CO_2-wettability of low to high rank coal seams: Implications for carbon sequestration and enhanced methane recovery

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Abstract

Coal seams offer tremendous potential for carbon geo-sequestration with the dual benefit of enhanced methane recovery. In this context, it is essential to characterize the wettability of the coal-CO_2-water system as it significantly impacts CO_2 storage capacity and methane recovery efficiency. Technically, wettability is influenced by reservoir pressure, coal seam temperature, water salinity and coal rank. Thus a comprehensive investigation of the impact of the aforementioned parameters on CO_2-wettability is crucial in terms of storage site selection and predicting the injectivity behaviour and associated fluid dynamics. To accomplish this, we measured advancing and receding water contact angles using the pendent drop tilted plate technique for coals of low, medium and high ranks as a function of pressure, temperature and salinity and systematically investigated the associated trends. We found that high rank coals are strongly CO_2-wet, medium rank coals are weakly CO_2-wet, and low rank coals are intermediate-wet at typical storage conditions. Further, we found that CO_2-wettability of coal increased with pressure and salinity and decreased with temperature irrespective of coal rank. We conclude that at a given reservoir pressure, high rank coal seams existing at low temperature are potentially more efficient with respect to CO_2-storage and enhanced methane recovery due to increased CO_2-wettability and thus increased adsorption trapping.

1. Introduction

Carbon capture and storage (CCS) is the most promising approach to mitigate anthropogenic CO_2 emissions and thus ensure a cleaner environment [1-5]. The storage of CO_2 in depleted oil and gas reservoirs [6-8] or deep saline aquifers [9-11] allows trapping of enormous volumes over a long period of time. Another option is injection of CO_2 into coal seams [12-15] with the dual benefit of enhanced coal bed methane recovery [16-18]. In conventional reservoirs, CO_2 is held trapped by means of four mechanisms which are structural trapping [19-22], capillary or residual trapping [8,23-25], dissolution trapping [26,27] and mineral trapping [28]. In coal seams, however, the dominant storage mechanism is adsorption trapping of CO_2 onto the coal matrix [12,29,30]. Typically the adsorption capacity of CO_2 is higher than that of methane, depending on coal rank [31-33]; consequently, CO_2 displaces methane towards the production well and itself gets sorbed within the micropores of the coal seam and remains trapped. The preferential adsorption and thus storage of CO_2 in coal seams, by forced migration of methane, is strongly influenced by wettability of the CO_2-water-coal system [12,34], which in turn is generally a function of reservoir pressure [34-37], temperature and salinity. Moreover, in coal seams wettability is also a function of coal rank, vitrinite reflectance, fixed carbon and ash content [35,38]. Therefore, it is essential to describe CO_2-wettability of coals of varying ranks, and how reservoir conditions (pressure, temperature and brine salinity) influences this wettability.

In this context, several studies reported CO_2-wettability of coals at ambient conditions [38-41], but only a limited amount of literature data for the more relevant higher pressures have been reported [34-37,42,43]. Table 1 presents a summary of the major experimental variables considered in previous studies, and this work.

Table 1: CO_2-wettability of coals: Summary of experimental conditions used.

Reference	Pressure	Temperature	Salinity	Coal type	Overall Coal rank
Chi et al. [42]	up to 6.2 MPa	298K	DI water	Not mentioned	Not mentioned

Siemons et al. [37]	up to 14 MPa	318K	DI water	Anthracite	High
Sakurovs and Lavrencic, [36]	up to 15 MPa	313 K	DI water	Bituminous	Medium
Kaveh et al. [43]	up to 16 MPa	318K	DI water	High volatile bituminous	Medium
Kaveh et al. [35]	up to 16 MPa	318K	DI water	Semi anthracite, High volatile bituminous	High and Medium
Saghafi et al. [34]	up to 6 MPa	295K	DI water	Medium volatile bituminous	Medium
This study	up to 20 MPa	308K, 323K and 343K	0wt% - 10wt% NaCl	Semi-anthracite, Medium volatile bituminous, Lignite	High, Medium and Low

Therefore there is a clear lack of data available on CO_2-wettability of coals as a function of coal rank, coal formation pressure, and particularly temperature and salinity (cp. Table 1). Thus there exists a gap in terms of proper understanding of CO_2-wettability of coal seams of different ranks at reservoir conditions. Moreover, although it is well established that coal seams offer enormous potential for enhanced methane recovery and CO_2 sequestration, yet certain important questions need to be addressed which are: 1) Which type of coal (low rank, medium rank, or high rank) are most suitable for CO_2 storage and enhanced coalbed methane recovery under the prevailing geothermal and reservoir pressure conditions? 2) Is the suitability of CO_2 sequestration in coal seams of a particular rank valid for a wide range of reservoir pressures, temperatures and salinity conditions? 3) What mechanisms are responsible for long term CO_2-storage in coals? To answer these questions and to generally improve the characterization of CO_2-wettability of coals, we experimentally measured water advancing and receding contact angles on three coal samples as a function of coal rank (low, medium and high ranks), vitrinite reflectance and fixed carbon at different CO_2 pressures (0.1 MPa to 20 MPa), temperatures (ranging from 308K to 343K), and brine salinities (0wt% NaCl-10wt% NaCl) using the pendent drop technique. The results of the study lead to a broad characterization of CO_2-wettability of coals and thus help optimize CO_2-storage and enhanced coal bed methane recovery operations. Our results indicate that CO_2-wettability of

coals is strongly influenced by coal rank such that the high rank coals are more CO_2-wet and low rank coals are least CO_2-wet at a given reservoir pressure, temperature and salinity.

2. Materials and methods

2.1. Coal Samples

Three coal samples [high rank (semi anthracite; from Hazelton, Pennsylvania, USA), medium rank (medium volatile bituminous; from Morgantown, West Virginia, USA), and low rank (lignite; from North Dakota, USA; Table 2)] were used in this research. The samples were cut to cuboid shape (~1cm x 1cm x 0.5cm) and the surface roughness of each substrate was measured with an atomic force microscope (AFM instrument model DSE 95-200); note that surface roughness significantly affects contact angle measurements [44,45]. The RMS surface roughness of the specific coal substrates used were 840nm, 880nm and 280nm for high, medium and low rank coals respectively.

