Investigations of CO₂-water wettability of coal: NMR relaxation method

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Abstract
Carbon geo-sequestration (CGS) and recovery enhancement with carbon dioxide injection (CO₂-ECBM) have brought increasing focus on the CO₂ and water wettability of coal. The CO₂ and water contact angles measured using existing conventional methods, such as the pendent drop tilting plate technique and the captive-bubble technique, show low reproducibility due to coal heterogeneity and operational complexity. In this study, a novel NMR-based approach was developed to evaluate the CO₂ and water wettability of coal. The experimental results of nine bituminous and anthracite coals show that water wettability can be linearly correlated with the changes of the $T_2$ spectra peak positions. Based on the measured contact angle from the profile of the water adhering to the coal powder disc and the $T_2$ from the NMR of coal powder, we proposed a linear formulation to evaluate the contact angle using the change of $T_{2g}$ of P3. Using this method, we analyzed the CO₂-water wettability characteristics of coal. The results show that CO₂ reduces the water wettability of coal. Low temperature and/or high CO₂ pressure can enhance the CO₂ wettability of coal. The change of water-coal wetting behavior with injection of CO₂, is resulted by three factors: change of CO₂ adsorption capacity of coal, change of interfacial tension, and dissolution of CO₂ in water. This study makes it possible to evaluate changes in the water and CO₂ wettability of coal, which is essential for evaluating the fluid-interaction mechanisms during the process of carbon geo-sequestration and enhanced coalbed methane recovery with carbon dioxide injection.

Keywords: CO₂ sequestration; coalbed methane; coal; wettability; relative permeability

1. Introduction
Coal seams offer great potential for carbon geo-sequestration (CGS) with the accompanying benefit of recovery enhancement with carbon dioxide injection (CO₂-ECBM) (Ozdemir, 2009; Gentzis, 2000; Busch and Gensterblum, 2011). CO₂ sequestration into coalbeds is largely controlled by the interactions between the coal matrix and CO₂ and other reservoir fluids. In particular, the wettability of coal controls the pore scale fluid configuration and thus has a strong effect on capillary pressure, relative permeability and fluid invasion mechanisms (Chalbaud et al, 2006; Chaturvedi et al., 2009; Han et al., 2010; Iglauer et al., 2015; Zhou et al., 2016).

In the context of reservoir engineering, coalbed methane (CBM) reservoirs consist of cleats and matrix pores that are saturated with water: fluid flows in large cleats according to Darcy’s law,
whereas the diffusion-driven transport of gas occurs in coal micropores. The performance of CO₂ for CGS or CO₂-ECBM may be different for hydrophobic (gas-wet) and hydrophilic (water-wet) reservoirs. For a hydrophobic reservoir, micropores are occupied by gas, which leads to the much faster transport of the injected gas into the coal matrix. In contrast, if pores are filled with water, the transport of the injected gas in a hydrophilic reservoir is very slow due to the difficulty of gas diffusion through the water (Siemons et al., 2006; Kaveh et al., 2012). Hence, it is essential to quantify the wettability of coal to improve our understanding of the mechanisms of gas/water flow in coal seams.

Several quantitative and qualitative methods were used to evaluate the wettability of rock, including the contact angle measurement (Johnson and Dettre, 1969), the Amott method (Amott, 1959), the USBM wettability index (Donaldson et al., 1969), spontaneous imbibition (Bobek et al., 1958), the flotation method (American Petroleum Institute, 1962), displacement capillary pressure (Benner et al., 1942) and others (Meng et al., 2017). Among these methods, the Amott, USBM wettability index and displacement capillary pressure methods measure wettability by operating displacement tests. However, it is extremely difficult to perform these tests in unconventional low-permeable samples, such as coal and gas shale (Xu and Dehghanpour, 2014; Iglauer, 2017), which thus limits their application to wettability measurements. The spontaneous imbibition rate/volume test allows us to indirectly indicate the wettability of coal and gas shale (Gao and Hu, 2016), but it fails to obtain any quantitative index for wettability characterization. Similarly, the flotation method, which is a fast and simplified operations measurement, is strongly influenced by coal particle size and the distribution of coal powder on the water, even though it is commonly used in the coal cleaning and flotation industry (Fuerstenau et al., 1987). Moreover, determining the immersion time in the flotation method is subjective and depends on personnel experience since there is no explicit standard of judgment on the immersion time.

