

1 **CO₂-wettability of low to high rank coal seams: Implications for carbon sequestration**
2 **and enhanced methane recovery**

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10

11 **Abstract**

12 Coal seams offer tremendous potential for carbon geo-sequestration with the dual benefit of
13 enhanced methane recovery. In this context, it is essential to characterize the wettability of
14 the coal-CO₂-water system as it significantly impacts CO₂ storage capacity and methane
15 recovery efficiency. Technically, wettability is influenced by reservoir pressure, coal seam
16 temperature, water salinity and coal rank. Thus a comprehensive investigation of the impact
17 of the aforementioned parameters on CO₂-wettability is crucial in terms of storage site
18 selection and predicting the injectivity behaviour and associated fluid dynamics. To
19 accomplish this, we measured advancing and receding water contact angles using the pendent
20 drop tilted plate technique for coals of low, medium and high ranks as a function of pressure,
21 temperature and salinity and systematically investigated the associated trends. We found that
22 high rank coals are strongly CO₂-wet, medium rank coals are weakly CO₂-wet, and low rank
23 coals are intermediate-wet at typical storage conditions. Further, we found that CO₂-
24 wettability of coal increased with pressure and salinity and decreased with temperature
25 irrespective of coal rank. We conclude that at a given reservoir pressure, high rank coal
26 seams existing at low temperature are potentially more efficient with respect to CO₂-storage
27 and enhanced methane recovery due to increased CO₂-wettability and thus increased
28 adsorption trapping.

29

30 1. Introduction

31 Carbon capture and storage (CCS) is the most promising approach to mitigate anthropogenic
32 CO₂ emissions and thus ensure a cleaner environment [1-5]. The storage of CO₂ in depleted
33 oil and gas reservoirs [6-8] or deep saline aquifers [9-11] allows trapping of enormous
34 volumes over a long period of time. Another option is injection of CO₂ into coal seams [12-
35 15] with the dual benefit of enhanced coal bed methane recovery [16-18]. In conventional
36 reservoirs, CO₂ is held trapped by means of four mechanisms which are structural trapping
37 [19-22], capillary or residual trapping [8,23-25], dissolution trapping [26,27] and mineral
38 trapping [28]. In coal seams, however, the dominant storage mechanism is adsorption
39 trapping of CO₂ onto the coal matrix [12,29,30]. Typically the adsorption capacity of CO₂ is
40 higher than that of methane, depending on coal rank [31-33]; consequently, CO₂ displaces
41 methane towards the production well and itself gets sorbed within the micropores of the coal
42 seam and remains trapped. The preferential adsorption and thus storage of CO₂ in coal seams,
43 by forced migration of methane, is strongly influenced by wettability of the CO₂-water-coal
44 system [12,34], which in turn is generally a function of reservoir pressure [34-37],
45 temperature and salinity. Moreover, in coal seams wettability is also a function of coal rank,
46 vitrinite reflectance, fixed carbon and ash content [35,38]. Therefore, it is essential to
47 describe CO₂-wettability of coals of varying ranks, and how reservoir conditions (pressure,
48 temperature and brine salinity) influences this wettability.

49 In this context, several studies reported CO₂-wettability of coals at ambient conditions [38-
50 41], but only a limited amount of literature data for the more relevant higher pressures have
51 been reported [34-37,42,43]. Table 1 presents a summary of the major experimental variables
52 considered in previous studies, and this work.

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57 Table 1: CO₂-wettability of coals: Summary of experimental conditions used.