2.2. Petrology, Ultimate and Proximate Analysis

The results of the proximate, ultimate and petrological analysis and the internal properties (density and volume) of the coal samples are listed in Table 2. Note that coal samples of different rank differ mainly in volatile matter, moisture, fixed carbon and vitrinite reflectance [46,47]. Petrology was analysed in accordance with Australian Standard AS2856 and ISO7404; proximate analysis were conducted using AS1038.3, ISO11722 and ASTM D3172-07a, and ultimate analysis were performed using AS1038.6 and ISO 609.

Table 2. Properties of coal samples used.

Sample	Rank	Semi-Anthracite	Medium-volatile Bituminous	Lignite
	Geological Location	Hazelton,	Morgantown,	North Dakota

		Pennsylvania	West Virginia	
	Overall rank (used in this work)	High rank	Medium rank	Low rank
Petrology	Vitrinite Reflectance (R_r, %*)	3.92	0.82	0.35
	Vitrinite (%)	89.6	73.1	83
	Liptinite (%)	0	3.4	4
	Inertinite (%)	7.6	18.8	10.8
	Minerals (%)	2.8	4.7	2.1
Proximate analysis	Moisture (air dried, %)	2.6	2	16.3
	Ash (%)	9.7	6.4	7.8
	Volatile Matter (%)	2.9	32.4	34.8
	Fixed carbon (%)	84.9	59.2	41.1
Ultimate analysis	Ash (%)	9.7	6.4	7.8
	Carbon (%)	82.6	78.6	54.6
	Total Hydrogen (%)	2.35	5.07	5.27
	Hydrogen (%)	2.06	4.85	3.45
	Nitrogen (%)	1.16	1.54	0.62
	Total Sulphur (%)	0.8	0.99	0.66
	Oxygen by difference (%)	3.68	7.62	2.87
Properties	Bulk density (g/cc)	1.30	1.28	1.44
	Dry sample volume (cc)	16.55	12.77	4.26
	Dry mass (g)	21.17	16.194	6.159
	RMS Surface Roughness (nm)	840	880	280

* All percentages in above table represent weight percent

2.3. Fluids

99.9 wt% CO_2 (from BOC, gas code – 082), de-ionized water (Conductivity: 0.02 mS/cm), and 5wt% and 10wt% NaCl brine (NaCl Source: Scharlab s.l., Spain, Purity: ≥0.995mass%) were used in the study. Acetone (99.9 wt%) was used to wash the coal samples.

2.3. Contact angle measurements

CO_2-brine wettability was measured using the pendent drop tilted plate technique [48]. The experimental setup is shown in Figure 1; it consists of a high pressure cell (which holds the

sample on a tilted plate), a CO_2 cylinder, two high precision syringe pumps (Teledyne D-500, pressure accuracy of 0.1%FS) for water and CO_2 and a video camera. Prior to each experiment, the coal substrates were washed with acetone and then cleaned in air plasma (Diemer Yocto instrument) for 2 minutes to ensure that no organic contaminants are deposited on the sample, which would introduce a bias [49].

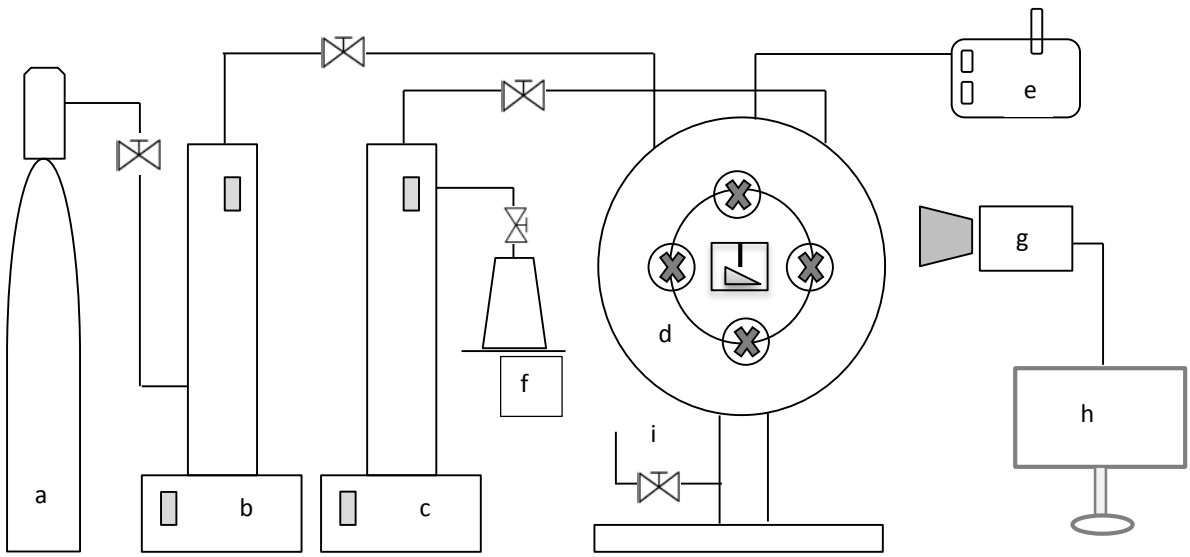

Figure 1. Experimental setup for contact angle measurements used in this study; (a) CO_2 cylinder (b) high precision syringe pump-CO_2, (c) high precision syringe pump-water, (d) high pressure cell with substrate housed on a tilted plate inside, (e) heating unit, (f) liquid feed/drain system, (g) high resolution video camera, (h) image visualization and interpretation software, (i) pressure relief valve.