The contact angle measurement is the most commonly used method for research of the wettability of coal (Wei et al., 1992; Orumwense, 1998; Anderson, 1986; Arnold and Aplan, 1989). However, the evaluated coal wettability may sometimes be inaccurate using the contact angle measurement because coal is an extremely heterogeneous material with significant variation in its physical and chemical properties, even on a polished coal sample surface. According to Keller (1987), the coal compositions of paraffinic hydrocarbon, aromatic carbon, and minerals are strongly hydrophobic, intermediate water-wet and strongly water-wet, respectively. Therefore, the heterogeneity in coal composition can result in high wettability heterogeneity with non-uniform spatial contact angle distribution in a coal sample (Wei et al., 1992; Siemons et al. 2006). To reduce the uncertainty during wettability measurements resulting from coal heterogeneity, coal powder discs, instead of a polished raw coal surface, are normally used to measure the contact angle (He and Laskowski, 1992; Zhou et al., 2016). However, the effect of disc porosity on the contact angle has still not effectively been solved (He and Laskowski, 1992). Moreover, it is difficult to prepare the sample and to compress coal discs with a polished plane, especially for anthracite coal with low clay mineral content. Thus, it is urgent to develop a quantitative methodology, with simple operation and high accuracy, to determine the water wettability of coal to perform successful CGS and CO₂-ECBM projects.
In the context of CGS and CO$_2$-ECBM, it is of great value to investigate variations in the water and CO$_2$ wettability of coal that are affected by the in situ reservoir temperature and pressure, as well as the gas adsorption and solution (Saghafi et al., 2014b; Kaveh et al., 2012; Sakurovs and Lavrencic, 2011; Siemons et al., 2006). In the literatures, contact angle measurement methods, including the pendent drop tilting plate technique (Arif et al., 2016) and the captive-bubble technique (Kaveh, et al., 2011; Ibrahim and Nasr-El-Din, 2016), have been used to obtain water/gas wettability in high-pressure CO$_2$-water conditions. According to the results of Siemons et al. (2006), Sakurovs and Lavrencic (2011) and Kaveh et al. (2012), the contact angles of CO$_2$ gas bubbles against coal surfaces in water cells decrease with increasing gas pressure, indicating that the coal became more CO$_2$-wet. Additionally, there is a linear relationship between the gas bubble contact angle and gas pressure (Sakurovs and Lavrencic, 2011). Arif et al. (2016) measured the advancing and receding water contact angles of different rank coals using the pendent drop technique. They found that the CO$_2$ wettability is independent of coal rank, and it increases with gas pressure and decreases with temperature. In these works, the contact angle of water-coal or gas-coal is measured from the profile of the water/gas bubble adhering to the surface. There are two major challenges in these measurements: the first is conducting the measurement in a high-pressure water/gas filled cell, and the other is that the measurement must be completed quickly. However, it is problematic to perform the measurement quickly, especially for the captive gas bubble technique, as it requires enough time for CO$_2$ to adsorb on the coal. Additionally, the fast measurement may induce uncertainty in the contact angle. Moreover, for the contact angle measurement by the captive gas bubble method, the dissolution of gas bubbles in water also introduces inaccuracy to the results (Saghafi et al., 2014a). In addition to the mentioned challenges, the measured contact angle also depends on the gas bubble size. More specifically, smaller bubbles have higher capacity to wet coal (Saghfi et al., 2014b). In general, conventional contact angle measurement methods are not capable of evaluating the wettability of real water-CO$_2$-coal systems in reservoirs.

The low field $^1$H Nuclear Magnetic Resonance (NMR) technique has been successfully used to quantitatively evaluate the wettability of porous media, such as conventional hydrocarbon reservoirs (Bortolotti et al., 2009; Johannesen et al., 2007; Zhang et al., 2000; Connolly et al., 2017) and soil (Manalo and Kantzas, 2003). For example, a recent research by Connolly et al. (2017) demonstrated that the successful use of the NMR to quantify capillary trapping during dynamic sandstone core flooding experiments at reservoir conditions. However, this method has not been applied successfully to measure the water-gas wettability of coal. In this work, we applied the NMR method to quantitatively characterize the wettability of coal. In contrast to existing methods, the NMR technique is nondestructive, fast and makes real-time measurements, in addition to providing reliable results. We also evaluate the changes in water wettability of coal under different CO$_2$ pressures and temperatures, which makes it possible to disclose the in situ interactions of fluids (water and CO$_2$) with coal in reservoir conditions. This study is significant for the following in-depth investigation of the potential effects of CO$_2$ and water wettability of coal on CGS and CO$_2$-ECBM.
2. Samples and methods

2.1. Samples

Nine coal block samples were collected from the underground coal mines of the Tarim, Ordos and Qinshui basins, China. All samples were carefully packed and immediately transported to the laboratory for vitrinite reflectance, maceral analyses and proximate analyses.

Six of the selected samples were crushed to powders of 0.18-0.25 mm in size. After moisture-equilibrium pretreatment, these powdered samples were conducted for CO$_2$ isothermal adsorption at a constant temperature of 25 °C and under pressures of up to 4.9 MPa following the Chinese GB/T 19560-2004 procedure.

2.2. Contact angle measurement

Contact angle measurements were performed on the high-pressure compressed disc artificial surface made from the powdered coal. Since coal is an extremely heterogeneous medium consisting of different macerals and minerals that have different surface properties, the crushed powder samples can average the surface of coal with different organic and inorganic compositions. To form a much smoother surface for the contact angle measurement, we used a very small particle size (0.074 mm) to prepare the powder samples. Each powder sample was dried in a vacuum-oven at 80 °C for 6 h and compacted at 30 MPa to form the coal discs. The compacted coal discs were kept in a vacuum container for constant angle measurements.