58

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

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61 Therefore there is a clear lack of data available on CO₂-wettability of coals as a function of
62 coal rank, coal formation pressure, and particularly temperature and salinity (cp. Table 1).
63 Thus there exists a gap in terms of proper understanding of CO₂-wettability of coal seams of
64 different ranks at reservoir conditions. Moreover, although it is well established that coal
65 seams offer enormous potential for enhanced methane recovery and CO₂ sequestration, yet
66 certain important questions need to be addressed which are: 1) Which type of coal (low rank,
67 medium rank, or high rank) are most suitable for CO₂ storage and enhanced coalbed methane
68 recovery under the prevailing geothermal and reservoir pressure conditions? 2) Is the
69 suitability of CO₂ sequestration in coal seams of a particular rank valid for a wide range of
70 reservoir pressures, temperatures and salinity conditions? 3) What mechanisms are
71 responsible for long term CO₂-storage in coals? To answer these questions and to generally
72 improve the characterization of CO₂-wettability of coals, we experimentally measured water
73 advancing and receding contact angles on three coal samples as a function of coal rank (low,
74 medium and high ranks), vitrinite reflectance and fixed carbon at different CO₂ pressures (0.1
75 MPa to 20 MPa), temperatures (ranging from 308K to 343K), and brine salinities (0wt%
76 NaCl-10wt% NaCl) using the pendent drop technique. The results of the study lead to a broad
77 characterization of CO₂-wettability of coals and thus help optimize CO₂-storage and
78 enhanced coal bed methane recovery operations. Our results indicate that CO₂-wettability of

79 coals is strongly influenced by coal rank such that the high rank coals are more CO₂-wet and
80 low rank coals are least CO₂-wet at a given reservoir pressure, temperature and salinity.

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83 **2. Materials and methods**

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85 *2.1. Coal Samples*

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

94

95 *2.2. Petrology, Ultimate and Proximate Analysis*

96 The results of the proximate, ultimate and petrological analysis and the internal properties
97 (density and volume) of the coal samples are listed in Table 2. Note that coal samples of
98 different rank differ mainly in volatile matter, moisture, fixed carbon and vitrinite reflectance
99 [46,47]. Petrology was analysed in accordance with Australian Standard AS2856 and
100 ISO7404; proximate analysis were conducted using AS1038.3, ISO11722 and ASTM D3172-
101 07a, and ultimate analysis were performed using AS1038.6 and ISO 609.

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106 **Table 2.** Properties of coal samples used.

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

		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

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109 2.3. Fluids

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111 99.9 wt% CO₂ (from BOC, gas code – 082), de-ionized water (Conductivity: 0.02 mS/cm),
 112 and 5wt% and 10wt% NaCl brine (NaCl Source: Scharlab s.l., Spain, Purity: ≥ 0.995 mass%)
 113 were used in the study. Acetone (99.9 wt%) was used to wash the coal samples.

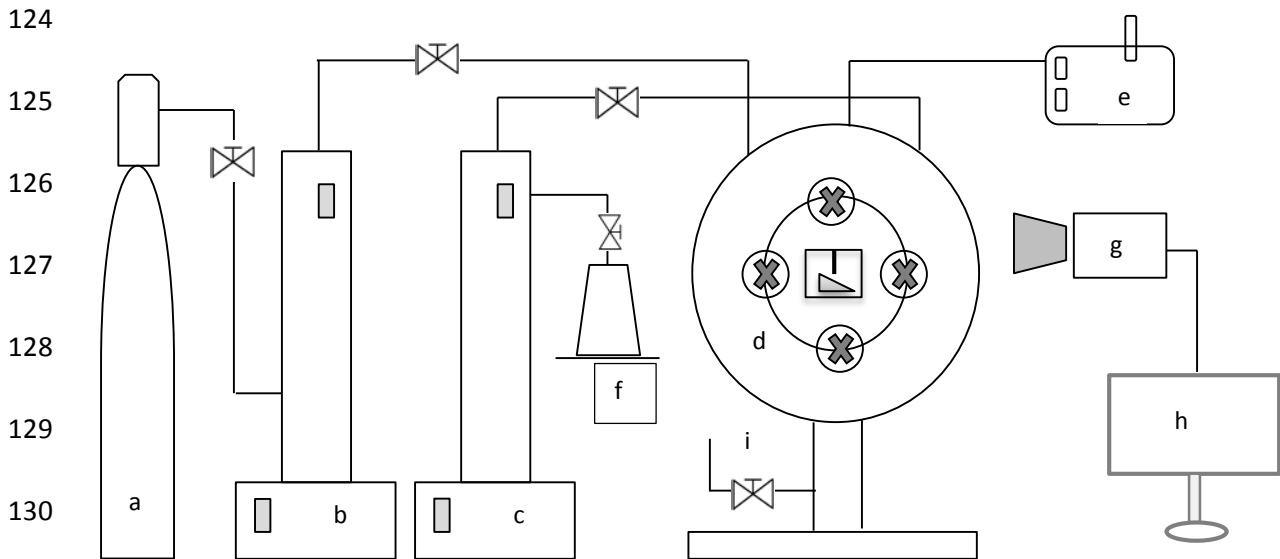
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116 2.3. Contact angle measurements