For each measurement, a clean and dry coal sample was placed inside the pressure cell onto the tilted plate. The temperature was set to a fixed value (308K, 323K, and 343K), and CO_2 pressure in the cell was increased with a high precision syringe pump to pre-determined values (0.1 MPa, 5 MPa, 10 MPa, 15 MPa, 20 MPa) by injecting CO_2 into the cell. Subsequently a droplet of de-gassed brine (average volume of ~6μL ± 1μL) was allowed to flow (at 0.4ml/min) and was dispensed onto the substrate through a needle. We note that the fluids used were not thermodynamically equilibrated, since earlier studies demonstrated that the contact angle θ is not significantly affected by mass transfer during the first 60seconds of

exposure (only insignificant change (2^{o}) was observed by [50,51]) and during this time all measurements were completed. Furthermore, non-equilibrated fluids are most relevant at the leading edge of the CO_2 plume, i.e. when CO_2 first encounters under saturated brine. A video camera (Basler scA 640–70 fm, pixel size = 7.4 μm; frame rate = 71 fps; Fujinon CCTV lens: HF35HA-1B; 1:1.6/35 mm) recorded the entire process, and contact angles were measured on images extracted from the movie files. Advancing (θ_a) and receding water contact angles (θ_r) were measured simultaneously at the leading and trailing edges of the droplet, just before the droplet started to move. The standard deviation of these measurements was ±3° based on replicate measurements; however for lignite the standard deviation reached ±5°, which is due to the more complicated nature of the sample.

3. Results and Discussion

In order to assess CO_2-storage and methane recovery potential, CO_2-wettability of coals was characterized as a function of rank at relevant thermophysical conditions by measuring advancing and receding contact angles on coal samples of high, medium and low ranks at various reservoir conditions (pressure range: 0.1-20 MPa, temperature range: 308K-323K and salinity range: 0wt%-10wt% NaCl). The outcomes of the study led to a precise realisation of the relationships between coal rank and corresponding CO_2 geo-storage and ECBM potential. The subsequent sections describe the results in detail.

3.1. Effect of Pressure on CO_2-wettability of coal

The effect of pressure was systematically tested on the three (high, medium, low rank) samples at 0.1 MPa, 5 MPa, 10 MPa, 15 MPa and 20 MPa for three different temperatures (308K, 323K, and 343K). Both, θ_a and θ_r, clearly increased with pressure at all temperatures for all coal samples (Figure 2-4). High rank coal was water wet ($\theta<50°$, [21]) at ambient pressure for all temperatures tested (308K-343K; Figure 2). As pressure increased from 0.1 MPa to 20 MPa at 323K, θ_a increased from 51° to 141° and θ_r increased from 45° to 129° (red lines in Figure 2), and thus high rank coal became CO_2-wet at high pressure ($\theta>130°$, [21]). Similarly, at 343K, as pressure increased from ambient to 20 MPa, θ_a increased from 58° to 118° and θ_r increased from 52° to 107°.

This increase in contact angle with pressure is consistent with independent experimental data on coal [34-37,42,43,52]. Specifically, Chi et al. [42] measured contact angles up to 6.2 MPa

at 298K for coals of unknown ranks and found that coal hydrophobicity increased with pressure. Siemons et al. [37] extended the testing pressure up to 14 MPa at 318K and analysed CO_2-water contact angle for an anthracite coal (high rank) and found that the system became CO_2-wet at 2.6 bar, however, in our case semi-anthracite became weakly CO_2-wet at around 7 MPa ($\theta_a > 110°$); this difference could be due to difference in rank of the samples (semi-anthracite in this study) and difference in experimental conditions (temperature and surface cleaning methods). Sakurovs and Lavrencic [36] experimentally determined CO_2-water contact angles using the captive bubble technique up to 15 MPa at 313K for low to medium rank coals (R_v% of their samples ranged from 0.62-1.4) and found an increase in CO_2-wettability with pressure for all samples. Kaveh et al. [35] compared CO_2-wettability of high volatile bituminous (medium rank) and semi anthracite (high rank) coals up to 16 MPa and at 318K; and reported that semi-anthracite became CO_2-wet ($\theta = 110°$) at 5.7 MPa which is close to our result (7 MPa); the slight difference could be due to different surface cleaning methods and temperature. Saghafi et al. [34] also studied CO_2-wettability of high rank coal up to 6 MPa at 295K, their sample turned CO_2-wet at 5 MPa ($\theta = 110°$).

The increase in contact angle with pressure is also consistent with experimental data on pure minerals such as mica [53-56] and quartz [50,51,55,57]. This transformation of wettability from water-wet to CO_2-wet by an increase in pressure is, apart from increased intermolecular interactions of CO_2 with solid surface [53,58], also related to the increased adsorption of CO_2 on the coal surface, which is evident from experimental CO_2 adsorption data on coals [33,59-62].

Since adsorption is the dominant storage mechanism in coals, and typically accounts for 98% of the total gas stored [12,63], high pressure storage conditions are preferred as they would lead to increased storage volumes. Moreover, increased CO_2-wettability of coal will lead to more uniform distribution of CO_2 within the micropores of the coal seams and thus improved displacement of methane towards the production wells. However, at high pressures coal swells [64-66], which leads to a significant permeability decrease [67], which again limits the Darcy flow (of the CO_2) and thus injectivity.

