Variation of mechanical properties of bituminous coal under CO\textsubscript{2} and H\textsubscript{2}O saturation

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ABSTRACT

CO\textsubscript{2} injections into coal seams can boost the recovery of coalbed methane (CBM), while simultaneously sequestering a greenhouse gas. However, alteration of the mechanical attributes of coal is observed during CO\textsubscript{2} injection. Most studies to date have focused on the influence of single-fluid saturation on coal, and few investigations have been dedicated to various and coupled-fluid saturations on the geomechanical attributes of coal. This work therefore examines the effect of CO\textsubscript{2}, water and water + CO\textsubscript{2} saturation on bituminous coal. It was found that the average uniaxial strength of the untreated coal samples is 46.07 MPa and it reduces after CO\textsubscript{2} and water saturation, this reduction increases with increasing CO\textsubscript{2} saturation pressure, especially for supercritical CO\textsubscript{2}, as the much higher adsorption affinity of supercritical CO\textsubscript{2} results in greater structural alteration. Further 5.29\% and 9.69\% strength reductions were found for water+6 MPa CO\textsubscript{2} and water+8 MPa CO\textsubscript{2} (supercritical) saturated samples, from 26.33 MPa to 19.00 MPa–23.90 MPa and 14.53 MPa, respectively, compared with the corresponding single CO\textsubscript{2} saturations, because of the enhanced structural alteration and mineral dissolution observed in SEM images. The coal structure is relaxed with increased Young's modulus after exposure to CO\textsubscript{2} or water. More progressive strain development was found for the water + CO\textsubscript{2} treated sample, which showed a more ductile collapse compared with the shear-dominated failure of the untreated sample. The weakening effect was further evidenced by acoustic emission (AE) results, according to which the AE energies decreased considerably after CO\textsubscript{2} or water saturation, and this reduction intensified for the water + CO\textsubscript{2} saturated sample with increase of crack initiation stress and reduction of stable crack propagation. The findings highlight that while single CO\textsubscript{2} or water saturation weakens coal strength, the coupled influence of water + CO\textsubscript{2} saturation, which is the most likely scenario in actual field operations, induces greater strength alteration and threatens the overall stability of the system.

1. Introduction

Natural gas is a major component of the world energy supply market and it is a much cleaner fossil fuel than other sources such as coal and oil (British Petroleum, 2017; Faramawy et al., 2016). Coalbed methane (CBM) is a natural gas trapped in coal seams. Unlike conventional natural gas reservoirs, where high gas flow rates can be achieved during the extraction process since high-pressure gas exists in permeable and porous reservoir rocks capped with impermeable layers, most CBM is physically adsorbed within coal inner surfaces with relatively low permeability (Zhang et al., 2016). Therefore, permeability enhancement techniques need to be adopted to increase the flow characteristics of reservoirs for the efficient and economical recovery of CBM. The enhanced coalbed methane method (ECBM), which is primarily conducted by injecting CO\textsubscript{2} into the coal seam to replace the CH\textsubscript{4} in place, has been implemented and tested as a feasible methane enhancement method (Fujioka et al., 2010; Pan et al., 2018; Ranathunga et al., 2017; Yamaguchi et al., 2009; Zhang et al., 2016) It also has the promising potential of immobilising a great amount of CO\textsubscript{2} in coal seams to reduce the level of this greenhouse gas in the atmosphere, which will contribute to the alleviation of global warming (MacDowell et al., 2017). Many scientists believed that the global climate change is caused by the increasing emissions of anthropogenic greenhouse gases into the atmosphere (Figueroa et al., 2008). Therefore, Paris Agreement is established to strengthen the cooperation between nations to combat climate change by limiting the rise of global temperature this century.
molecules are therefore displaced by CO₂ molecules which contributes through coal matrix for CO₂ and CO₂ molecules can enter more confined pore areas where CH₄ molecules are restricted. The adsorbed CH₄ molecules are therefore displaced by CO₂ molecules which contributes to methane recovery as well as CO₂ sequestration. However, significant changes of coal structure occur during the adsorption of CO₂. These structural changes to the coal are due to a series of physical and chemical interactions between coal and CO₂ (Larsen, 2004; Xie et al., 2015; Ranathunga et al., 2016), which alter the adsorption behaviour, the flow behaviour and the geomechanical properties of coal. To date, most studies have concerned the adsorption characteristics and permeability variations during the interaction between coal and CO₂ and less attention has been paid to alterations in the mechanical properties (Vishal et al., 2015).

One of the most common phenomena in the interaction process is coal matrix swelling due to the adsorption of CO₂; the swollen coal matrix facilitates the re-arrangement of the macromolecules in coal to a more non-covalently associated structure with lower free energy (Larsen et al., 1997). As a result, the strained coal is relaxed, which impairs its mechanical performance. Coal strength reduction is an unwanted scenario during CO₂ sequestration since the structural alteration of coal seam due to the adsorption of CO₂ might create the risk of the injected CO₂ to back migrate into the atmosphere (Gale, 2004). Besides, the reduction of coal strength may also cause hazardous incidents such as gas outburst as a result of the increase pore pressure inside the weakened coal seam (Zhi and Elsworth, 2016; He et al., 2016). Therefore, these mechanical property alterations of coal due to the interaction with CO₂ affect the methane recovery process as well as the long-term safety of CO₂ sequestration in coal seams.

