In-situ X-ray micro-computed tomography imaging of the microstructural changes in water-bearing medium rank coal by supercritical CO2 flooding

Citation for published version:

Digital Object Identifier (DOI):
10.1016/j.coal.2019.01.002

Link:
Link to publication record in Heriot-Watt Research Portal

Document Version:
Peer reviewed version

Published In:
International Journal of Coal Geology

Publisher Rights Statement:
© 2019 Elsevier B.V.

General rights
Copyright for the publications made accessible via Heriot-Watt Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy
Heriot-Watt University has made every reasonable effort to ensure that the content in Heriot-Watt Research Portal complies with UK legislation. If you believe that the public display of this file breaches copyright please contact open.access@hw.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.
Accepted Manuscript

In-situ X-ray micro-computed tomography imaging of the microstructural changes in water-bearing medium rank coal by supercritical CO2 flooding

Yihuai Zhang, Maxim Lebedev, Yu Jing, Hongyan Yu, Stefan Iglauer

PII: S0166-5162(18)30568-8
DOI: https://doi.org/10.1016/j.coal.2019.01.002
Reference: COGEL 3141
To appear in: International Journal of Coal Geology

Received date: 15 June 2018
Revised date: 10 January 2019
Accepted date: 11 January 2019

Please cite this article as: Yihuai Zhang, Maxim Lebedev, Yu Jing, Hongyan Yu, Stefan Iglauer, In-situ X-ray micro-computed tomography imaging of the microstructural changes in water-bearing medium rank coal by supercritical CO2 flooding. Cogel (2018), https://doi.org/10.1016/j.coal.2019.01.002

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.
In-situ X-ray micro-computed tomography imaging of the microstructural changes in water-bearing medium rank coal by supercritical CO\textsubscript{2} flooding

Yihuai Zhang\textsuperscript{1,2,*}, Yihuai.Zhang@hw.ac.uk, Maxim Lebedev\textsuperscript{2}, Yu Jing\textsuperscript{3,4}, Hongyan Yu\textsuperscript{5}, Stefan Iglauer\textsuperscript{4}

\textsuperscript{1}The Lyell Centre, Heriot-Watt University, Edinburgh EH14 4AS, Scotland, United Kingdom
\textsuperscript{2}WA School of Mines: Minerals, Energy, and Chemical Engineering, Curtin University, 26 Dick Perry Avenue, 6151 Kensington, Australia
\textsuperscript{3}School of Minerals and Energy Resources Engineering, UNSW, 2052 Kensington, Sydney, Australia
\textsuperscript{4}School of Engineering, Edith Cowan University, 270 Joondalup Drive, 6027 Joondalup, Australia
\textsuperscript{5}State Key Laboratory of Continental Dynamics; Department of Geology, Northwest University, Xi’an, 710069 China

*Corresponding author.

Abstract

Carbon dioxide geosequestration into deep unmineable coal seams is a technique which can mitigate anthropogenic greenhouse gas emissions. However, coal composition is always complex, and some minerals such as calcite chemically react when exposed to the acidic environment (which is created by scCO\textsubscript{2} mixing with formation water). These reactive transport processes are still poorly understood. We thus imaged a water-bearing heterogeneous coal (calcite rich) core before and after scCO\textsubscript{2} injection in-situ at high resolution (3.43 µm) in 3D via X-ray micro-tomography. Indeed, the calcite- fusinite mix phase was partially dissolved, and absolute porosity and connectivity significantly increased. We thus suggest that such a process could be used as an acidizing method for enhanced coal bed methane (ECBM) production, thus significantly improving the permeability performance,
CO₂ injectivity and the associated methane permeability.