117 CO₂-brine wettability was measured using the pendent drop tilted plate technique [48]. The
 118 experimental setup is shown in Figure 1; it consists of a high pressure cell (which holds the

119 sample on a tilted plate), a CO₂ cylinder, two high precision syringe pumps (Teledyne D-500,
 120 pressure accuracy of 0.1%FS) for water and CO₂ and a video camera. Prior to each
 121 experiment, the coal substrates were washed with acetone and then cleaned in air plasma
 122 (Diemer Yocto instrument) for 2 minutes to ensure that no organic contaminants are
 123 deposited on the sample, which would introduce a bias [49].



133 **Figure 1.** Experimental setup for contact angle measurements used in this study; (a) CO₂
 134 cylinder (b) high precision syringe pump-CO₂, (c) high precision syringe pump-water, (d)
 135 high pressure cell with substrate housed on a tilted plate inside, (e) heating unit, (f) liquid
 136 feed/drain system, (g) high resolution video camera, (h) image visualization and
 137 interpretation software, (i) pressure relief valve.

139 For each measurement, a clean and dry coal sample was placed inside the pressure cell onto
 140 the tilted plate. The temperature was set to a fixed value (308K, 323K, and 343K), and CO₂
 141 pressure in the cell was increased with a high precision syringe pump to pre-determined
 142 values (0.1 MPa, 5 MPa, 10 MPa, 15 MPa, 20 MPa) by injecting CO₂ into the cell.
 143 Subsequently a droplet of de-gassed brine (average volume of $\sim 6\mu\text{L} \pm 1\mu\text{L}$) was allowed to
 144 flow (at 0.4ml/min) and was dispensed onto the substrate through a needle. We note that the
 145 fluids used were not thermodynamically equilibrated, since earlier studies demonstrated that
 146 the contact angle θ is not significantly affected by mass transfer during the first 60seconds of

147 exposure (only insignificant change (2°) was observed by [50,51]) and during this time all
148 measurements were completed. Furthermore, non-equilibrated fluids are most relevant at the
149 leading edge of the CO₂ plume, i.e. when CO₂ first encounters under saturated brine. A video
150 camera (Basler scA 640–70 fm, pixel size = 7.4 μm ; frame rate = 71 fps; Fujinon CCTV lens:
151 HF35HA-1B; 1:1.6/35 mm) recorded the entire process, and contact angles were measured on
152 images extracted from the movie files. Advancing (θ_a) and receding water contact angles (θ_r)
153 were measured simultaneously at the leading and trailing edges of the droplet, just before the
154 droplet started to move. The standard deviation of these measurements was $\pm 3^\circ$ based on
155 replicate measurements; however for lignite the standard deviation reached $\pm 5^\circ$, which is due
156 to the more complicated nature of the sample.

157

158

159 **3. Results and Discussion**

160 In order to assess CO₂-storage and methane recovery potential, CO₂-wettability of coals was
161 characterized as a function of rank at relevant thermophysical conditions by measuring
162 advancing and receding contact angles on coal samples of high, medium and low ranks at
163 various reservoir conditions (pressure range: 0.1-20 MPa, temperature range: 308K-323K and
164 salinity range: 0wt%-10wt% NaCl). The outcomes of the study led to a precise realisation of
165 the relationships between coal rank and corresponding CO₂ geo-storage and ECBM potential.
166 The subsequent sections describe the results in detail.