Theoretically, changes in the mechanical properties of coal due to the adsorption of CO₂ can be explained by Gibbs’ adsorption theory (Gibbs, 1878) and the Griffith failure criterion (Griffith, 1921). According to the Griffith failure criterion (Griffith, 1921), the adsorption of a substance with higher chemical potential reduces the surface energy of the adsorbent, which leads to lower tensile stress required to generate a new crack, and the material is therefore weakened upon the adsorption of more chemically-reactive adsorbate. A number of studies have been conducted in the past in an attempt to identify the weakening effect of CO₂ adsorption on coals of different ranks (Hu et al., 2016; Ranathunga et al., 2016; Viete and Ranjith, 2006; Vishal et al., 2015). For example, Viete and Ranjith (2006) observed around 13% reduction in UCS values and 26% reduction in Young’s modulus after saturating brown coals with 1.5 MPa CO₂. Ranathunga et al. (2016) extended their research by using brown coal samples subjected to supercritical CO₂ saturation and calculated a larger magnitude strength reduction. For example, a 57.50% and 40.12% reduction was found for UCS and Young’s modulus, respectively, after 8 MPa supercritical CO₂ saturation. This greater reduction is believed to be correlated to the much higher adsorption potential of supercritical CO₂ to coal compared with that of subcritical CO₂. Similar strength reductions were observed for both high ranks of coal with exposure to CO₂ (Perera et al., 2016); however, high rank coal exhibited a greater strength reduction compared to low rank coal. This is attributed to the fact that high rank coal undergoes a much longer coalification process, which leaves high rank coal with a well-developed cleat system, which can offer more places for the CO₂ molecules, resulting in a greater strength reduction being associated with structural alteration (Perera et al., 2016).

Although CO₂ is the major fluid that interacts with coal during CO₂ injection, this process is linked with other fluid-coal interactions. Therefore, it is important to understand the mechanical responses of coal subjected to other saturation fluids. Natural coal seams are usually permeated with water, as the primary recovery of methane is achieved by pumping out water of the reservoir to reduce the pressure on coal seams. Therefore, the effect of the presence of water on the alteration of the mechanical properties of coal needs to be examined. However, few studies to date have performed the necessary investigations (Perera et al., 2016; Vishal et al., 2015; Yao et al., 2015; Zhang et al., 2018). For example, Yao et al. (2015) observed a comparable strength reduction for two different types of coal as the UCS and Young’s modulus values decreased after water saturation. They explained this coal strength reduction as the softening effect of water saturation. Similar to the results after CO₂ saturation, greater strength reduction was recorded for high rank coal. However, almost all the experiments reported to date were performed under single fluid saturation and the coupled effects of CO₂ and water saturation on the variations of the geo-mechanical attributes of coal are not well understood. While the existence of water may reinforce the weakening effect created by CO₂ adsorption to coal (Vishal et al., 2015), others have reported that the presence of moisture creates obstacles for CO₂ being adsorbed into coal by competing with the CO₂ molecules for sorption sites (Busch et al., 2007; Pan et al., 2010). Hence, the complication of the coupled influence of both CO₂ and water on the changes of the mechanical properties of coal needs to be investigated. Vishal et al. (2015) performed a series of experiments on water-saturated coals with exposure to 3 MPa CO₂ and observed that the samples failed at the early loading stage with the highest strength reduction compared with the samples saturated with a single fluid (CO₂ or water). However, they considered only subcritical CO₂ (3 MPa) saturation, and the effect of supercritical CO₂ + water saturation on alterations of the mechanical properties of coal still remains a matter of research interest. Generally, the ideal places for carrying out CO₂-ECBM projects are deep-seated coal seams where supercritical CO₂ is likely to be encountered, as the phase transition of CO₂ from subcritical to supercritical happens at the critical points of 7.38 MPa and 31.8 °C. Therefore, the main objective of this study is to fill this gap by examining the effect of various saturation fluids on the mechanical attributes of coal, with a special focus on CO₂ saturation, water saturation and CO₂ + water saturation. As stated previously, the target coal seams for implementing CO₂-ECBM projects are primarily deep coal seams where high rank coal is generally present. Therefore, high rank coal samples were used in this study.
2. Experimental methodology

A series of unconfined compressive strength tests (UCS) was performed on black coal samples subjected to various saturation fluids including CO₂, water and CO₂ + water. An acoustic emission (AE) system, a non-contact and material-independent optical 3-D deformation measurement system and the scanning electron microscopy (SEM) technique were adopted to assist in the analysis of results. The results were then compared and discussed to identify the effect of various saturation media on the mechanical property variations of bituminous coal.

2.1. Sample preparation

Bituminous coal with 59.81% fixed carbon content was employed in this study. The coal samples used in this study were recovered from the No.3 coal seam of the Permo-Carboniferous system in Tashan coal mine, China. The average moisture content (wet basis) and density were 1.31% and 1.45 g/cm³, respectively. The ash content was 13.16% while the volatile matter content was 30.07%. The lower heating value of coal is 32706 kJ/kg. Coal samples with 38 mm in diameter were cut and end-trimmed to 76 mm in length using the LECO cutting machine and a diamond-tipped grinding machine in the Monash University Deep Earth Energy Research Laboratory (DEERL). Great care was taken during the end-trimming process, and each sample was first mounted and fixed on the base support during the grinding process, rotating the base created a pair of parallel end faces, which is difficult to obtain if the sample is directly rotated from the base. Therefore, the load applied on the sample during the compression process was guaranteed to be uniformly distributed across the sample surface. Great care was taken during the grinding to reduce the possible damage to the sample. After the grinding treatment, samples with visible fractures were discarded to further minimise the heterogeneity of the tested sample, and the remaining samples were encased in polyethylene film and isolated in an opaque plastic container, sealed with tape. The container was stored in the curing room at DEERL to minimise disturbance to the inherent characteristics of the coal sample. Fig. 5(a) illustrates a close view of a typical coal sample.