**Keywords:** microCT; ECBM; carbon storage; dissolution; acidizing

1. Introduction

Carbon geosequestration into deep geological formations is currently the best choice for zero carbon emissions and climate change mitigation. Proposed storage sites include sandstone, carbonate rock, oil shale and coal seams. CO₂ injection into deep un-mineable coal seams can enhance coalbed methane recovery, and this process has gained substantial interest in recent decades (Al-Yaseri et al., 2017a; Pan et al., 2018; Ranathunga et al., 2017b; Yang et al., 2016; Zhang et al., 2017). Technically, CO₂ is injected into the coal matrix’ micro/nano pores where it displaces the original (adsorbed) methane, while CO₂ is trapped inside the matrix (adsorption trapping) and closes potential leakage routes (i.e. cleats/fractures) by matrix swelling (Zhang et al., 2016a). However, such coal matrix–CO₂ induced coal swelling is complex and can significantly change the physical properties of the host rock, e.g. many studies proved that the coal seams’ (geometrical) structures and associated permeability change after CO₂ injection (Day et al., 2008; Perera et al., 2011; Ranathunga et al., 2015, 2017a; Siriwardane et al., 2009; Vishal, 2017; Zhang et al., 2016a). Karancan (2007) claimed that this CO₂ sorption-swelling and related volumetric strains were heterogeneous processes depending on the lithotypes present. Day et al. (2008) used digital cameras and directly observed coal swelling in CO₂ at pressures up to 15 MPa and temperatures up to 55 °C for Australian coals. Zhang et al. (2016a) injected scCO₂ into a coal core sample and observed that the permeability dramatically decreased, while micro fractures closed (observed by X-ray tomography). However, most of the experiments and simulations were conducted at dry (ideal) conditions, although formation water always exists in coal seams (An et al., 2015; Liu and Rutqvist, 2010; Liu et al., 2016; Wang et al., 2009) – thus a key parameter (water) was ignored, which has a significant effect on the above mentioned processes as discussed here.
Furthermore, it is well established that the injected CO$_2$ dissolves in the formation water, and this CO$_2$–enriched brine is acidic at reservoir conditions (pH values drop to 3-4, Deng et al., 2015; Menke et al., 2017). Moreover, it is clear that coal is always heterogeneous and consists of not only of organics, but also inorganic materials such as carbonate, quartz and clay (e.g. Yu et al., 2018; Zhang et al., 2018a; Ward et al., 2018). Especially in low to medium rank coal, such inorganics exist abundantly. Such inorganic materials (e.g. carbonates) may be sensitive to the acidic environment and thus it is hypothesized here that CO$_2$ injection may significantly change the petrophysical coal properties.

Thus, in this study, we analyzed such a process via x-ray micro-tomography (microCT) with which the coal microstructural changes can be observed at micrometer scale at reservoir conditions (Lebedev et al., 2017a, 2017b; Zhang et al., 2018b).

2. Methodology

To study these effects, microCT in-situ imaging was employed, as it can observe the microstructural changes caused by such fluid-rock interaction in 3D at reservoir conditions (Lebedev et al., 2017a), where resolutions up to 300 nm voxel size can be realized (e.g. An et al., 2017; Hosseinzade Khanamiri and Torsæter, 2018; Iglauer and Lebedev, 2018; Jing et al., 2016, 2017; Ramandi et al., 2018; Roshan et al., 2018; Shi et al., 2018; Yang et al., 2017; Zhang et al., 2016b, 2016c). Such in-situ microCT techniques successfully overcome the shortcomings of the traditional imaging tools such as SEM which only can obtain 2D surface images at ambient pressure conditions.

2.1. Materials

A coal sample which contained calcite was obtained from the Pingdingshan coal mine, China. The coal had been identified as sub-bituminous containing 36 % ($\pm$ 1%) volatile matter and 54 % ($\pm$ 2%) fixed carbon content (measured by Chinese standard GB/T 212 -2008 and DL/T 1030-2006), the petrophysical properties of this coal are tabulated in Table 1. The coal
Microstructures were also imaged by SEM (Phenom XL, 15 KV energy, the sample was polished to flat before the test), Fig. 1; coal matrix, porosity and calcite mineral phase can be identified: the coal matrix mainly included vitrinite and fusinite, the porosity consisted of fusinite primary pores and micro cleats, and the calcite phase existed as well crystallized calcite and small calcite mineral particles developed inside the fusinite pores – a calcite-fusinite mixed phase. For the microCT experiments, a cylindrical coal plug (5 mm diameter and 10 mm length) was cut (parallel to the sedimentary bedding) for the following microCT in-situ flooding test.

