coal swelling or permeability reduction – UHS in coal seams is thus feasible from a fundamental physico-chemical (high H₂ adsorption) and petro-physical (high injection and withdrawal rates are possible) perspective. This work therefore provides essential insights into coal permeability behaviour when exposed to H₂ gas; and thus aids in the implementation of a large-scale hydrogen economy.
Acknowledgements

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Conflicts of Interest

There are no conflicts to declare.

Data Availability Statement

The data presented in this paper is stored in the NERC EDS National Geoscience Data Centre (UK), and can be accessed here:

https://www2.bgs.ac.uk/ngdc/citeddata/catalogue.html

https://www2.bgs.ac.uk/nationalgeoscientificdatacentre/citedData/catalogue/84502681-f445-4a01-9dad-c561a94e7c87.html

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References


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