2.1.1. CO₂ saturation

Prior to CO₂ saturation, the samples were oven-dried at 105 °C for 24 h to remove the moisture. A high-pressure high-temperature saturation apparatus was used for CO₂ saturation, as shown in Fig. 1(a). This apparatus mainly consists of a gas bottle, a syringe pump, a pressure cell and a heating unit. After the samples were placed in the cell, CO₂ was first introduced into the pressure cell from the gas bottle. Then the heating band started heating the cell, and the temperature was set at 37 °C and controlled by a temperature monitoring unit. Next, the cell was pressurised using the syringe pump to the required pressure. Five different saturation pressures were applied in this study, namely, 2, 4, 6, 8 and 10 MPa. Since the temperature was set at 37 °C for all the saturation pressures, both subcritical (2, 4, 6 MPa) and supercritical CO₂ saturation (8, 10 MPa) could be achieved. Samples were saturated under these conditions for three weeks before the pressure was gradually released at a rate of 0.02 MPa/min in an attempt to minimise possible damage to the sample due to rapid pressure changes (Ranathunga et al., 2016). The samples were then recovered from the cell, wrapped in polyethylene film and tested within 20 min to minimise any changes to the saturation condition.

2.1.2. Water saturation

Water saturation was performed using the desiccator shown in Fig. 1(b). Three pre-weighed coal samples were placed in the desiccator filled with de-ionised water for over three weeks during which the weight of each sample was recorded over time. After the weight of the samples became stable, the samples were collected from the desiccator and stored in the curing room for another two weeks to allow the moisture to be evenly distributed in them. Similar to the CO₂ saturation, UCS testing was conducted within 20 min after the samples were removed from the curing room.

2.1.3. CO₂ + water saturation

Although coal seams are permeated with various fluids in-situ, almost all the related studies to date were conducted using a single saturation medium. The mechanical property alterations of coal with exposure to CO₂ and water at the same time still remain a matter of study. Therefore, two sets of CO₂ + water saturations were added to the experiment, namely subcritical CO₂ (6 MPa) with water and supercritical CO₂ (8 MPa) with water. The high-pressure saturation apparatus was again adopted for CO₂ + water saturation. First, three samples were put into the pressure cell filled with de-ionised water, then the pressure chamber was pressurised up to 6 MPa and this pressure was maintained for over three weeks with the temperature being kept at 37 °C throughout the saturation period. The same procedures were followed.
for producing the supercritical CO$_2$+water saturated samples. The pressure cell was then de-pressurised at a rate of 0.02 MPa/min and the samples were tested within 20 mins after being removed from the cell.

2.2. Experimental testing methods

Uniaxial compressive tests were performed using the Shimazu compression tester (AG-300kNXplus) in the DEERL with an accuracy in force measurement within ± 0.5%. During compression, the load displacement rate was maintained at 0.1 mm/min to fail the sample and the corresponding stress and displacement were captured over time using an advanced data acquisition system. The transient elastic waves generated during the compression process were captured by the AE system (Hou et al., 2016; Lee and Rathnaweera, 2016). Strain variations (both axial and lateral) during the test were recorded using a 3-D deformation measuring system equipped with two high-resolution cameras. Strain measurement was obtained by converting the movement of pixels in an image into displacement vectors using the in-built software. In order to capture the displacement during compression, the surface of the sample needs to present sufficient image variations in tone and contrast. This was achieved by colouring the sample with matt white paint and spraying black paint dots all over the sample surfaces. Strain development and AE signals were captured simultaneously with the compression process.

Micro-scale structural alteration of coal samples was observed using scanning electron microscopy (SEM). SEM analysis was conducted with the aid of the FEI Quanta 3-D FEG FIB electron microscope at the Monash Centre for Electron Microscopy (MCEM). During each saturation process, several coal slices 2 mm thick were saturated together with the standard coal samples. After each saturation duration, these slices were removed for SEM analysis.

3. Experimental results and discussion

In this study, as three samples were assigned to each saturation condition, a total of 27 samples were tested. Table 1 summarises the average UCS values, Young’s modulus and Poisson’s ratios under each saturation condition. Since the strength values varied marginally for samples under the same saturation condition, samples with the highest UCS values were selected to represent each saturation condition to facilitate the following discussion.

3.1. Stress-strain behaviour

Fig. 2 shows the stress-strain responses of the samples. The Young’s modulus and Poisson’s ratio of each sample were then obtained using the elastic region from the stress-strain curve, as indicated in Table 1. Based on the information from Table 1 and Fig. 2, with respect to the CO$_2$-saturated samples, significant strength reductions were observed, and this reduction is much higher for the supercritical CO$_2$- saturated samples. For example, the average UCS reductions for coal samples saturated with subcritical CO$_2$ (6 MPa) and supercritical (8 MPa) are 42.84% and 58.77%, respectively. While a 5.56% UCS reduction increment was observed as the average UCS reduction increased from 37.28% (4 MPa CO$_2$ saturation) to 42.84% (6 MPa CO$_2$ saturation), a much higher 15.93% increment was recorded when the average UCS