Table 1: The Physical properties of the coal sample (Zhang et al., 2016b, 2017).

<table>
<thead>
<tr>
<th>M_{ad} (%)</th>
<th>V_{daf} (%)</th>
<th>A_{ad} (%)</th>
<th>C_{f} (%)</th>
<th>E (GPa)</th>
<th>υ (-)</th>
<th>ρ (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.90</td>
<td>36.00</td>
<td>4.20</td>
<td>54.00</td>
<td>2.60</td>
<td>0.31</td>
<td>1.35</td>
</tr>
</tbody>
</table>

Note: M_{ad} is the moisture content (%); V_{daf} is the volatile matter (%); A_{ad} is the ash yield (%); C_{f} is the fixed carbon content (%); E is Young’s Modulus (GPa); and υ is Poission’s ratio (-); ρ is the bulk density (g/cm³).

Fig. 1. SEM images of the coal sample; (A) a large amount of calcite is evident (white color); (B) the vitrinite and calcite-fusinite mix; (C) the primary pores (diameters less than 3 μm) in the fusinite with calcite particles inside; (D) detailed micro structures of the fusinite.

2.2. MicroCT in-situ flooding test

Here the cylindrical coal plug was mounted inside a novel X-ray transparent core holder (Zhang et al., 2016a; Lebedev et al., 2017b; Iglauer and Lebedev, 2018) which was as a part of the microCT in-situ imaging core flooding system, see Fig. 2. This core flooding system included two parts: the microCT instrument itself (ZEISS Xradia VersaXRM 500 instrument, a 2000 × 2000 pixel detector was used and the X-ray accelerating voltage was set to 60 kV in this experiment), and the high pressure – high temperature (HPHT) flooding system. The in-situ microCT core flooding test was then conducted following the below steps:
1. The coal plug was saturated with 5 wt% NaCl brine (coal plug was immersed into the brine under vacuum for 1 week) before the coal sample was mounted into the core holder (made of Polyether ether ketone). More details about this X-ray transparent core holder can be found in Lebedev et al. (2017a) and Iglauer and Lebedev (2018).

2. All the tubes were filled with 5 wt% NaCl brine with a syringe pump (Teledyne ISCO 500D, B in Fig. 2) after the coal plug was mounted into the core holder; note that all flow tubes and fluids were continuously isothermally heated to 50°C (323 K) with heat jackets by continuously circulating warm water, and the core holder was heated by electric tape.

3. First the saturated coal plug was imaged (voxel size: 3.43 μm) under a confining pressure of 5 MPa (no pore pressure, thus 5 MPa effective stress was applied – the effective stress was kept constant during the whole experiment at a temperature of 50°C / 323K. The confining pressure was applied by compressed deionized (DI) water by confining pump (C in Fig. 2).

4. Then the coal plug was flooded with supercritical CO₂ (scCO₂) at 10 MPa backpressure (via pump B, Fig. 2), while a 15 MPa confining pressure were applied (i.e. the experiment was conducted at a constant effective stress of 5 MPa). The CO₂ injection rate was 0.25 ml/min, and approximately 5000 pore volumes of CO₂ were injected in this experiment.

5. The sample was then microCT imaged again at in-situ reservoir condition (i.e. at 15 MPa confining pressure, 10 MPa pore pressure, and a temperature of 50°C / 323K).

All images were filtered with a 3D non-local means filter (Buades et al., 2005) to denoise the image (a local five voxel neighborhood was used during smoothing) and a watershed algorithm (Schlüter et al., 2014) was used subsequently for phase segmentation, based on the (different) X-ray relative radiodensity of the materials. Finally, the images were qualitatively
and quantitatively analysed (see Fig. 3 for details). Note that all image processing here was performed with Avizo 9.2 software.

Fig. 2. High pressure-High temperature (HPHT) in-situ microCT coreflooding apparatus: (A) CO$_2$ injection pump, (B) back pressure / production pump, (C) confining pressure pump, (D) microCT (ZEISS Xradia VersaXRM 500 instrument), (E) photo showing the inside of the microCT scanner, (F) X-ray transparent core holder assembly, (G) microCT image processing, (H) CO$_2$ cylinder.