Contact angle measurements were conducted using an automatic contact angle meter equipped with 3 mega-pixel cameras and an LED light source. A special syringe and needle were used to fix the volume of the droplet to 10 μL to exclude the impact of drop size on the contact angle measurement. The profile of the drop on the coal disc was photographed through a zooming lens, and then the contact angle of the drop was measured (Fig. 1). The representative contact angles for each sample are the mean values of the contact angles measured on 30 different spots on each disc.
2.3. NMR measurements

The samples used for NMR measurements are powdered samples with coal particles of 0.18-0.25 mm. The powder samples were dried in a vacuum-oven at 80 °C for 6 h and then were put into a special made poly-Teflon sample cell for the NMR measurement. For the powdered samples in the sample cell, there are two types of pore voids: the inter-particle voids between coal particles, and intra-particle porosity within individual particles. It is well-accepted that the intra-particle porosity is much smaller than the inter-particle voids; thus, the intra-particle porosity can be neglected. Therefore, the inter-particle void porosity of packed coal powder can be calculated by:

\[ \phi = 1 - \frac{m}{\rho V_c} \]

where \( \phi \) is the inter-particle void porosity; \( V_c \) is the volume of the poly-Teflon sample cell; \( m \) is the powdered coal mass and \( \rho \) is the coal density. To keep all the samples in vials with the same void porosity, the same volume of coal powder was prepared by measuring the coal density \( \rho \) and coal powder weight. Then, we can obtain the same inter-particle void porosity by packing the coal powder with the same volume into the same vials. In this study, the inter-particle porosity of the sample, \( \phi \), remains constant at 30%.

Four series of experiments, A-D, were completed (Table 1). For the sample preparation of the series A-D, coal powder and 1 mL of distilled water were put into the sample cell, and then the sample cell was wrapped with plastic sheeting to keep the surface water from evaporating and the coal powder from oxidizing. First, the wrapped sample cell was placed in the NMR magnetic coil.
for experiment series-A. In this series, the $T_2$ spectra of nine samples were measured every hour to monitor the change of water in the coal. Second, experiment series-B was conducted on 6 coal powder samples to study the effect of CO$_2$ on the water wettability. In series-B, the relative changes of the $T_2$ spectra were measured at a constant 4-MPa CO$_2$ gas pressure and experimental temperature of 25 °C. Third, in series-C, the operation for samples SYQ and WTP was the same as experiment series-B except for the CO$_2$ pressures (2 and 6 MPa). Finally, experiment series-D was conducted for samples FK and GH with the same process as series-B except at different temperatures (35 and 45 °C). The purpose of conducting series-D is to investigate the effects of temperature on the water and CO$_2$ wettability of coal.

Table 1 Four experimental series and their experimental conditions

<table>
<thead>
<tr>
<th>Experiment Series</th>
<th>Sample</th>
<th>Fluid</th>
<th>Pressure (MPa)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>TA, FK, YX, SYQ, CYH, HY, GH, SJZ, WTP</td>
<td>Water</td>
<td>0.1</td>
<td>25</td>
</tr>
<tr>
<td>B</td>
<td>TA, FK, SYQ, GH, SJZ, WTP</td>
<td>CO$_2$</td>
<td>4</td>
<td>25</td>
</tr>
<tr>
<td>C</td>
<td>SYQ, WTP</td>
<td>CO$_2$</td>
<td>2 and 6</td>
<td>25</td>
</tr>
<tr>
<td>D</td>
<td>FK, GH</td>
<td>CO$_2$</td>
<td>4</td>
<td>35 and 45</td>
</tr>
</tbody>
</table>

In this study, the Carr–Purcell–Meiboom–Gill (CPMG) sequence was used to measure the $T_2$ distributions. The parameters of the NMR measurement are as follows: the echo spacing is 0.3 ms, the echo-train is 64, the wait time is 3 s and the echo number is 18000.

3. Results and discussion

3.1. Characterization of coal samples

The results of the vitrinite reflectance, maceral analyses and proximate analyses are listed in Table 2. The selected coals are high-volatile bituminous coal to anthracite coal, representing a broad range of coal ranks and litho-type compositions. The mean maximum vitrinite reflectance in oil ($R_o$, %) of the coal ranges from 0.8% to 3.13%. The coal macerals are mainly characterized by intermediate to high vitrinite corresponding to intermediate to low inertinite, plus minor proportions of liptinite.

The results of the CO$_2$ adsorption experiments are given in Table 3. The Langmuir volumes of the selected six coal samples range from 27.54 to 57.73 m$^3$/t (as-received-base), with the minimum value for the sample TA.