<table>
<thead>
<tr>
<th>Saturation condition</th>
<th>Average UCS (MPa)</th>
<th>ΔUCS(%)</th>
<th>Average E (GPa)</th>
<th>ΔE (%)</th>
<th>Average $\nu$</th>
<th>Δ$\nu$(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>46.07</td>
<td>–</td>
<td>3.37</td>
<td>–</td>
<td>0.263</td>
<td>–</td>
</tr>
<tr>
<td>2 MPa CO$_2$</td>
<td>30.50</td>
<td>33.80</td>
<td>2.21</td>
<td>34.36</td>
<td>0.286</td>
<td>8.75</td>
</tr>
<tr>
<td>4 MPa CO$_2$</td>
<td>28.90</td>
<td>37.28</td>
<td>2.08</td>
<td>38.32</td>
<td>0.291</td>
<td>10.65</td>
</tr>
<tr>
<td>6 MPa CO$_2$</td>
<td>26.33</td>
<td>42.84</td>
<td>1.87</td>
<td>44.46</td>
<td>0.298</td>
<td>13.31</td>
</tr>
<tr>
<td>8 MPa CO$_2$</td>
<td>19.00</td>
<td>58.77</td>
<td>1.27</td>
<td>62.43</td>
<td>0.331</td>
<td>25.86</td>
</tr>
<tr>
<td>10 MPa CO$_2$</td>
<td>17.18</td>
<td>62.71</td>
<td>1.14</td>
<td>66.04</td>
<td>0.345</td>
<td>31.18</td>
</tr>
<tr>
<td>Water</td>
<td>32.06</td>
<td>30.41</td>
<td>1.88</td>
<td>44.16</td>
<td>0.307</td>
<td>16.73</td>
</tr>
<tr>
<td>Water+6 MPa</td>
<td>23.06</td>
<td>48.13</td>
<td>1.66</td>
<td>50.69</td>
<td>0.321</td>
<td>22.05</td>
</tr>
<tr>
<td>Water+8 MPa</td>
<td>14.53</td>
<td>68.46</td>
<td>0.97</td>
<td>71.29</td>
<td>0.364</td>
<td>38.40</td>
</tr>
</tbody>
</table>

Note: one sample under 8 MPa CO$_2$ saturation showed significantly low strength values, probably due to damage during the transportation process. Therefore, it was eliminated from discussion of the results.
reduction increased from 42.84% (6 MPa CO₂ saturation) to 58.77% (8 MPa CO₂ saturation). For the water-saturated coal samples, an average UCS reduction of 30.41% was recorded compared with untreated samples. Strength reduction was reinforced for coal samples saturated with CO₂ + water compared with single water saturation and the corresponding CO₂ saturation, as the average UCS of water + 6 MPa CO₂ saturated samples and water + 8 MPa CO₂ saturated samples were determined to be 23.90 MPa and 14.53 MPa respectively. This indicates a further 5.29% strength reduction compared with 6 MPa CO₂ saturated samples, and a 9.69% strength reduction compared to 8 MPa CO₂ saturated samples.

With respect to the stress-strain responses of coal samples during compression, more ductile characteristics were observed for CO₂ treated coal samples. As shown in Fig. 2(a), brittle failure was found after peak stress for untreated samples, while for CO₂ saturated samples, gradual stress reduction with greater strain was observed until sample failure. This softening behaviour was further enhanced when the samples were exposed to supercritical CO₂, since those samples showed a milder stress reduction gradient with larger axial and lateral strain. Similarly, fewer brittle characteristics were captured for water-saturated samples, and a more progressive stress reduction was found for water + CO₂ saturated samples. It can therefore be concluded that CO₂ saturation, water saturation and water + CO₂ saturation change the failure mechanism of coal samples from brittle to more ductile because of the improved ductile characteristics. This can be further confirmed by the variation of Young’s modulus, which is discussed in Section 3.2.

As stated earlier, the adsorption of a more chemically-reactive adsorbate leads to the reduction of surface energy of the adsorbent, and consequently reduced strength (Gibbs, 1878; Griffith, 1921). CO₂ is generally considered to be a fluid with high chemical potential, and the porous nature of coal allows the coal matrix to absorb a considerable amount of CO₂, resulting in an altered coal structure, as indicated in Table 4 with SEM images. The pre-existing cleats and fractures within the sample expand with the adsorption of CO₂, and new fractures are induced during this process, which contributes to the strength reduction of CO₂ treated samples. This can be further justified by the failure patterns of the samples as shown in Fig. 4, Fig. 4(a) and (b) present the post-failure patterns of an unsaturated sample and a subcritical CO₂ permeated sample, respectively. The unsaturated coal sample reveals a burst shear-dominated collapse along the axial direction while the subcritical CO₂ treated sample shows axial splitting along the major cleat seated in the direction of loading accompanied by a shear-like collapse, which suggests that the major cleats of the sample were weakened after CO₂ saturation.

The greater strength reduction for the supercritical CO₂-saturated sample correlates with greater structural alterations. As supercritical CO₂ is credited with a higher affinity to coal than subcritical CO₂ (Bae and Bhatia, 2006), more CO₂ is adsorbed in coal, which induces greater swelling of coal since swelling is proportional to the sorption volume (Cui et al., 2007). Furthermore, the greater swelling phenomenon leads to greater cleat expansion and the generation of new fractures in the coal. The failure pattern of a supercritical CO₂-treated sample shown in Fig. 4(c) shows that the presence of many fractures along the loading direction indicates the collapse of the supercritical CO₂—treated sample occurred as a result of failures along the major and minor cleats. In addition, coal is considered to be an organic sedimentary rock which includes different organic matters, while supercritical CO₂ has shown its ability to serve as an unconventional alternative source to traditional organic solvents (Peach and Eastoe, 2014). As the adsorbed supercritical CO₂ acts as a solvent of the organic compounds in coal, a certain amount of small hydrocarbon molecules can therefore be mobilised and extracted from coal, further contributing to the alteration of the coal structure. For all the above reasons, greater strength reduction occurs when coal samples encounter supercritical CO₂.