Fig. 3. Flowchart illustrating the microCT image processing sequence.

3. Results and discussion

3.1. Microstructural morphological changes

Clearly, the sub-bituminous coal was highly heterogeneous as evident on the SEM and microCT images, see Figs. 1 and 4. As in the SEM images, several phases were identified on the water-saturated plug tomograms: the coal matrix (dark grey – low X-ray density), the mineral phase (calcite, white – high X-ray density), and calcite-fusinite mix phase (grey – medium X-ray density). Note that no micro fractures/cleats were observed in the water saturated coal sample; this is in contrast to observations made in dry coal samples (e.g. Ramandi et al., 2016; Zhang et al., 2018c) including the dry coal imaged by SEM (Fig. 1).

Such closure of the micro fractures/cleats can be explained by water adsorption into the coal matrix and associated organic matrix swelling, see Zhang et al., 2016c. We also presented the range of microCT X-ray relative radiodensity for the different phases (see Table 2 for details) from our scanning.

Fig. 4. MicroCT image (3.43 μm voxel edge length) of the coal sample (brine saturated): (A) 2D slice through the raw image: coal matrix is dark grey (low X-ray density), calcite mineral is white (high X-ray density), and the calcite- fusinite mixed phase is grey (medium X-ray
density); (B) 3D visualization of the raw image (colours indicate different microCT X-ray relative radiodensity, compare Table 2).

Table 2. The summary of microCT X-ray relative radiodensity of the various phases observed, and the color range used in Figures 1 and 7.

<table>
<thead>
<tr>
<th>Phase</th>
<th>X-ray relative radiodensity</th>
<th>Color range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voids (pores)</td>
<td>0-200</td>
<td>![Blue to Red Gradient]</td>
</tr>
<tr>
<td>Coal matrix (without minerals)</td>
<td>200-20000</td>
<td>![Blue to Red Gradient]</td>
</tr>
<tr>
<td>Fusinite-calcite mixed</td>
<td>20000-35000</td>
<td>![Pink to Green Gradient]</td>
</tr>
<tr>
<td>Minerals (calcite)</td>
<td>&gt;35000</td>
<td>![Red to Yellow Gradient]</td>
</tr>
</tbody>
</table>

After the scCO₂ was injected into the water bearing coal, the scCO₂ mixed with the brine caused significant chemical dissolution and clearly wormholes were created (see both 2D and 3D images, Fig. 5). Chemically, the calcite inside the coal reacted with the carbonic acid, which is formed by the chemical reaction of H₂O with CO₂ (Busenberg and Plummer, 1986; Iglauer, 2011; Zhang et al., 2018c; Adamczyk et al. 2009), thus the solid (s) calcite is dissolved into aqueous Ca²⁺ (aq), HCO₃⁻ (aq) and CO₃²⁻ (aq) ions;

\[
\begin{align*}
H_2O (l) + \text{scCO}_2(sc) & \leftrightarrow H_2O (l) + CO_2(aq) \\
H_2O (l) + CO_2(aq) & \leftrightarrow H_2CO_3(aq) \\
H_2CO_3(aq) & \leftrightarrow HCO_3^- (aq) + H^+ (aq) \\
HCO_3^- (aq) & \leftrightarrow CO_3^{2-} (aq) + H^+ (aq) \\
CaCO_3(s) + \text{H}^+ (aq) & \leftrightarrow Ca^{2+} (aq) + HCO_3^- (aq) \\
CaCO_3(s) + H_2CO_3(aq) & \leftrightarrow Ca^{2+} (aq) + 2HCO_3^- (aq)
\end{align*}
\]
Fig. 5. MicroCT image (3.43 \( \mu \)m voxel edge length) for the coal sample after scCO\(_2\) flooding; the dissolved area is black (lowest X-ray density number), coal matrix is dark grey (low X-ray density number), the well-formed calcite mineral is white (high X-ray density number), and calcite-fusinite mix phase is grey (medium X-ray density number); (A) 2D slice, (B) 3D cut view.