167

168 *3.1. Effect of Pressure on CO₂-wettability of coal*

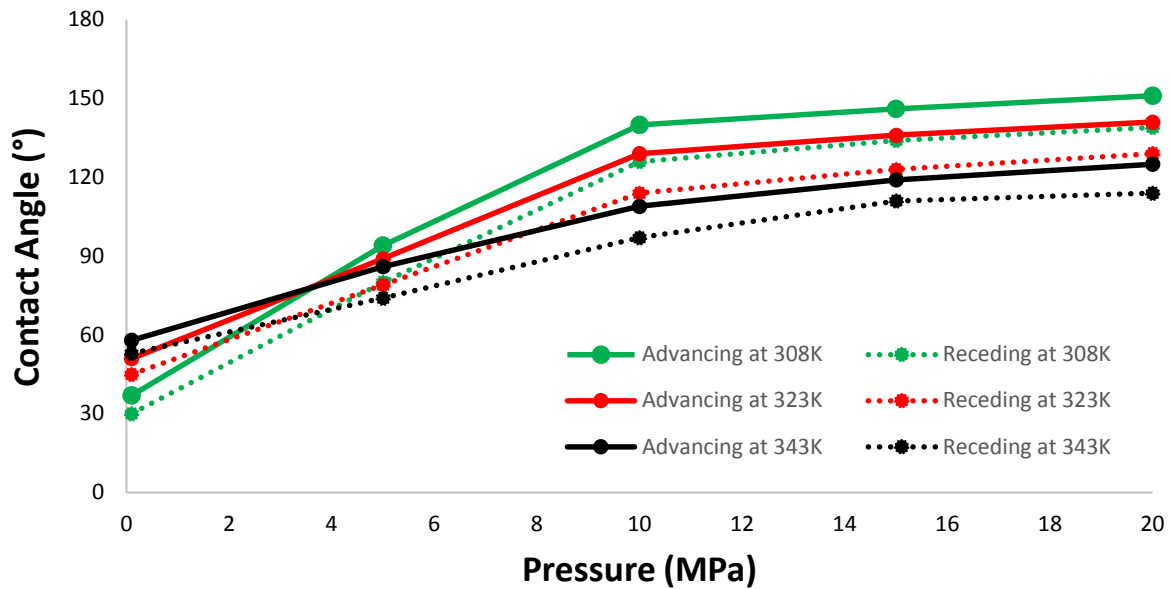
169 The effect of pressure was systematically tested on the three (high, medium, low rank)
170 samples at 0.1 MPa, 5 MPa, 10 MPa, 15 MPa and 20 MPa for three different temperatures
171 (308K, 323K, and 343K). Both, θ_a and θ_r , clearly increased with pressure at all temperatures
172 for all coal samples (Figure 2-4). High rank coal was water wet ($\theta < 50^\circ$, [21]) at ambient
173 pressure for all temperatures tested (308K-343K; Figure 2). As pressure increased from 0.1
174 MPa to 20 MPa at 323K, θ_a increased from 51° to 141° and θ_r increased from 45° to 129° (red
175 lines in Figure 2), and thus high rank coal became CO₂-wet at high pressure ($\theta > 130^\circ$, [21]).
176 Similarly, at 343K, as pressure increased from ambient to 20 MPa, θ_a increased from 58° to
177 118° and θ_r increased from 52° to 107° .

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

180 at 298K for coals of unknown ranks and found that coal hydrophobicity increased with
181 pressure. Siemons et al. [37] extended the testing pressure up to 14 MPa at 318K and
182 analysed CO₂-water contact angle for an anthracite coal (high rank) and found that the system
183 became CO₂-wet at 2.6 bar, however, in our case semi-anthracite became weakly CO₂-wet at
184 around 7 MPa ($\theta_a > 110^\circ$); this difference could be due to difference in rank of the samples
185 (semi-anthracite in this study) and difference in experimental conditions (temperature and
186 surface cleaning methods). Sakurovs and Lavrencic [36] experimentally determined CO₂-
187 water contact angles using the captive bubble technique up to 15 MPa at 313K for low to
188 medium rank coals ($R_v\%$ of their samples ranged from 0.62-1.4) and found an increase in
189 CO₂-wettability with pressure for all samples. Kaveh et al. [35] compared CO₂-wettability of
190 high volatile bituminous (medium rank) and semi anthracite (high rank) coals up to 16 MPa
191 and at 318K; and reported that semi-anthracite became CO₂-wet ($\theta = 110^\circ$) at 5.7 MPa which
192 is close to our result (7 MPa); the slight difference could be due to different surface cleaning
193 methods and temperature. Saghafi et al. [34] also studied CO₂-wettability of high rank coal
194 up to 6 MPa at 295K, their sample turned CO₂-wet at 5 MPa ($\theta = 110^\circ$).