Interestingly, when the CO₂ saturation pressure increased from 8 to 10 MPa, only small increments in the average UCS reduction were observed, as indicated in Fig. 3. A number of studies have shown that significant permeability reduction due to coal matrix swelling can be expected after exposing coal to supercritical CO₂ (Cui et al., 2007; Day et al., 2010; Pan et al., 2010; Qu et al., 2014; Ranathunga et al., 2017). Furthermore, physical compression of coal samples in a high-pressure environment further contributes to reductions in permeability due to the narrowed cleats. Therefore, the passage of CO₂ through coal is compromised due to the reduced permeability, which leads to less weakening of coal when the supercritical CO₂ pressure is further increased.

Compared with the results obtained by Ranathunga et al. (2016), who examined the effect of various CO₂ saturation pressures on variations in the mechanical properties of brown coal, greater UCS reductions were captured in the present study using bituminous coals. This is attributed to the fact that the longer coalification process that bituminous coal experiences leaves bituminous coal with a more developed cleat system, allowing a greater amount of CO₂ to be adsorbed into the coal matrix, which generates greater strength reductions. In addition, the relatively soft nature of brown coal indicates that brown coal is more sensitive to pressure, and greater contraction of brown coal occurs with increasing pressure, which restricts the flow path for CO₂ passage. Therefore, lower strength reduction after CO₂ saturation can be expected for low rank coal. It should be noted that other physical characteristics including cleat density and fracture abundance and patterns also influence the overall strength of coal.

For the water-saturated samples, the polar sites in coal surfaces favour bonding with water molecules through hydrogen bonds, and clusters of water molecules are generated as more and more molecules gather around through hydrogen bonding with other molecules nearby (Day et al., 2008). Therefore, coal’s surface energy is reduced due to the increase of water molecules inside it and consequently, sample strength is reduced. In addition, coal swells with the adsorption of moisture, and the expansion of either surface of the fractures produces considerable compression in the coal sample, which causes impaired mechanical characteristics. The failure pattern of a water-treated sample further demonstrates the weakening effect upon water adsorption. As shown in Fig. 4(d), the sample failed along the major cleats seated in the loading direction, which emphasizes that water saturation causes considerable changes in response to stresses. Compared with the results obtained by Vishal et al. (2015), who adopted two sets of bituminous coal samples and calculated strength reductions of 25.5% and 7.0% after water saturation, respectively, higher UCS reduction (30.41%) was observed in the present study. The average UCS value for the untreated sample in...
this study is 46.07 MPa, which is more than three times the values in their study (15.29 and 15.03 MPa). This indicates that the coal sample used here has a more compacted mass property, as shown in Fig. 5. Moreover, the brighter appearance of the sample used in this study suggests that more vitrinite is present, which indicates that the rank of the coal used here is higher than the coal used by Vishal et al. (2015). Generally, the more fine-developed the cleat system in higher rank coals permits a greater moisture intake, resulting in a greater response to water saturation. The two sets of coal samples in their study were recovered from the same coalfield, which highlights the inherent heterogeneity of the geo-mechanical characteristics of coal, even for the same rank coal from the same reservoir. Therefore, the coal samples used in the present study were carefully selected to minimise heterogeneity.

Compared to the UCS reductions of single fluid (CO₂ or water)-saturated samples, samples treated with both CO₂ and water exhibited greater UCS reductions. This shows that the coupled effect of water and CO₂ saturation on strength deterioration is more prominent than single fluid saturation. Studies have shown that the injection of CO₂ into coal can change the contact angle of water on the coal surface, and therefore alter the wettability of coal (Ibrahim and Nasr-El-Din, 2016; Sakurovs and Lavrencic, 2011). Compared with the adsorption capacity of CO₂ in dry coals, the amount of CO₂ adsorbed in wet coal significantly decreases due to the sorption competition between water molecules and

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Fig. 4. Physical appearance after failure (a) unsaturated, (b) subcritical CO₂-saturated (6 MPa), (c) supercritical CO₂—saturated (8 MPa), (d) water saturated, (e) water + 6 MPa CO₂, (f) water + 8 MPa CO₂.

Fig. 5. Physical appearance of sample used a) in present study. b) in Vishal et al. (2015).
CO₂ molecules. However, this reduction correlates with coal rank, and high rank coal tends to be less affected by the presence of moisture, as the lower proportion of polar sites in high rank coal limits the interactions between water molecules and polar sites (Arif et al., 2016; Day et al., 2008). Therefore, it can be inferred that water saturation did not cause much reduction of CO₂ adsorption into coal in the present study, since the coal samples used in the study are bituminous coal, and the greater UCS reductions for CO₂ + water saturated samples were the results of the coupled and enhanced effects of CO₂ and water.