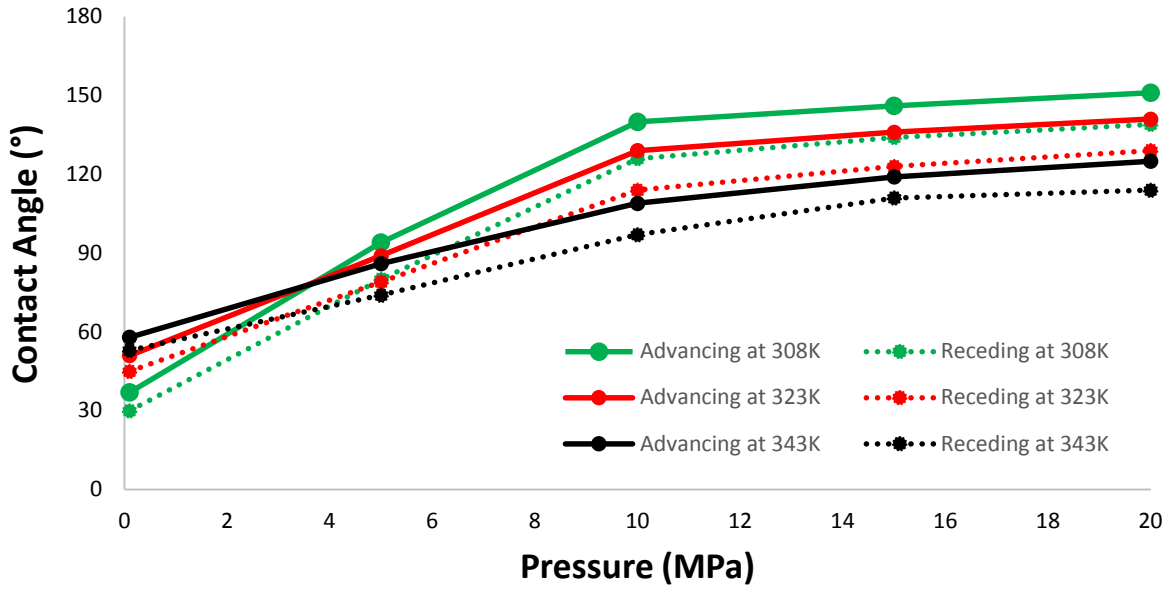

Figure 2. CO_2-DI water contact angles on high rank coal (semi-anthracite) at tested pressures (0.1 MPa-20 MPa) and temperatures (308K-343K).

Furthermore, we found that the rate of contact angle increase with pressure is sharper for the pressure range 0.1 MPa-10 MPa (Figure 2). For example, at 323K, θ_a measured 51° at 0.1 MPa and 129° at 10 MPa resulting in a net increase of 78°, whereas the net increase in θ_a for the pressure range 10 MPa-20 MPa was only 12°. This implies that injection of CO_2 in high rank coals at very high pressure may yield only marginal benefits in terms of additional volume stored because of only marginal improvement in CO_2-wettability. Generally, the increase in contact angle with pressure flattened out for pressures 10 MPa-20 MPa.

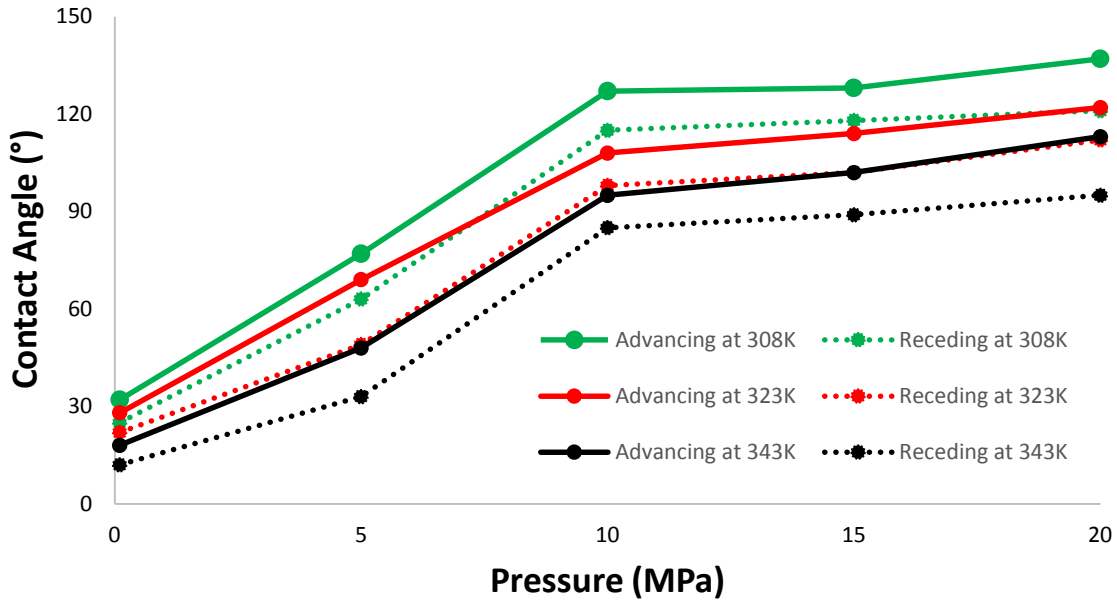

Figure 3. CO_2-DI water contact angles on medium rank coal (medium volatile bituminous) at tested pressures (0.1 MPa-20 MPa) and temperatures (308K-343K).

The medium rank coal sample (medium volatile bituminous coal) remained water-wet (at ambient conditions) with a maximum θ_a value of 32° (Figure 3). When pressure increased from 0.1 MPa to 20 MPa at 323K, θ_a increased from 28° to 122° and θ_r increased from 18° to 113°. Consequently, the system, which was water-wet at ambient conditions, turned weakly CO_2-wet at reservoir conditions ($110° \leq \theta \leq 130°$; [21]). Likewise high rank coal, the increase in contact angle for medium rank coal was sharp up to 10 MPa; however, the increase gradually flattened (between 10-20 MPa). The results, therefore, imply that CO_2 storage capacity in medium rank coals increases with pressure at all temperatures owing to the increased CO_2-wetting which implies to increased adsorption trapping; however, this storage capacity increase is only marginal at higher pressures, e.g. from 15 MPa to 20 MPa. Therefore, from an economic standpoint, for practical storage purposes an optimal injection pressure must be selected.