195 The increase in contact angle with pressure is also consistent with experimental data on pure
196 minerals such as mica [53-56] and quartz [50,51,55,57]. This transformation of wettability
197 from water-wet to CO₂-wet by an increase in pressure is, apart from increased intermolecular
198 interactions of CO₂ with solid surface [53,58], also related to the increased adsorption of CO₂
199 on the coal surface, which is evident from experimental CO₂ adsorption data on coals [33,59-
200 62].

201
202 Since adsorption is the dominant storage mechanism in coals, and typically accounts for 98%
203 of the total gas stored [12,63], high pressure storage conditions are preferred as they would
204 lead to increased storage volumes. Moreover, increased CO₂-wettability of coal will lead to
205 more uniform distribution of CO₂ within the micropores of the coal seams and thus improved
206 displacement of methane towards the production wells. However, at high pressures coal
207 swells [64-66], which leads to a significant permeability decrease [67], which again limits the
208 Darcy flow (of the CO₂) and thus injectivity.



210

211 **Figure 2.** CO₂-DI water contact angles on high rank coal (semi-anthracite) at tested
 212 pressures (0.1 MPa-20 MPa) and temperatures (308K-343K).

213

214 Furthermore, we found that the rate of contact angle increase with pressure is sharper for the
 215 pressure range 0.1 MPa-10 MPa (Figure 2). For example, at 323K, θ_a measured 51° at 0.1
 216 MPa and 129° at 10 MPa resulting in a net increase of 78°, whereas the net increase in θ_a for
 217 the pressure range 10 MPa-20 MPa was only 12°. This implies that injection of CO₂ in high
 218 rank coals at very high pressure may yield only marginal benefits in terms of additional
 219 volume stored because of only marginal improvement in CO₂-wettability. Generally, the
 220 increase in contact angle with pressure flattened out for pressures 10 MPa-20 MPa.

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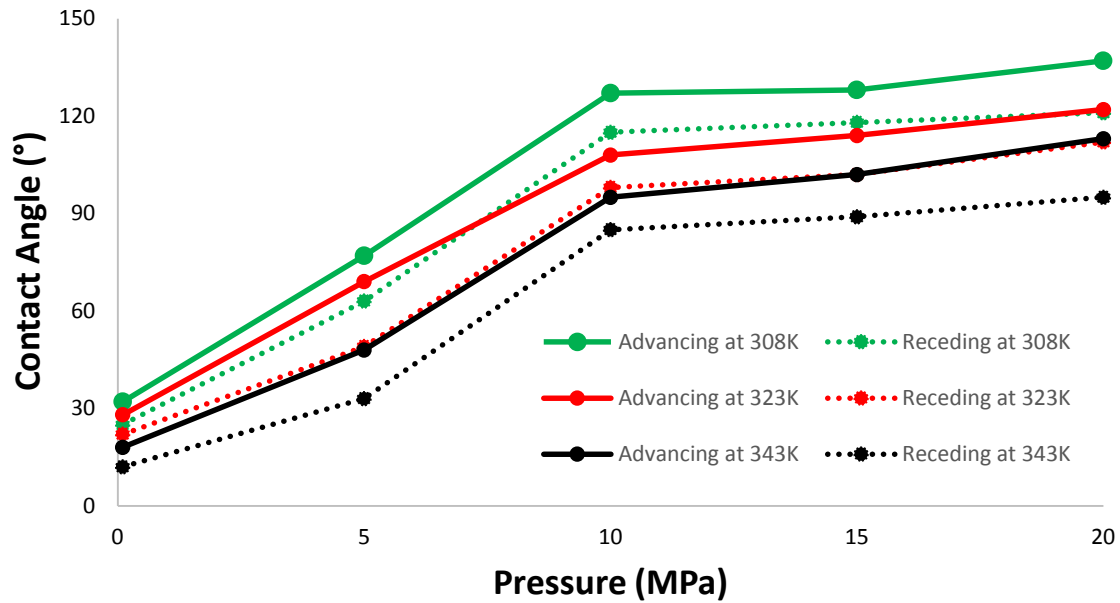