These dissolved areas were also highly heterogenous (see Fig. 6 and Fig. 7); we found that most of the dissolution was localized in the calcite-fusinite mix phase, this can be explained by the less consolidated nature of the fusinite, which has a lot of nano/micro pores, as evident in the high resolution SEM images (see C and D in Fig. 1). This is the primary porosity system in the coal matrix, and the calcite particles inside the fusinite thus had a larger contact area (with the acid) when compared to the well-developed compact calcite phase (e.g. compare in Fig. 1A). As the contact area is directly proportional to chemical dissolution, more calcite dissolved in the fusinite phase. Similar to the former reactive flow transport
studies in carbonate rocks (Liu and Mostaghimi, 2018; Lebedev et al., 2017b) the injected acid preferentially migrated through the dissolved area (due to its higher permeability). Furthermore, most of the ‘wormhole’ dissolution happed near the inlet area, see Fig. 7 and Fig. 9, although this also depended on sample heterogeneity, consistent with former CO$_2$ acid brine injection studies in carbonate rocks (Lebedev et al., 2017b).

Moreover, the microCT X-ray attenuation number of the calcite significantly decreased after CO$_2$ flooding (see Fig. 6 which shows the same area before and after the scCO$_2$ injection; colored by microCT X-ray attenuation number at the same scale). Thus, we conclude that the acid did not just form large ‘wormholes’, but also increased the nanoporosity in the calcite. Through digital image processing (see Fig. 8 for the same slice of raw images, after non-local filtering, and after application of the watershed segmentation algorithm), the coal matrix, calcite mineral and voids area were segmented. The newly formed pore volume (by calcite dissolution) measured on the microCT images amounted to 2.78% of the total bulk volume, see Figs. 8 and 9 for the 3D view.
Fig. 6. 2D images (3.43 μm voxel edge length) of the same area before and after scCO$_2$ injection with colored by microCT X-ray relative radiodensity at same scale; (A) before scCO$_2$ injection; (B) after the scCO$_2$ injection.

Fig. 7. 3D visualization (3.43 μm voxel edge length) for the sample after the scCO$_2$ injection; with colored by microCT X-ray relative radiodensity, (A1), (A2), and (A3) are three extracted parts: (A1) is near the inlet area, (A2) is in the middle of the sample, and (A3) is near the outlet area.
Fig. 8. The microCT image processing (white/green is calcite; black/blue is the wormhole, and dark grey/red is the coal matrix), (A) raw image; (B) image after non-local means filter process; and (C) segmented image after watershed segmented algorithm.
Fig. 9. 3D visualizations of the different phases in the coal sample (3.43 μm voxel edge length resolution) after scCO₂ flooding, note that the arrow indicates the fluid flow direction.

3.2. **Comparison of scCO₂ injection into dry coal samples**

Clearly, scCO₂ flooding of water-bearing coal results in a very different response when
compared with scCO\(_2\) flooding of dry coal, where Zhang et al. (2016a) found that scCO\(_2\) induced coal matrix swelling and micro fractures/cleats closure, and associated reduced permeability (note that the coal sample used in our experiment was as same as in Zhang et al. (2016a); however, in the water-bearing coal sample significant dissolution happened (i.e. the calcite dissolved, see above). We thus suggest that water saturation is one of the key parameters in the context of CO\(_2\) storage in such coal seams.

3.3. Application to ECBM and CO\(_2\)-geosequestration

In summary, the scCO\(_2\) injection into the water-bearing coal sample created new pore space by dissolving calcite, which substantially increased porosity and pore connectivity. We thus suggest that such a process could be an environmentally friendly and relatively non-hazardous acidizing method in ECBM for such carbonate rich coal seams. This way methane production and/or CO\(_2\) injectivities may be significantly enhanced, which is currently a limiting factor in ECBM due to coal matrix swelling (and the associated dramatic permeability reduction) (Zhang et al., 2016a). However, note that such acidizing may also significantly affect the rock mechanical properties (Zhang et al., 2016d), which should also be taken into account in future research work.