Table 2 Results of petrological composition analysis and coal proximate analysis of selected coals.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Basin</th>
<th>Coalmine</th>
<th>$R_o$</th>
<th>Vol. %</th>
<th>Proximate Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$V^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(%)</td>
</tr>
</tbody>
</table>
The measured contact angles for the nine samples vary from 53° to 118° (Table 3). Coal sample FK is the strongest water-wet, with a contact angle of 53°, whereas HY is the weakest water-wet, with a contact angle of 118°. The contact angle is related to coal rank and coal petrological composition. As shown in Fig. 2, the contact angles increase with coal rank at \( R_o \) values of 0.8%-1.8%, and then they decrease slightly with increasing coal rank at \( R_o \) values of >1.8%. The maximum of the contact angle is observed at coal rank from medium-volatile bituminous coal to low-volatile bituminous coal, which agrees well with the results reported by Horsley and Smith (1951). Moreover, contact angles show a positive correlation with vitrinite group contents (Fig. 2) because the vitrinite group is more hydrophobic than the inertinite group (Arnold and Aplan, 1989).

Table 3 The CO\(_2\) isothermal adsorption analyses and contact angles of water on selected coal disc surfaces.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>TA</th>
<th>FK</th>
<th>YX</th>
<th>SYQ</th>
<th>CYH</th>
<th>HY</th>
<th>GH</th>
<th>SJZ</th>
<th>WTP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir volume (m(^3)/t)</td>
<td>27.54</td>
<td>38.73</td>
<td>-</td>
<td>31.64</td>
<td>-</td>
<td>-</td>
<td>57.73</td>
<td>42.78</td>
<td>48.14</td>
</tr>
<tr>
<td>Langmuir pressure (MPa)</td>
<td>0.69</td>
<td>0.7</td>
<td>-</td>
<td>2.13</td>
<td>-</td>
<td>-</td>
<td>1.35</td>
<td>1.47</td>
<td>1.09</td>
</tr>
<tr>
<td>Contact angle(°)</td>
<td>79</td>
<td>53</td>
<td>79</td>
<td>74</td>
<td>87</td>
<td>118</td>
<td>96</td>
<td>93</td>
<td>84</td>
</tr>
</tbody>
</table>
Fig. 2. The relationship between contact angles and a-mean maximum vitrinite reflectance in oil ($R_o$); b-volume percentage of the vitrinite group.

3.2. Determination of contact angle by the NMR method

3.2.1 Changes of $T_2$ spectra after water addition

According to the basics of NMR measurements, the $T_2$ of water in a homogeneous internal field gradient can be described by Eq. (2) (Howard et al., 1993; Kenyon et al., 1988),

$$\frac{1}{T_2} = \frac{1}{T_{2s}} + \rho_2 \frac{S}{V}$$

where $B$ is bulk relaxation; $\rho_2$ is the surface relaxivity and $S/V$ is the surface-to-volume ratio (Lowden et al., 1988). Bulk fluid relaxation relaxes slowly and signal peaks appear at longer relaxation times, which is an intrinsic property of the fluid. Surface relaxation relaxes rapidly and is affected by the interactions of the fluid with the surface (Coates et al., 1999; Yao et al., 2010, 2014).

The measured $T_2$ spectra of the coal powder samples with the addition of water indicate that different phases of water exist in the coal powder. As shown in the black solid line spectra in Fig. 3, there are three distinct $T_2$ spectrum peaks: P1, P2 and P3. P1, which is located at approximately 0.1-10 ms, represents the water in adsorption pores (with diameters of less than 0.1 $\mu$m) of individual coal particles. P2, located at approximately 10-100 ms, results from the surface relaxation of water in the seepage pores (more than 0.1 $\mu$m in diameter) of the individual coal particles (Sun et al., 2016). P3 (approximately 100-1000 ms) represents water in the inter-particle void space, which is dominated mainly by bulk water relaxation. Compared with the P1 and P3 peaks, the P2 peak appears to be too small. This means that the porosity of the seepage pores is relatively low in coal with a particle size of 0.2-0.3 mm (in diameter). Moreover, P2 is not detected for samples WTP and TA, which may result from the fast fluid exchange between bulk water and the water in the seepage pores.
The different $T_2$ spectrum curves for the same coal sample in Fig. 3 show different water conditions within the coal sample, i.e., representing the movement of water in the coal powder with time. There is a notable trend of increasing P1 and decreasing P3 after the addition of water into the coal powder. Meanwhile, P3 shifts leftward (toward the fast relaxation part). This suggests that the bulk water in the inter-particle space moves into the intra-particle pores, leading to decreases in the area of P3 and increases in the area of P1. The changes of the P3 position indicate that the bulk water between individual particles spreads to more inter-particle surfaces. The movement of water leads to the $T_2$ relaxation being influenced more by the coal particle surfaces, resulting in the shift of P3.