For low rank coals, contact angles increased with pressure at all temperatures as shown in Figure 4. For example, at 308K, a sharp increase was observed for pressure 0.1 MPa to 10 MPa, and the curve flattened afterwards. However, at 323K, the change in contact angle with pressure followed a slightly inconsistent trend such that contact angles first increased gradually up to 5 MPa (θ_a increased from 38° to 50° when pressure increased from 0.1 MPa to 5 MPa), then sharply up to 10 MPa (θ_a measured from 92°), and then a small increase was

observed up to 20 MPa (θ_a increased to 116°). The maximum contact angle measured for low rank coals was 122° (at 20 MPa and 308K) indicating that the most hydrophobic wettability regime for low rank coals is 'weakly CO_2-wet' implying reduced CO_2 trapping by means of adsorption. Similar trends were observed for higher temperature (323K and 343K).

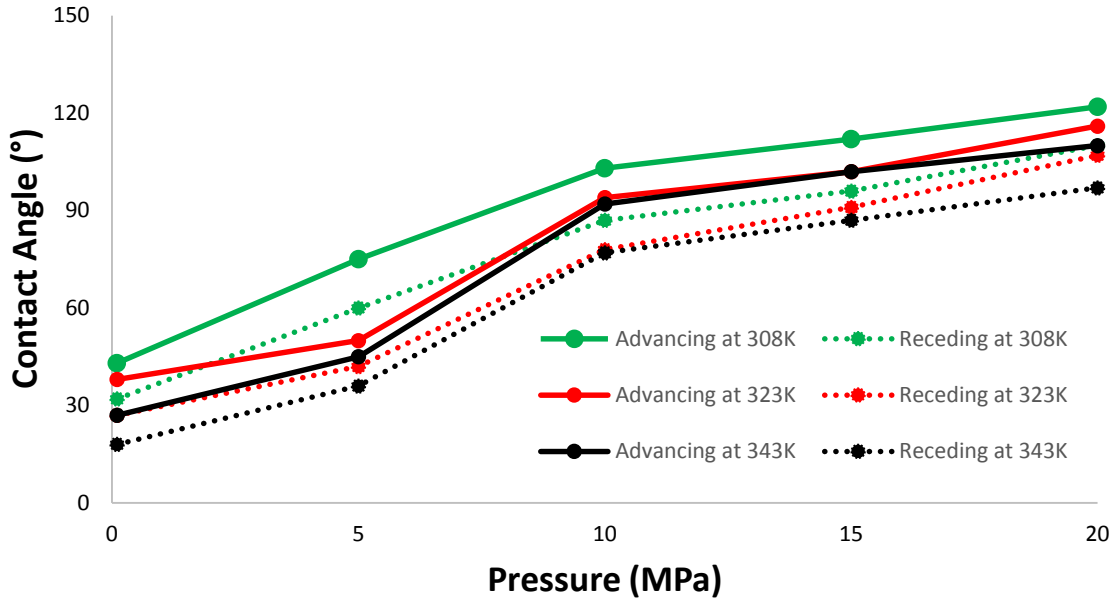

Figure 4. CO_2-DI water contact angles on low rank coal (lignite) at tested pressures (0.1 MPa-20 MPa) and temperatures (308K-343K).

3.2. Effect of temperature on CO_2-wettability of coal

The trends of contact angle variation with temperature are presented in Figures 2-4. For all coal samples analysed, both, θ_a and θ_r, decreased with temperature at all pressures tested, with the exception that for high rank coal, θ_a and θ_r increased with temperature at ambient pressure (0.1 MPa). For example, when temperature increased from 308K to 343K at 0.1 MPa, θ_a increased from 37° to 58° for high rank coal, while it decreased from 32° to 18° for medium rank coal and from 43° to 27° for low rank coal. At higher pressures (5 MPa-20 MPa), however, all coal types showed a clear decrease in θ_a and θ_r with temperature (Figures 2-4). For simplicity a summary of contact angle variation with temperature is shown in Figure 5. At 15 MPa, for high rank coal, when temperature increased from 308K to 323K, θ_a decreased from 146° to 119°, implying wettability transformation from strongly CO_2-wet to weakly CO_2-wet. Similarly, for medium rank coal, θ_a decreased from 128° to 102° when temperature

increased from 308K to 343K. However, for low rank coal, θ_a first decreased from 112° to 102° when temperature increased from 308K to 323K, and then became constant when temperature increased further (from 323K to 343K). In summary, CO_2-wettability of coal decreased with increasing temperature irrespective of the coal rank. There is no published data on the effect of temperature on CO_2-water-coal contact angles, however, the decrease in contact angle with temperature has also been reported for pure minerals such as mica [53,54] or quartz [56-58].

We demonstrate that two distinct mechanisms may be held responsible for the decrease in contact angle with temperature. The first mechanism is the interplay of the three interfacial tensions [53,58], which is expressed by the Young-Laplace equation as follows:

$$\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{vl}} \qquad (1)$$

In eq. (1), γ_{sv} and γ_{sl} are the solid-CO_2 interfacial tension and solid-brine interfacial tension, respectively, whereas γ_{vl} is CO_2-brine interfacial tension. Since most of the previous studies [51,53,57,68] agree that CO_2-brine interfacial tension increases with temperature, it is evident from equation (1) that the difference of solid-CO_2 interfacial tension and solid-brine interfacial tension (numerator of equation) should increase with temperature to cause a corresponding decrease in contact angle with temperature.