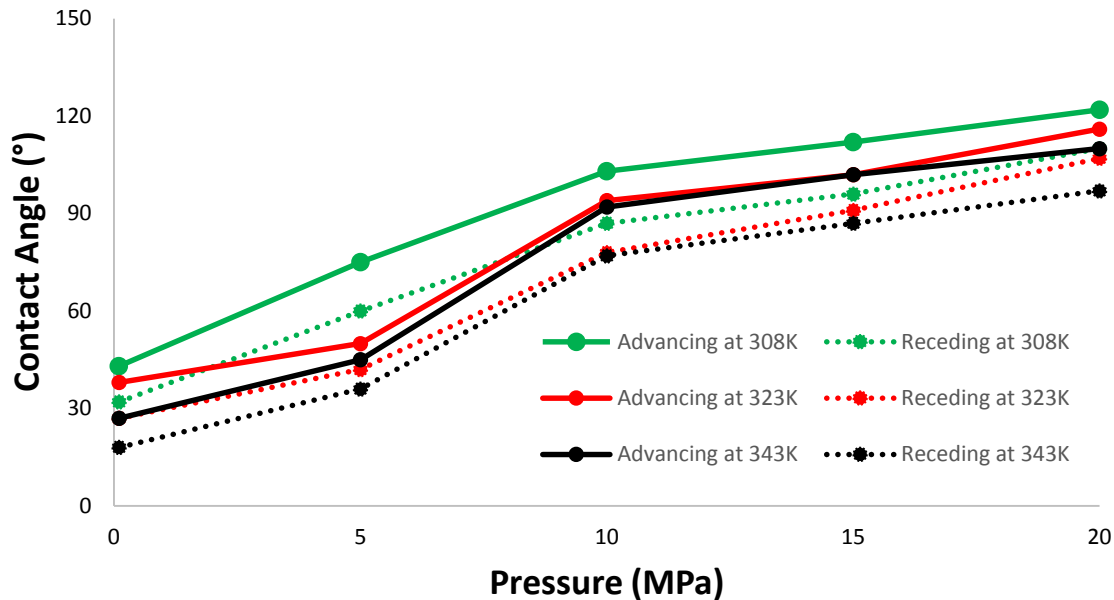
Figure 3. CO₂-DI water contact angles on medium rank coal (medium volatile bituminous) at tested pressures (0.1 MPa-20 MPa) and temperatures (308K-343K).

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 CO₂-wet at reservoir conditions ($110^\circ \leq \theta \leq 130^\circ$; [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 CO₂ storage capacity in medium rank coals increases with pressure at all temperatures owing to the increased CO₂-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

245 observed up to 20 MPa (θ_a increased to 116°). The maximum contact angle measured for low
 246 rank coals was 122° (at 20 MPa and 308K) indicating that the most hydrophobic wettability
 247 regime for low rank coals is ‘weakly CO₂-wet’ implying reduced CO₂ trapping by means of
 248 adsorption. Similar trends were observed for higher temperature (323K and 343K).

249



250

251 **Figure 4.** CO₂-DI water contact angles on low rank coal (lignite) at tested pressures (0.1
 252 MPa-20 MPa) and temperatures (308K-343K).

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254

255 3.2. Effect of temperature on CO₂-wettability of coal

256

257 The trends of contact angle variation with temperature are presented in Figures 2-4. For all
 258 coal samples analysed, both, θ_a and θ_r , decreased with temperature at all pressures tested, with
 259 the exception that for high rank coal, θ_a and θ_r increased with temperature at ambient pressure
 260 (0.1 MPa). For example, when temperature increased from 308K to 343K at 0.1 MPa, θ_a
 261 increased from 37° to 58° for high rank coal, while it decreased from 32° to 18° for medium
 262 rank coal and from 43° to 27° for low rank coal. At higher pressures (5 MPa-20 MPa),
 263 however, all coal types showed a clear decrease in θ_a and θ_r with temperature (Figures 2-4).
 264 For simplicity a summary of contact angle variation with temperature is shown in Figure 5.
 265 At 15 MPa, for high rank coal, when temperature increased from 308K to 323K, θ_a decreased
 266 from 146° to 119° , implying wettability transformation from strongly CO₂-wet to weakly
 267 CO₂-wet. Similarly, for medium rank coal, θ_a decreased from 128° to 102° when temperature

268 increased from 308K to 343K. However, for low rank coal, θ_a first decreased from 112° to
 269 102° when temperature increased from 308K to 323K, and then became constant when
 270 temperature increased further (from 323K to 343K). In summary, CO₂-wettability of coal
 271 decreased with increasing temperature irrespective of the coal rank. There is no published
 272 data on the effect of temperature on CO₂-water-coal contact angles, however, the decrease in
 273 contact angle with temperature has also been reported for pure minerals such as mica [53,54]
 274 or quartz [56-58].