4. Conclusions

Carbon geosequestration in deep geological formations has been suggested as the most efficient way to mitigate climate change by reducing CO\(_2\) emissions into the atmosphere (Al-Yaseri et al., 2017b, 2017c; Al-Khdheawi et al., 2017, 2018; Benson, 2015; Liu et al., 2018; Metz, 2005). Deep unmineable coal seams are key target formations; however, CO\(_2\) adsorption into the coal matrix causes coal matrix swelling and a dramatic reduction in permeability, thus limiting the industrial potential of these CO\(_2\) sinks (Zhang et al., 2016a).
Furthermore, the injected CO$_2$ mixes with formation water and creates an acidic environment, which impacts on acid-sensitive minerals (such as calcite), which are present in coal seams. This effect is, however, still poorly understood.

We thus investigated such fluid-coal interactions at the micro meter pore-scale via 3D microCT (Lebedev et al., 2017b; Zhang et al., 2016c; Kong et al., 2018) in-situ core flooding experiments; scCO$_2$ was injected into a heterogeneous water-bearing bituminous coal at reservoir conditions (15 MPa confining pressure, 10 MPa pore pressure, and 323 K). The coal’s microstructure (mainly the calcite-fusinite mix phase) partially dissolved after CO$_2$ flooding. The dissolved volume significantly increased the porosity and pore connectivity in the coal sample. We thus propose that such a process could be an environmentally friendly and relatively harm free acidizing method in ECBM, which can significantly increase permeability and thus methane production and CO$_2$ injectivity, at least when carbonates are present.

Acknowledgements

The measurements were performed using the microCT system courtesy of the National Geosequestration Laboratory (NGL) of Australia, funding for the facility was provided by the Australian Government. This work was also supported by resources provided by the Pawsey Supercomputing Centre, which provided the Avizo 9.2 image processing software, with funding from the Australian Government and the Government of Western Australia.

References

1694.
An, S., Yao, J., Yang, Y., Zhang, W., Zhao, J. and Li, A., 2017. The microscale analysis of
reverse displacement based on digital core. Journal of Natural Gas Science and
Engineering, 48, p.138-144.
Buades, A., Coll, B., and Morel, J.-M., A non-local algorithm for image denoising, in
Busenberg, E., and Plummer, L., 1986, A comparative study of the dissolution and crystal
growth kinetics of calcite and aragonite, Studies in diagenesis, Volume 1578, US
Day, S., Fry, R., and Sakurovs, R., 2008, Swelling of Australian coals in supercritical CO₂:
International Journal of Coal Geology, v. 74, no. 1, p. 41-52.
Deng, H., Fitts, J. P., Crandall, D., McIntyre, D., and Peters, C. A., 2015, Alterations of
fractures in carbonate rocks by CO₂-acidified brines: Environmental science &
technology, v. 49, no. 16, p. 10226-10234.
Hosseinzade Khanamiri, H., and Torsæter, O., 2018, Fluid Topology in Pore Scale Two-Phase
Flow Imaged by Synchrotron X-ray Microtomography: Water Resources Research.
Iglauer, S., 2011, Dissolution trapping of carbon dioxide in reservoir formation brine—a
Iglauer, S., and Lebedev, M., 2018, High pressure-elevated temperature x-ray micro-
computed tomography for subsurface applications: Advances in Colloid and Interface
Science.
Jing, Y., Armstrong, R. T., Ramandi, H. L., and Mostaghimi, P., 2016, Coal cleat
Karacan, C. Ö., 2007, Swelling-induced volumetric strains internal to a stressed coal
associated with CO2 sorption: International Journal of Coal Geology, v. 72, no. 3-4, p. 209-220.


Metz, B., 2005, Carbon dioxide capture and storage: special report of the intergovernmental panel on climate change, Cambridge University Press.


Yu, H., Zhang, Y., Lebedev, M., Han, T., Verrall, M., Wang, Z., Al-Khdheewa, E., Al-Yaseri,


• The calcite-fusinite mix phase partially dissolved was observed in-situ in 3D as scCO$_2$
  injected into water-bearing bituminous coal.

• Morphological results showed the dissolved volume significantly increased the porosity
  and pore connectivity.

• An environmentally friendly and relatively harm free acidizing method in ECBM was
  proposed.
Figure 5