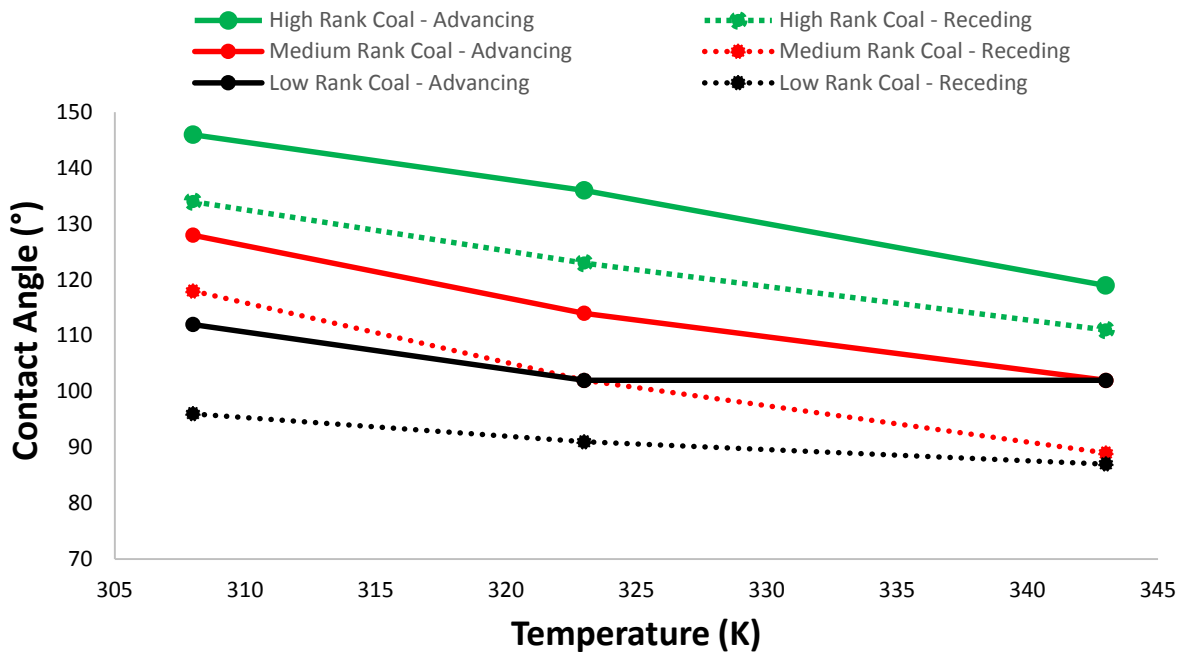

Figure 5. Effect of temperature on CO_2-wettability for all coal samples used in the study. For simplicity measurements are shown only for 15 MPa.

Secondly, the decrease in the contact angle with temperature can be attributed to the CO_2 adsorption behaviour on coal. The experimental studies on the effect of temperature on CO_2 adsorption [69-74] report that there is a clear decrease in CO_2 adsorption on coal surfaces with temperature. This reduced CO_2-affinity is thus reflected in the contact angles. Perera et al. [71] mentioned that the decrease in adsorption capacity with temperature is due to the increase in kinetic energy and rate of diffusion of CO_2, which tend to release gas molecules from the coal matrix resulting in a corresponding reduction in net amount of adsorbed gas. We thus conclude that low temperature coal seams have higher CO_2 storage capacities in comparison to high temperature coal seams.

3.3. Effect of coal rank on CO_2-wettability

In order to demonstrate the impact of coal rank on CO_2-wettability and thus on methane production and CO_2 storage potential in coals, we plotted advancing water contact angles (only for simplicity) as a function of pressure and temperature (Figure 6). It is clear that at any given CO_2 pressure, apart from the ambient, high rank coal offers highest CO_2-wetting potential, and CO_2-wettability substantially decreases with rank. Low rank coals (e.g. Lignite) are least CO_2-wet and medium rank coal (e.g. Bituminous) are intermediate. These results are in agreement with Kaveh et al. [35] who compared CO_2-wettability of semi-anthracite and high volatile bituminous coals, and they measured higher contact angles for semi-anthracite coals, and thus they concluded that hydrophobicity of coals increases with coal rank. Moreover, Sakurovs and Lavrencic [36] also concluded that high ranks coals were easier to wet with CO_2 at high pressures and that the increase in CO_2-wettability promoted the rate of penetration of CO_2 into the coals. It can therefore be established that CO_2-wettability of coals is a strong function of coal rank and that high rank coals are more CO_2-wet. We point out that this behaviour is related to the increase in CO_2 adsorption capacity with an increase in coal rank as evidenced by the literature data on adsorption isotherms of coals of varying rank [32,75].

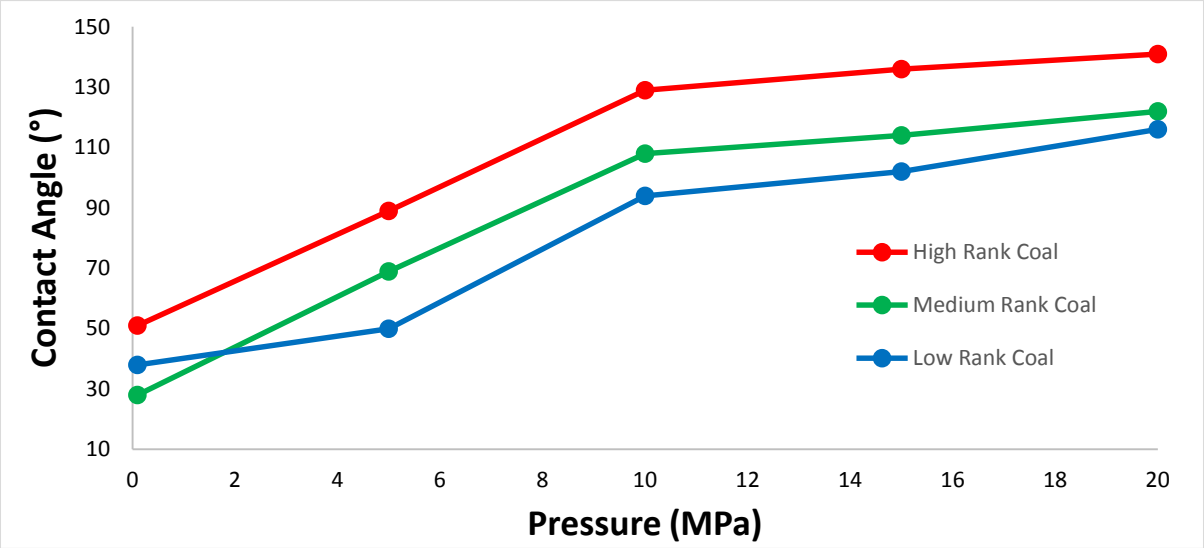

Figure 6. Effect of coal rank on CO_2-wettability.