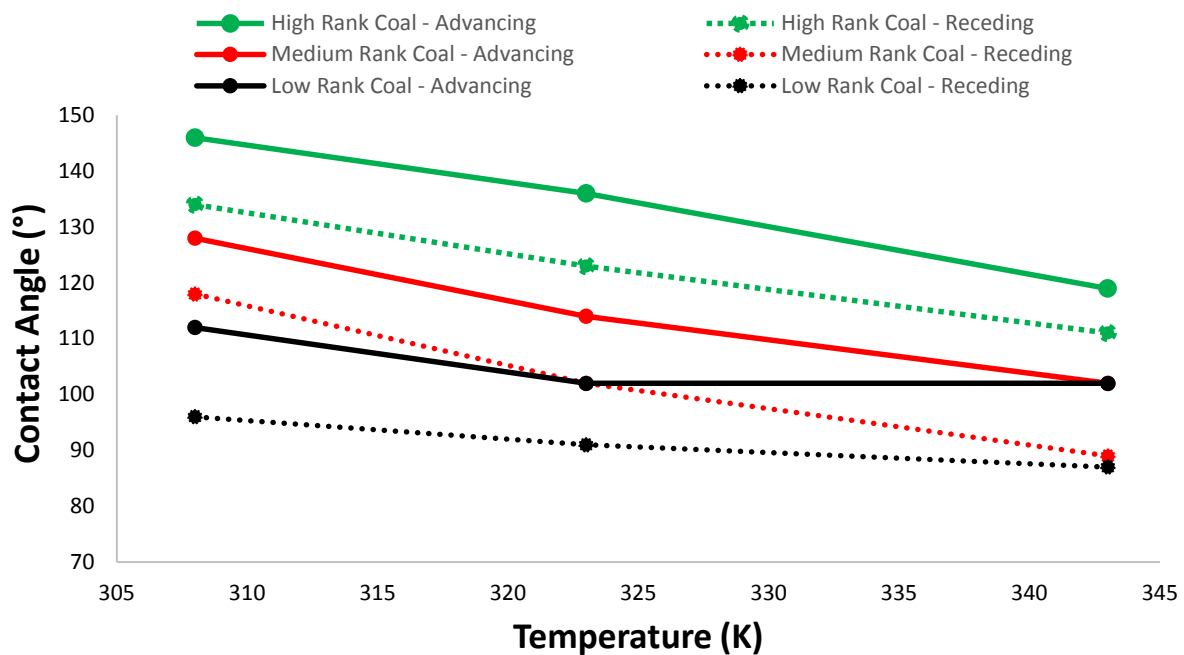
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276 We demonstrate that two distinct mechanisms may be held responsible for the decrease in
 277 contact angle with temperature. The first mechanism is the interplay of the three interfacial
 278 tensions [53,58], which is expressed by the Young-Laplace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

$$279 \quad \cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{vl}} \quad (1)$$

280 In eq. (1), γ_{sv} and γ_{sl} are the solid-CO₂ interfacial tension and solid-brine interfacial tension,
 281 respectively, whereas γ_{vl} is CO₂-brine interfacial tension. Since most of the previous studies
 282 [51,53,57,68] agree that CO₂-brine interfacial tension increases with temperature, it is evident
 283 from equation (1) that the difference of solid-CO₂ interfacial tension and solid-brine
 284 interfacial tension (numerator of equation) should increase with temperature to cause a
 285 corresponding decrease in contact angle with temperature.

286



287

288

289 **Figure 5.** Effect of temperature on CO₂-wettability for all coal samples used in the study.
290 For simplicity measurements are shown only for 15 MPa.