To eliminate or reduce the negative effects of fluid interactions on the measurement results, the weighted average of $T_2$, $T_{2g}$ (as defined in Eq. (3)), is used to quantify the change of peak position during a series of NMR measurements, and it is given as

$$T_{2g} = \exp\left[\sum \frac{\ln(T_{2i})A_i}{A_{total}}\right]$$

(3)
where $T_{2g}$ is the weighted geometric average of the $T_2$ distribution, $T_{2i}$ is the $i$th transverse relaxation time, $A_{total}$ is the total signal amplitude of the $T_2$, and $A_i$ is the signal amplitude of the $i$th $T_2$. A greater value of $T_{2g}$ indicates that the fluid resides in larger pores or is more affected by the bulk phase; conversely, a smaller value reflects fluid residing in smaller pores. The change of $T_{2g}$ indicates a shift of the $T_2$ spectra position, indicating the movement of fluid in pores (Guo and Kantzas, 2009). Thus, the $T_{2g}$ of P3 is calculated to quantify the change in the peaks. Moreover, the normalized $T_{2g}$ was used to measure the degree of peak changes for different coals.

Fig. 4 shows that the normalized $T_{2g}$ of P3 decreases with water residence time for the nine coal samples. The reduction trends of $T_{2g}$ are different from each other for these coal samples. For the same coal sample, the fastest decrease is noticed in the first 48 hours; then, the change decreases during 48-72 hours, which means the water in coal tends to approach an approximate equilibrium state after 48 hours. Thus, we assume that the water reaches an equilibrium state after 72 hours, when the change of the $T_{2g}$ spectra between 60 to 72 hours can be neglected.

![Fig. 4. The normalized $T_{2g}$ of P3 decreases for different coals.](image)

### 3.2.2. Determination of coal wettability by NMR

The ultimate normalized $T_{2g}$ of P3 has a positive linear correlation against the measured contact angles for coal discs (Fig. 5). As shown in this figure, a smaller ultimate normalized $T_{2g}$ of P3 value in the equilibrium state corresponds to a more water-wet coal sample. In contrast, a larger ultimate normalized $T_{2g}$ of P3 value relates to a less water-wet coal. This is because for stronger water-wet coal, a large surface wettability force drives the water in the inter-particle space accesses into more coal particle surfaces. In this situation, the migration of water is represented by the leftward movement of $T_2$ distribution and a smaller $T_{2g}$ value. We use the interfacial tension theory provided by Thomas Young (Young et al., 1805) to explain the mechanism of water migration. According to Young et al. (1805), the contact angle of a liquid drop on an ideal solid surface is defined by the mechanical equilibrium of the drop under the action of three interfacial tensions. The interactions between the three interfacial tensions are expressed by the Young-Laplace equation,
where $\delta_{lg}$ is the gas-water interfacial tension; $\delta_{sg}$ is the gas-solid interfacial tension; $\delta_{ls}$ is the solid-water interfacial tension and $\theta$ is the contact angle of water on the solid surface. In Eq. (4), $\delta_{sg}-\delta_{ls}$ is defined as surface wettability tension, which is the driving force of water migration on coal particle surfaces.

As mentioned above, for all samples, the inter-particle porosity and coal particle size are the same. Therefore, the different water spreading among coal powder results from different surface wettability tension for the coal samples. Moreover, the $\delta_{lg}$ remains constant for different coal samples at the same conditions (temperature, pressure and media). Thus, there is a negative correlation between surface wettability tension and $\theta$. For stronger water-wet coal with a small contact angle, a large surface wettability force drives the water to spread onto more coal particle surfaces. When the water in the inter-particle space spreads on more particles, the $T_2$ relaxation is influenced more by surface relaxation and leads to the $T_2$ value becoming smaller. Conversely, in the weaker water-wet coal powder, the water spreads to less coal particle surfaces, leading to slighter $T_2$ changes. Therefore, the changes of the $T_{2g}$ of P3 show a positive correlation with surface wettability tension. Note that the gravity effect can be neglected for different coal powders because we used the same inter-particle porosity, coal particle size and experimental operations in this study.

As shown in Fig. 5, the contact angle of water on the coal surface, $\theta$, could be correlated as a linear equation of $T_{2g}$ of P3 at the end of the test (t=72 hours). The fitted linear correlation is given as below,

$$\theta = 84.6 \times T_{2g} + 52.5$$

(5).

Eq. (5) is then applied as a general model to determine the contact angles of real coal samples based on the NMR measurements of the $T_{2g}$ of P3.

### 3.2.3. Uncertainty analysis of the model

Assessing the reproducibility of the NMR experiments is important for evaluating the
credibility of the proposed model. In this study, we chose sample SJZ to repeat the NMR experiments at 25 °C. Two groups of reproducibility experiments were conducted for coal sample SJZ (Fig. 6a and 6b). Figure 6c compares the results from the two reproducibility experiments with those from experiment series-A. As shown in Fig. 6c, the $T_{2g}$ values of P3, at the equilibrium state of water (72 hours), are almost the same for the three groups of experiments. The absolute deviation between the three sets of data at 72 hours after water dripping is within 1% for sample SJZ, which is acceptable in terms of deviation; thus, the model of wettability determination by NMR experiments is repeatable for all other samples.

Fig. 6. a,b-Reproducibility experiments for the SJZ wettability measurement; c-The normalized $T_{2g}$ of P3 peak decreases in the three groups of experiments.