3.4. Effect of brine salinity on CO_2-wettability of coal

Water can exist in coals seams in the form of free water in cleats, chemically bound hydration water, and water adsorbed onto the surface of the matrix blocks [76,77]. The cleat system is initially filled with water and it provides the flow path for production by Darcy's law. We thus analysed the impact of brine salinity on CO_2-brine-coal wettability for various salinities (0wt% NaCl, 5wt%NaCl and 10wt% NaCl) at 15 MPa and 323K on all the coal samples studied in this work; as salinity is expected to vary in subsurface coal seams [78].

Both, θ_a and θ_r, increased with salinity for all coal samples (Figure 7). This increase was stronger for the brine salinity increase from 0wt% NaCl to 5wt% NaCl; e.g. for medium rank coal, θ_a increased from 114° to 127° and θ_r increased from 102° to 112° when salinity increased from 0wt% NaCl to 5wt% NaCl brine. For the salinity increase from 5wt% NaCl to 10wt% NaCl, the increase in contact angle was very small; e.g. for medium rank coal, θ_a increased from 127° to 132° and θ_r increased from 112° to 116° when salinity increased from 5wt% NaCl to 10wt% NaCl brine. Moreover, we found similar trends for low, medium and high rank coals (Figure 7). In the literature, there is a lack of data on the effect of salinity on CO_2-wettability of coal, yet our results are consistent with Ibrahim et al. [52], who analysed contact angles of CO_2-brine-coal systems for brine salinities varying between 0 g/L-15 g/L NaCl), and who reported that contact angles were highest for 15 g/L and lowest for DI water.

Brine salinity thus does not exhibit major influence on contact angles at typical reservoir conditions.

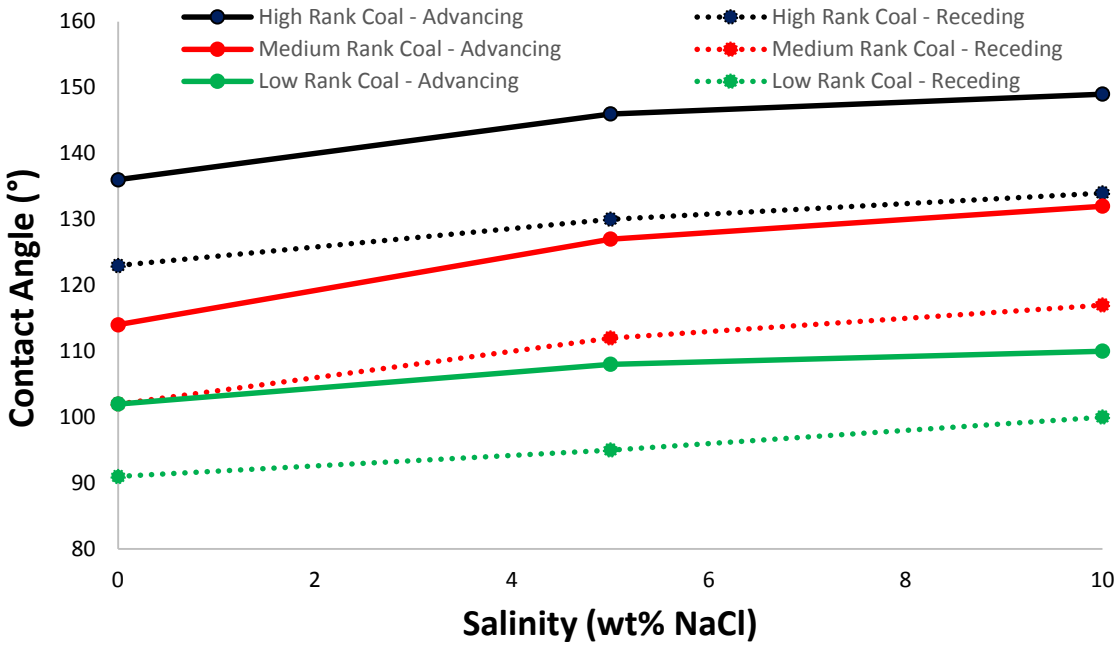

Figure 7. Effect of salinity on CO_2-wettability of coals at 323K and 15 MPa.

3.5. Relation between vitrinite reflectance, fixed carbon and coal wettability

There is a strong positive correlation between virtinite reflectance and water contact angle. Similarly, fixed carbon (which is the solid combustible residue that remains after coal is heated and volatile matter is expelled) strongly correlates with the water contact angle (Figure 8). Practically, coals with higher vitrinite reflectance are more CO_2-wet and thus will store more CO_2 by means of adsorption; coals with higher fixed carbon content also have better CO_2-wetting characteristics. At 20 MPa and 323K, coal with a vitrinite reflectance (R_r, %) of 3.8 is strongly CO_2-wet (θ_a = 140°), whereas at the same reservoir conditions medium rank coal (R_r = 0.82) is weakly CO_2-wet (θ_a = 122°) and low rank coal (R_r = 0.35) is intermediate-wet (θ_a = 116°); thus CO_2 injection into low rank coals will require higher injection pressures to completely wet the surface in comparison to medium and high rank coals. Thus we conclude that coals of higher vitrinite reflectance and fixed carbon exhibit better CO_2 adsorption storage capacity, because of their better CO_2-wettability. This effect

can be attributed to the non-polar nature of vitrinite matter which promotes de-wetting of the surface.