This enhanced strength reduction became more pronounced for samples with exposure to supercritical CO₂ + water, as shown in Fig. 6. Li et al. (2017) indicated the complicated geochemical reactions which occur during the interaction between coal and supercritical CO₂ + water. Clay minerals precipitate during the contact between carbonate water and mineral matters in coal (Li et al., 2017), and these clay minerals expand upon the adsorption of water, which causes strength reduction of coal. Besides, the solvated water in supercritical CO₂ is significantly reactive to mineral matter (McGrail et al., 2009), and the interplay between coal and supercritical CO₂ + water results in the mobilization and dissolution of mineral matter to a certain degree, which leads to reduced strength. This is further discussed in Section 3.4 with the interpretation of Fig. 9. In addition, extraction of organic substances due to supercritical CO₂ further contributes to weakening coal mass. The failure pattern of a water + CO₂− saturated sample clearly highlights that considerable strength reduction takes place as multiple failure planes along the loading direction, as indicated in Fig. 4(e) and (f). Moreover, the SEM images in Table 4 show that generation of micro-cracks within the coal sample occurred after the sample was treated with supercritical CO₂ + water. Although the presence of moisture in coal limits the amount of CO₂ adsorbed, resulting in less alteration of water-saturated coal samples compared to dry samples, water-saturated samples have already partly altered because of water adsorption, which indicates that the total structural alteration due to the adsorption of water and CO₂ is greater than the single CO₂ adsorption-induced structural alteration in dry coals. Overall, the above reasons collectively cause greater strength deterioration for water + CO₂− saturated samples.

It should be noted that in real field applications, coal seam is subjected to considerable lithostatic pressures and temperatures. Such conditions are not included in this test due to the extensive time required to saturate and fail the sample subjected to confining pressures. Strength reduction due to the adsorption of CO₂ or water in real application scenarios is expected to be lower than the values observed in this study, because higher effective stress correlates with lower permeability which restricts the interaction between coal and sorption fluids. Although the unconfined compressive test could not completely represent the real field case, it provides general information on the variations of mechanical behaviours of coal with CO₂ and water saturation, and also can act as a reference to future works which incorporates the confining stress on the weakening effect of coal mass subjected to fluid saturations.

3.2. Young's modulus variations

The stiffness alterations of the coal samples were then analysed by examining the Young's modulus variations. As shown in Table 1, after saturation with CO₂, all the coal samples exhibit a reduction in Young's modulus, and this reduction increases with increasing CO₂ saturation pressure, especially for supercritical CO₂-saturated samples. For example, the average Young's modulus reduction increased from 38.32% to 44.46% and showed a 6.14% increment when the CO₂ saturation pressure changed from 4 MPa to 6 MPa, while a nearly triple increment of 17.97% was found when the CO₂ saturation pressure increased from 6 MPa to 8 MPa. Water saturation caused a 44.16% reduction of average Young's modulus as it dropped from the original value of 3.37 GPa–1.88 GPa, and this reduction was further enhanced for samples saturated with water + 6 MPa CO₂ (50.69%) and water + 8 MPa CO₂ (71.29%).

The reduction of Young's modulus after CO₂ or water saturation indicated that the ductile properties of coal samples had improved during the saturation period. Studies have shown that the interaction between the adsorbed CO₂ and coal structure causes swelling of coal, and the CO₂ effused into the organic matter causes the structural rearrangement of coal samples during which the dissolved CO₂ acts as a plasticizer, softening the coal mass and improving the ductile properties (Larsen, 2004; Larsen et al., 1997). This can also be used to explain the Young's modulus reduction of water-saturated samples, since coal also swells after the adsorption of moisture. In addition, SEM images in Table 4 show an altered surface roughness of water saturated sample, previous studies of fracture mechanics have found that increasing moisture content causes the fracture toughness to be reduced by enlarging the fracture process zone which embraces considerable micro-cracking (Nara et al., 2012; Zhou et al., 2018). The reduced fracture roughness and the free water present in fractures of water-saturated samples reduce resistance during fracture development, which facilitates the propagation of the fractures and improves the ductility of water-saturated samples. Besides, since the SEM images clearly present a smoother surface texture after each saturation, this smoothed surface enhances the normal stresses at specific asperities, as the changes of surface roughness cannot be homogenous for the two surfaces between a specific cleat (Hol et al., 2014), this would further contributes to the reduction of stiffness. Similar to the UCS variation, greater Young's modulus reduction was found for water + CO₂-saturated samples, especially for the water + 8 MPa CO₂-saturated sample. As explained previously, coal shows higher matrix swelling with the adsorption of supercritical CO₂ which causes greater structural alteration, and this greater structural alteration is further enhanced by the presence of water. In addition, supercritical CO₂ exists in an intermediate phase between gaseous CO₂ and liquid CO₂, and its liquid-like density, gas-like viscosity and surface tension allow greater infiltration into coal, especially in the aqueous-phase environment. As a result, more organic constituents are mobilised and extracted, which adds to the plasticization of the coal sample by rearranging the coal structure from the original strained state to a more relaxed form.

However, for samples saturated only with CO₂, with further increasing the saturation pressure to 10 MPa, only small Young's modulus reductions were found, as shown in Table 1. Since prominent permeability reductions occur for coal samples upon exposure to supercritical CO₂, the swelling and the plasticization of coal abate.
dissolution of organic and mineral matter significantly alters the coal structure, and the rearranged coal structure is no longer able to absorb a large amount of CO₂ when the pressure is further increased. In other words, CO₂ is less soluble in this rearranged coal structure. Overall, it can be inferred that, based on the results of the present study, coal strength can be greatly impaired by CO₂ or water adsorption, and this weakening effect intensifies with CO₂ saturation pressure, especially for supercritical CO₂ saturation. The maximum reduction in coal strength occurred for the coupled water + CO₂ treated sample, which is the most likely scenario encountered in field operations for either ECBM recovery or CO₂ sequestration. The strength reduction of the host coal seam affects the permeability and integrity of the seam. Permeability reduction restrains the injection process of CO₂ as well as the drainage of CH₄, while the weakened coal seam poses a great threat to long-term CO₂ storage. This highlights the importance of maintaining the low-level water pressure of the host seam during field operations.