However, there are two key uncertainties in the NMR wettability measurements. The first is related to the change in the coal mineral content during grinding and sieving. Jayaweera et al. (1989) concluded that ash content varied among different particle sizes, i.e., the ash content increased with decreasing mean particle diameter results from sieving method. In this study, we crushed and sieved using different size mesh sieves to get different size coal powders, and the remaining material on the topside sieve was crushed and sieved again. This procedure was continued until the whole portion eventually passed through the sieves. During the process of sieving, the minerals went through the sieves to smaller-sized coal powder. Thus, the mineral contents in the specific coal powder are slightly less than those of the raw coal samples. Another uncertainty is the coal oxidation during the 72-hour experiment. Although it is unavoidable, we attempted to keep the coal powder sample from oxidizing by accelerating the grinding operation.
and then keeping the coal powder in a vacuum.

3.3 Effects of CO₂ injection on the change of water wettability of coal

After CO₂ injection into the coal reservoir, the reservoir properties (e.g., pore size distribution, permeability and wettability) will change due to a series of physical and chemical reactions between coal, water and CO₂ (Zhang et al., 2016; Iglauer, 2017). Thus, the laboratory analysis of water and the CO₂ wettability of coal can provide a better understanding of the simulation of underground CO₂ injection in the in situ reservoir.

In experiment series-B, six representative samples were selected from the nine coal samples in experiment series-A. The coal powders were kept in 4 MPa CO₂ after the addition of water, and then the $T_2$ spectra were measured to research the water wettability after the CO₂ treatment. Figure 7 shows the changes of the $T_2$ spectra after the water addition in CO₂ for the samples. Like the peak changes in experiment series-A, P1 increases and P3 decreases for all samples. Moreover, the P3 peak moves to the smaller $T_2$ with time. Comparing the normalized $T_{2g}$ of P3 in experiment series-A and series-B for six samples shows that the normalized $T_{2g}$ of P3 increases with the injection of CO₂ (Fig. 8). As discussed in the previous section, the increase of $T_{2g}$ indicates that the spread of water on coal particle surfaces becomes weak for all samples in CO₂.

Experiment series-C and series-D were carried out to investigate the effect of pressure and temperature on the wettability changes of coal resulting from CO₂ injection. Figure 9 shows the $T_2$ spectra changes with time for samples SYQ and WTP under 2 MPa, 4 MPa and 6 MPa CO₂. Figure 10 shows the changes of normalized $T_{2g}$ of P3 with time after the addition of CO₂ at different pressures. With pressure increasing from 2 MPa to 6 MPa, the normalized $T_{2g}$ of P3 increases. The higher CO₂ pressure has a greater effect on the water spread on coal particle surfaces for both the bituminous and anthracite coals, which indicates that the high CO₂ pressure shows a positive effect on the decreases of water-wetting.

Figure 11 shows the change of $T_2$ spectra for samples FK and GH with time at 25 °C, 35 °C and 45 °C. With increasing temperature, the change ranges of the P3 area and position become larger. As shown in Fig. 12, after the addition of water and at different temperatures, the curves of normalized $T_{2g}$ of P3 first decrease and finally tend to maintain a certain value. Moreover, the higher the temperature, the smaller the $T_{2g}$ of P3, i.e., high temperature has a negative effect on the decrease of coal water wettability.
Fig. 7. $T_2$ spectra of coal samples after water addition in 4 MPa CO$_2$ (a-TA; b-FK; c-SYQ; d-GH; e-SJZ; f-WTP)

Fig. 8. The normalized $T_2$ of P3 decreases under atmospheric and CO$_2$ conditions
Fig. 9. $T_2$ spectra of coal samples at different CO$_2$ pressures after water addition (a,b,c-SYQ; d,e,f-WTP)

Fig. 10. The normalized $T_{2g}$ of P3 decreases at different CO$_2$ pressures (a-WTP; b-SYQ)
3.4 Discussion

3.4.1 Effect of coal properties on water and CO₂ wettability

The results of experiment series-B show that the $T_{2g}$ of P3 increases with CO₂ injection and varies with different coal rank. Using Eq. (5) and the ultimate normalized $T_{2g}$ of P3, we can obtain the contact angle of water in the 4-MPa CO₂ condition. As shown in Table 4, the contact angle of water increases with CO₂ injection, indicating that water wettability becomes weak for both anthracite and bituminous coals after being exposed to CO₂. However, the degree of change in wettability varies, and it is defined by the difference of the water contact angle between
experiment series-A and series-B ($\Delta \theta$) (Table 4).