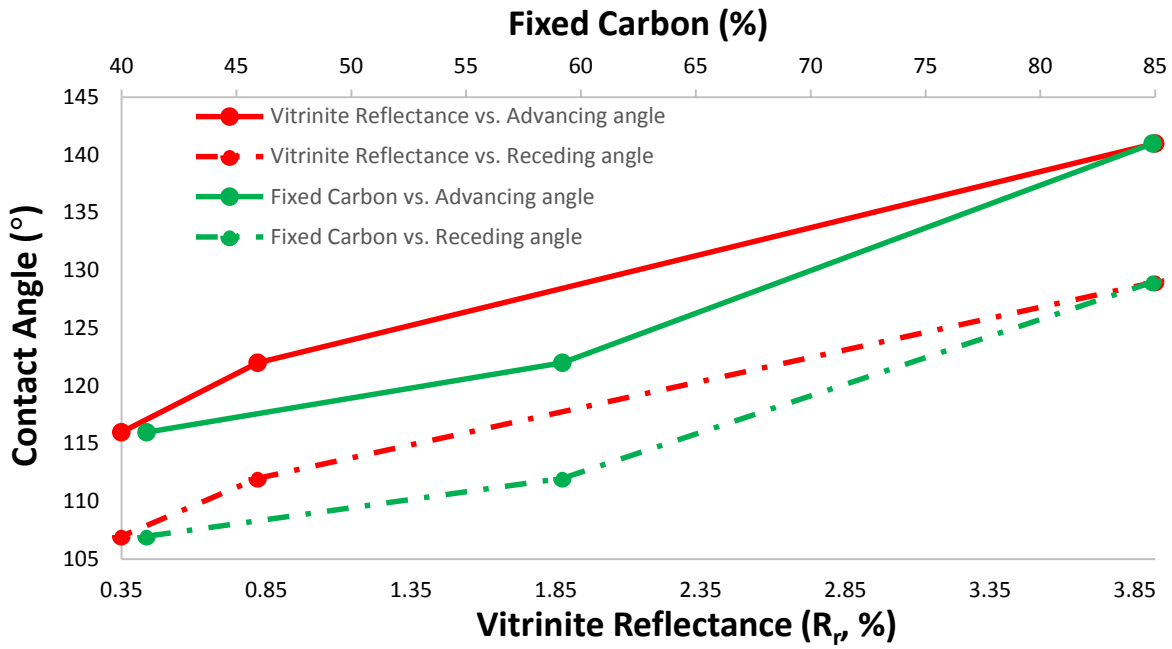

Figure 8. Variation of CO_2-wettability with vitrinite reflectance and fixed carbon content.

4. Implications

We measured CO_2-wettability of coals of varying ranks; which is essential to assess the CO_2 storage potential of coal seams, and also to assess enhanced hydrocarbon gas production from unmineable coal seams. The measured data implies that CO_2 storage in coal seams is strongly influenced by pressure, seam temperature, brine salinity, rank of the coal, vitrinite reflectance and fixed carbon. As an example, consider three potential candidate coal bed methane formations of different ranks (high, medium and low) at a depth of 1km and at temperature of 323K. The required CO_2 injection pressure will be approximately 10 MPa (estimated using formation pressure gradient ~ 10 MPa/km). We note that at 10 MPa and 323K, the values of the receding water contact angles for high, medium and low rank coals are 114°, 95° and 77°, respectively, implying that high rank coal is weakly CO_2-wet, medium rank coal is intermediate-wet and low rank coal is weakly water-wet at storage conditions (note: θ_r is considered here owing to the advancement of the CO_2 phase, which displaces brine; or alternatively 'drainage', Broseta et al. [54]). Consequently, the adsorption trapping capacities will be higher for high rank coal seams and least for low rank coal. Thus high rank coal will

be more suitable for CO_2 storage considering that adsorption of CO_2 is the dominant trapping mechanism [12,63]. Moreover, CO_2 injection into high rank coal at 10 MPa and 323K will wet the surfaces of coal with CO_2 better as compared to medium and low rank coals. Consequently, CO_2 will be distributed more uniformly into the micropores and thus recovery efficiency of methane will improve. It is also important to mention that with the increase in pressure and thus CO_2-wettability, coal will swell inducing a permeability reduction [64-66] and this effect limits CO_2 storage in coal seams.

In summary, once injected, CO_2 will occupy the smallest pores (micropores of coal matrix) and brine will occupy larger pores (cleats), and as a result brine will be watered-out. In addition, it is experimentally proven that methane wettability of coal is lower than that of CO_2 [34], and the sorption capacities of CO_2 relative to CH_4 on the coal surface are 1.1 – 9.1 times higher depending upon the coal rank [31,79-81]. Thus methane, which was adsorbed on the coal surfaces, will be displaced rather easily by CO_2.

5. Conclusions

We measured water contact angles to characterize CO_2-wettability of coals of low, medium and high rank as a function of reservoir pressure (0.1 MPa - 20MPa), temperature (308K-343K) and brine salinity (0wt% - 20wt%NaCl). The results demonstrate that both, θ_a and θ_r, increase with pressure, consistent with [34-37] and the increase is quite rapid up to 10 MPa and it flattens if pressure is increased further (10 MPa-20MPa, Figure 2-4), implying that injection pressures must be optimized to ensure economic feasibility. The increase in contact angles with pressure is attributed to a) increased CO_2-mineral intermolecular interactions due to increased CO_2 density [53,58], and b) increased CO_2 adsorption at high pressures [33,59-62]. Further we found that θ_a and θ_r decrease with temperature which is consistent with independent experimental CO_2-adsorption data [69-74]. The influence of salinity was not significant, and θ_a and θ_r increased only slightly with elevated salt content. Moreover, and importantly, the CO_2-wettability increased with the increase in coal rank, which is in agreement with other studies [35,36]. Specifically, we found that high rank coals (e.g. semi-anthracite) are strongly CO_2-wet at typical storage conditions, while medium rank coals (e.g. medium volatile bituminous) are weakly CO_2-wet and low rank coals (e.g. Lignite) are intermediate wet, i.e. CO_2-wettability showed a positive correlation with vitrinite reflectance

and fixed carbon content. Finally, we predict that high rank coal seams existing at high temperatures and high pressures are more feasible for CO_2 storage due to increased CO_2-wettability.

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