### 3.3. Acoustic emission analysis

Acoustic signals were collected and analysed to interpret the crack propagation of the coal samples during monotonous loading using a PCI-2-based acoustic emission (AE) system. Two AE sensors were glued on either side of the sample using electron wax. The amplifiers were adopted to intensify the low-frequency acoustic waves during crack development. Based on the measured background noise level, a threshold value of 40 dB was selected. The AE energy released during sample compression was received by the sensors and processed in the data acquisition system when the amplitude of the signals exceeded the threshold value.

Three stages, namely crack closure, stable crack propagation and unstable crack propagation, can be identified during crack development until the sample fails, based on the cumulative AE energies. Crack closure is defined as the stage from the very beginning of the contact between the sample and load until the inherent cracks within the sample close due to compression, during which insignificant AE energies are captured. Then the stable crack propagation stage commences from crack initiation stress (σci) until crack damage stress (σcd). At this stage the load applied on the sample causes some minor damage to the sample with a stable increase of cumulative AE energies. With further increase in load, the unstable crack propagation stage initiates until the sample fails with a rapid increase of cumulative AE energies due to rapid fracture generation. Table 2 shows the stress threshold values obtained from the AE readings for the tested samples, and Fig. 7 incorporates the cumulative AE energies with compression stress for untreated, 6 MPa CO₂ (subcritical) saturated and 8 MPa CO₂ (supercritical) saturated samples.

According to Fig. 7, in terms of the variation of cumulative AE energies with stress, the same behaviours were displayed for untreated and CO₂-saturated samples, with a minor increase of AE energies during stable crack propagation followed by a rapid increase of AE energies in unstable crack propagation. However, the total cumulative AE energies for CO₂-saturated samples decreased considerably compared with the untreated sample. This is because after CO₂ saturation, many micro-fractures had already been induced inside the sample, the intense and strained coal structure was converted into a more relaxed and low-energy state due to coal swelling, which reduces the energy needed for crack generation during loading.

### Table 2

<table>
<thead>
<tr>
<th>Saturation condition</th>
<th>σci (MPa)</th>
<th>σcd (MPa)</th>
<th>UCS (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsaturated</td>
<td>23.46</td>
<td>44.88</td>
<td>48.35</td>
</tr>
<tr>
<td>2 MPa CO₂</td>
<td>18.29</td>
<td>28.96</td>
<td>32.01</td>
</tr>
<tr>
<td>4 MPa CO₂</td>
<td>16.53</td>
<td>27.37</td>
<td>30.23</td>
</tr>
<tr>
<td>6 MPa CO₂</td>
<td>14.88</td>
<td>25.18</td>
<td>27.69</td>
</tr>
<tr>
<td>8 MPa CO₂</td>
<td>9.26</td>
<td>18.10</td>
<td>19.32</td>
</tr>
<tr>
<td>10 MPa CO₂</td>
<td>7.18</td>
<td>14.96</td>
<td>17.85</td>
</tr>
<tr>
<td>Water CO₂</td>
<td>26.72</td>
<td>31.25</td>
<td>33.04</td>
</tr>
<tr>
<td>Water + 6 MPa CO₂</td>
<td>16.91</td>
<td>20.35</td>
<td>23.35</td>
</tr>
<tr>
<td>Water + 8 MPa CO₂</td>
<td>13.33</td>
<td>15.28</td>
<td>16.01</td>
</tr>
</tbody>
</table>

### Fig. 8

Cumulative AE energies vs. axial stress for natural, 6 MPa and 8 MPa CO₂-saturated samples.
increase of the crack initiation stress of the water-saturated sample as indicated in Table 2 compared with the value of the untreated sample further illustrates the reduction of energy release due to the presence of water in cracks.

The effect of water + CO₂ saturation on AE energy release was then considered. As depicted in Fig. 8, the total AE energies for water + CO₂− treated samples reduced considerably compared with the respective single CO₂ saturation sample, and this reduction is significantly higher for the sample saturated with water+8 MPa CO₂, which further verifies the reinforced weakening effect with the presence of both water and CO₂. According to Figs. 7 and 8, there are notable reductions of stable crack propagation duration for the water + CO₂ saturated sample compared with that for the single CO₂ or water saturation. In addition to the weakening effect of water and CO₂ adsorption, the lubricating effect of free water is reinforced by the presence of increased initial cracks, and this further leads to the increment of crack initiation stress for water + CO₂ saturated samples compared with the associated single fluid saturations, as indicated in Table 2.

### 3.4. Strain behaviour and microstructural analysis

The strain behaviours of the samples were captured by a 3-D deformation measuring system and the axial strains at failure of the samples under different saturation conditions are summarized in Table 3.