Table 4 Water contact angle calculations using Eq. (5) in the series-A and series-B experiments

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>TA</th>
<th>FK</th>
<th>SYQ</th>
<th>GH</th>
<th>SJZ</th>
<th>WTP</th>
</tr>
</thead>
<tbody>
<tr>
<td>water contact angle $\theta_1$ (°) (experiment series-A)</td>
<td>73.7</td>
<td>60.8</td>
<td>78.4</td>
<td>99.4</td>
<td>90.8</td>
<td>70.3</td>
</tr>
<tr>
<td>water contact angle $\theta_2$ (°) (experiment series-B)</td>
<td>88.4</td>
<td>84.7</td>
<td>85.2</td>
<td>125.5</td>
<td>99.7</td>
<td>104.4</td>
</tr>
<tr>
<td>$\Delta \theta (\theta_2 - \theta_1)$</td>
<td>14.7</td>
<td>23.9</td>
<td>6.8</td>
<td>26.1</td>
<td>8.9</td>
<td>34.1</td>
</tr>
</tbody>
</table>

The $\Delta \theta$ is correlated with the CO$_2$ adsorption capacity, vitrinite content, fixed carbon content, and vitrinite reflectance of coal (Fig. 13). There is a slight positive correlation between the increase of the water contact angle and the CO$_2$ adsorption volume (Fig. 13a). Sakurovs and Lavrencic (2011) and Kaveh et al. (2011) suggested that the water-coal wetting behavior was affected by the adsorption of CO$_2$ on the coal surface. Although there is no proof of a direct relationship between CO$_2$ wettability and CO$_2$ adsorption, it can be assumed that coal with a large volume CO$_2$ adsorption capacity has stronger CO$_2$ wettability. Since adsorption is the dominant storage mechanism in coal, and it typically accounts for 98% of the total gas stored, further investigation is required to establish the relationship between CO$_2$-wettability and CO$_2$-adsorption.

Moreover, the adsorption of CO$_2$ into micropores in the coal matrix leads to a significant decrease in permeability, which may limit the Darcy flow of the CO$_2$. A recent research by Zhang et al. (2016) demonstrated that CO$_2$ injection can change coal microstructure and permeability. Thus, further investigation is required to affirm whether the coal matrix swelling due to CO$_2$ injection is another reason for the change of CO$_2$ wettability or not.

The contact angle changes also show a slight positive relationship with vitrinite volume and fixed carbon content (Fig. 13b and c). As mentioned above, the vitrinite group is hydrophobic. Moreover, Sakurovs and Lavrencic (2011) found that the fixed carbon content increased the hydrophobicity of coal. Thus, those weak water-wet contents of coal may become more CO$_2$-wet during CO$_2$ injection. The relationship between coal rank (vitrinite reflectance) and $\Delta \theta$ is relatively weak (Fig. 13d).

3.4.2 The effect of pressure on water and CO$_2$ wettability

Experiment series-C shows that higher CO$_2$ pressure has a greater effect on the decrease of water wettability for both bituminous and anthracite coals, i.e., the coals become more CO$_2$-wet.

To compare the water wettability of coal at different pressures, we calculated the contact angles of water using Eq. (5). The results are presented in Fig. 14. With increasing pressure of 0.1-6 MPa, the contact angle of water increased from 70.3° to 111.2° for WTP and from 78.4° to 88.2° for SYQ, which indicates the increase of CO$_2$ wettability. The increase of CO$_2$ wettability and the decrease of water wettability with CO$_2$ pressure are consistent with the existing experimental data.

Sakurovs and Lavrencic (2011) experimentally determined the CO$_2$-coal contact angle using the
captive bubble technique for low to medium rank coal ($R_o$ ranged from 0.62 to 1.4) and found an increase in CO$_2$ wettability with pressure for all samples. Siemons et al. (2006) measured the CO$_2$ contact angle for anthracite coal and found that it became CO$_2$-wet ($\theta > 90$) at 0.26 MPa. However, Arif et al. (2016) determined that semi-anthracite became weakly CO$_2$-wet at approximately 7 MPa ($\theta > 110$). Kaveh et al. (2011) found that semi-anthracite become CO$_2$-wet at 5.7 MPa and that high-volatile bituminous coal become CO$_2$-wet at 8.7 MPa. In our research, anthracite coal WTP became CO$_2$-wet at pressures of less than 2 MPa; however, bituminous coal SYQ became CO$_2$-wet at pressures of >6 MPa. As shown in Fig. 14, the contact angle changes more for anthracite than it does for bituminous coal with increasing pressure from 0 to 6 MPa.

![Fig. 13. The relationship between $\Delta \theta$ and a-CO$_2$ adsorption capacity; b-vitrinite volume content of coal; c-fixed carbon content of coal; d-mean maximum vitrinite reflectance in oil ($R_o$).](image)
According to previous studies (Kaveh et al., 2011; Sakurovs and Lavrencic, 2011; Siemons et al., 2006), three factors affect the water-coal wetting behavior with increasing CO₂ pressure, as shown in Fig. 15. The first one is the CO₂ adsorption capacity of coal. As discussed above, coal with higher CO₂ adsorption capacity is more CO₂-wet. The increase of CO₂ pressure leads to the more CO₂-wet (Fig. 15a). Moreover, similar trends in the literature data on CO₂ adsorption (Busch et al., 2003) also explain why the increased rate of contact angle is evident for pressures of 0.1-2 MPa in this study. The second factor is the change of interfacial tension with CO₂ pressure (Fig. 15b). Arif et al. (2016) indicated that the δtg of coal-CO₂ decreases with increasing CO₂ pressure (Fig. 15b). According to Eq. (4), surface wettability tension decreases with increasing CO₂ pressure. The third factor is CO₂ solution in water. The dissolution of CO₂ in water can decrease the pH, leading to the reduction of the negative charge density at the solid/water interface and thus reducing the electrokinetic potential of the coal particles (Ibrahim and Nasr-El-Din, 2016). Consequently, the δls of coal-water increases due to the negative contribution of the electrostatic component to surface energy, which causes the surface wettability tension to become less effective in CO₂, according to Eq. (4). With increasing CO₂ pressure, the CO₂ solubility increases, leading to high H⁺ concentrations (Wiebe and Gaddy, 1940); thus, the coal becomes more hydrophobic (Ibrahim and Nasr-El-Din, 2016).
Fig. 15. The factors affecting the water-coal wetting behavior with pressure and temperature (a) CO$_2$ adsorption; (b) interfacial tension; (c) CO$_2$ dissolution