According to Table 3, the maximum strain at failure for the samples increases with increasing CO₂ pressure. This emphasizes that the ductile properties of the coal samples improved after exposure to CO₂ and this improvement is considerably stronger for supercritical CO₂ adsorption, which is in accordance with the previous analysis of stress-strain behaviour and Young's modulus variations. The water-treated sample exhibited a higher strain value of 1.24% compared with an untreated sample (1.03%) due to the enhancement of ductile properties after water adsorption. Greater strains were observed for samples treated with water + CO₂, which further confirms that the adsorption of water and CO₂ at the same time causes greater improvement in ductile properties than single fluid saturation.

In addition, the microstructural alterations of coal after each saturation were obtained from SEM images in order to further understand the observed mechanical behaviours. An untreated sample was used as a control. Images were taken at a 10 mm working distance, with 10 kV accelerated voltage and a 47 pA probe current. As shown in Table 4, an untreated sample exhibits a relatively rough surface with large pores, while smoother surfaces with smaller pores were present on CO₂-treated samples. This further supports the previous analysis of strength reduction due to structural rearrangement for CO₂-saturated samples.

Similar results have been reported by previous researchers (Gathitu et al., 2009; Masoudian et al., 2014; Ranathunga et al., 2016). In addition, strip structures appear in the images of CO₂-saturated coal samples, and these striations are believed to be carbon structures which possess similar structural patterns to maceral collinite. These carbon structures are generated as a result of the interaction between CO₂ and coal (Davis et al., 1986). Some micro-cracks were also observed in the SEM images of the CO₂-treated samples, and these micro-cracks are believed to be the cause of the strength reduction for CO₂-saturated samples, since the adsorbed CO₂ in the coal converts the strained coal structure to a more relaxed form, and these micro-cracks in the coal may be the result of coal structure relaxation as the development of cracks is accompanied by strain energy release until the coal structure reaches a low energy state.

Similar to the CO₂-saturated sample, an altered micro-structure occurred in the water saturated sample and these structural changes are clearly greater in water + CO₂− saturated samples. Water + CO₂ saturated samples were also found to be covered with a layer of dust-like material after they were recovered from the saturation cell. The dust was collected and analysed using SEM and energy-dispersive-X-ray (EDX) and the results are indicated in Fig. 9. As EDX is not an ideal tool to perform quantitative analysis, it is best regarded as qualitative in nature. Therefore, according to the figure, the dust-like materials are minerals extracted from coal and identified as CaCO₂. The injection of CO₂ into an aqueous environment under pressure results in greater CO₂ dissolution, and the reaction sequence of CO₂ dissolution can be interpreted using Eq. (1):

\[
\text{CO}_2(g) + H_2O \rightleftharpoons \text{CO}_2(aq) + H_2O \rightleftharpoons H^+ + HCO_3^- \tag{1}
\]

Carbonate reactions between the dissolved CO₂ and calcite therefore take place in this enhanced acidic environment during the saturation period for water + CO₂− treated samples as follows:

\[
2\text{HCO}_3^- + Ca^{2+} \rightleftharpoons \text{CaCO}_3 + \text{CO}_2 + H_2O \tag{2}
\]

These observations suggest that mineral dissolution intensifies with the joint presence of water and CO₂, which causes greater strength reduction for water + CO₂-treated samples.

### 4. Conclusions

Deep coal seams have been shown to be a sensible option for permanent CO₂ disposal, with or without concomitant coalbed methane. The injection of CO₂ into coal seams changes the geo-mechanical attributes of coal, and the presence of moisture in coal complicates the interaction between coal and CO₂. Therefore, this experimental study was conducted to evaluate the effect of CO₂, water, and CO₂+water saturation on coal. A series of strength experiments was carried out on bituminous coal samples. Strain variations and failure patterns were obtained using a 3-D deformation measuring system. The micro-structures were profiled with SEM images and acoustic energy release was captured employing an acoustic emission system. The following major conclusions can be drawn:

**Coal strength reduces with CO₂ saturation as a result of structural alterations due to the adsorption of CO₂, and this reduction increases with increasing saturation pressure, especially for supercritical CO₂ saturation, because supercritical CO₂ has greater adsorption affinity, which results in greater structural alteration.**

Water saturation weakens coal strength, and this weakening effect is enhanced in the presence of CO₂, with a further 5.29% and 9.69% reduction when introducing 6 MPa and 8 MPa CO₂, respectively. This suggests that desirable seam reservoirs should keep the water pressure at lower levels during CO₂ injection.

Water or CO₂ saturation causes coal samples to relax with increased Young's modulus, and a more progressive stress reduction was obtained for water + CO₂− treated samples. The free water in cracks facilitates crack propagation, resulting in improved ductile behaviour. Larger strains were observed until sample collapse compared with untreated samples which showed shear-dominated collapse.

Acoustic emission energies reduce significantly after CO₂ or water saturation, especially for water + CO₂ saturated samples due to the generation of micro-cracks as well as the lubricating effect of free water in cracks, and this also leads to increased crack initiation stress and reduction of stable crack propagation.

The micro-structure of coal obtained from SEM images further supports the above conclusions on the effect of CO₂ and water saturation.
saturation on coal’s mechanical characteristics, with altered surface roughness, generation of micro-cracks and mineral dissolution after saturation.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jngse.2018.11.010.

References


Table 4
Microstructural alterations of samples.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Natural</th>
<th>Subcritical CO2-treated</th>
<th>Supercritical CO2-treated</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEM images</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Condition</td>
<td>water</td>
<td>Water+6MPa CO2</td>
<td>Water+8MPa CO2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 9. (a) SEM image of extracted mineral; (b) EDX analysis of extracted mineral.