3.4.3 The effect of temperature on water and CO$_2$ wettability

As shown in Fig. 16, for both anthracite and bituminous coal at 4 MPa CO$_2$, the contact angle of water calculated by Eq. (5) decreases with increasing temperature. It can be concluded that high temperature decreases the effect of CO$_2$ on the water wettability of coal. For anthracite coal, there is a clear decrease from 125.5° to 110.7° with increasing temperature. However, for bituminous coal, the contact angle first decreases from 75.3° to 71.1° and then becomes almost constant. The impact of temperature on coal wettability after CO$_2$ treatment can also be explained by the three factors shown in Fig. 15. First, the increasing temperature reduces CO$_2$ wettability because high temperature reduces the CO$_2$ adsorption capacity of coal. The reduced CO$_2$ affinity makes coal more water-wet (Kaveh et al., 2011; Sakurovs and Lavrencic, 2011; Siemons et al., 2006; Ibrahim and Nasr-El-Din, 2016) (Fig. 15a). Second, increasing temperature induces the reduction of water surface tension (Gittens' research, 1969; Chiquet et al., 2007; Zhou et al., 2017) (Fig. 15b). The water contact angle decreases with temperature at 0.1 MPa without the solution and adsorption of CO$_2$ (Arif et al., 2016). Additionally, the decrease in contact angle with temperature has been reported for pure minerals such as mica or quartz (Chiquet et al., 2007). Finally, the water solubility of CO$_2$ decreases with temperature (Wiebe and Gaddy, 1940); thus, reduced H$^+$ concentrations can result in the increase of the water-wetting behavior of coal (Fig. 15c).

Fig. 16. The contact angles decrease with increasing temperature (a-GH; b-FK)

4. Implications

The NMR provides a novel technique to measure the water and CO$_2$ wettability of coal during CO$_2$ sequestration that can simulate in situ reservoir conditions. We determine the wettability of coal by fitting the $T_{2g}$ of P3 and its contact angle against the coal surface. This method can also be used in other porous media, such as gas shale, although a different fitting formula must be established based on a series of measurements of NMR spectra and the contact angles of other...
The experimental data show that CO₂ storage in coal seams is strongly influenced by coal properties, gas pressure and reservoir temperature. The coal with high CO₂ adsorption capacity, high fixed carbon content and high vitrinite content shows more CO₂-wetting. Considering the fact that the sequestration capacity of coal is mainly dominated by CO₂ adsorption and the CO₂ wettability of coal, coal with high CO₂ adsorption capacity is more suitable for trapping CO₂. Therefore, CO₂ will occupy the micropores and water will occupy larger pores after CO₂ injection. Consequently, CO₂ will be distributed more uniformly in micropores and displace more methane and water. In addition, high CO₂ pressure and low reservoir temperature increase the CO₂-wettability of coal for both anthracite and bituminous coals. Consequently, high pressure and low temperature are two favorable factors for CGS and CO₂-ECBM.

5. Conclusion

In this study, water was dropped into coal powder and measured by NMR technology to determine the wettability of coal. The bulk water peaks of nine coal samples increase and shift to smaller $T_2$ values after the addition of water. The changes of the P3 position were quantitatively analyzed to determine the water wettability of coal. The wettability of coal from NMR results matches well with the contact angle measurements on coal discs. Although there are some uncertainties in the experiment, NMR provides a quantitative method to determine coal wettability.

NMR also provides a way to study water-CO₂ wettability with regard to coal properties, pressure and temperature. CO₂ injection can weaken the water wettability by replacing water from coal surface with adsorbed CO₂. Meanwhile, high CO₂ pressure increases the CO₂ wettability, and high temperature decreases the effect of CO₂ on the water wettability of coal. The change of water-coal wetting behavior with injection of CO₂, is resulted by three factors: change of CO₂ adsorption capacity of coal, change of interfacial tension, and dissolution of CO₂ in water. Analyzing wettability with NMR has the potential to target coal seams for CO₂ sequestration. Additionally, it can be used to determine the wettability of gas shale during CO₂ sequestration into gas shale reservoirs.

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