291

292 Secondly, the decrease in the contact angle with temperature can be attributed to the CO₂
293 adsorption behaviour on coal. The experimental studies on the effect of temperature on CO₂
294 adsorption [69-74] report that there is a clear decrease in CO₂ adsorption on coal surfaces
295 with temperature. This reduced CO₂-affinity is thus reflected in the contact angles. Perera et
296 al. [71] mentioned that the decrease in adsorption capacity with temperature is due to the
297 increase in kinetic energy and rate of diffusion of CO₂, which tend to release gas molecules
298 from the coal matrix resulting in a corresponding reduction in net amount of adsorbed gas.
299 We thus conclude that low temperature coal seams have higher CO₂ storage capacities in
300 comparison to high temperature coal seams.

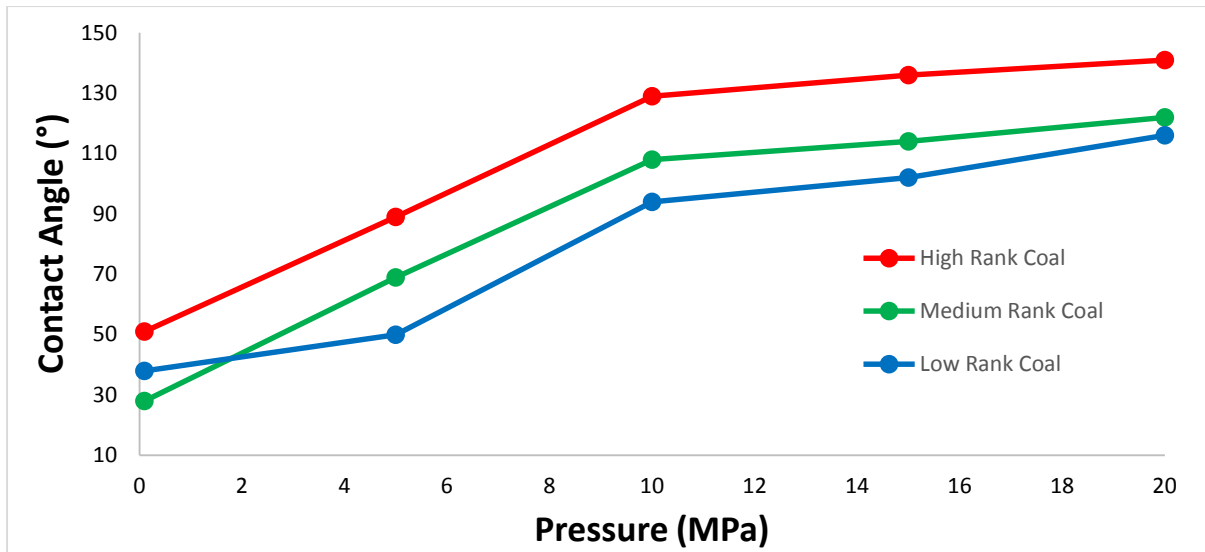
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302 3.3. *Effect of coal rank on CO₂-wettability*

303

304 In order to demonstrate the impact of coal rank on CO₂-wettability and thus on methane
305 production and CO₂ storage potential in coals, we plotted advancing water contact angles
306 (only for simplicity) as a function of pressure and temperature (Figure 6). It is clear that at
307 any given CO₂ pressure, apart from the ambient, high rank coal offers highest CO₂-wetting
308 potential, and CO₂-wettability substantially decreases with rank. Low rank coals (e.g.
309 Lignite) are least CO₂-wet and medium rank coal (e.g. Bituminous) are intermediate. These
310 results are in agreement with Kaveh et al. [35] who compared CO₂-wettability of semi-
311 anthracite and high volatile bituminous coals, and they measured higher contact angles for
312 semi-anthracite coals, and thus they concluded that hydrophobicity of coals increases with
313 coal rank. Moreover, Sakurovs and Lavrencic [36] also concluded that high ranks coals were
314 easier to wet with CO₂ at high pressures and that the increase in CO₂-wettability promoted
315 the rate of penetration of CO₂ into the coals. It can therefore be established that CO₂-
316 wettability of coals is a strong function of coal rank and that high rank coals are more CO₂-
317 wet. We point out that this behaviour is related to the increase in CO₂ adsorption capacity
318 with an increase in coal rank as evidenced by the literature data on adsorption isotherms of
319 coals of varying rank [32,75].

320



322

323 **Figure 6.** Effect of coal rank on CO₂-wettability.

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326 *3.4. Effect of brine salinity on CO₂-wettability of coal*

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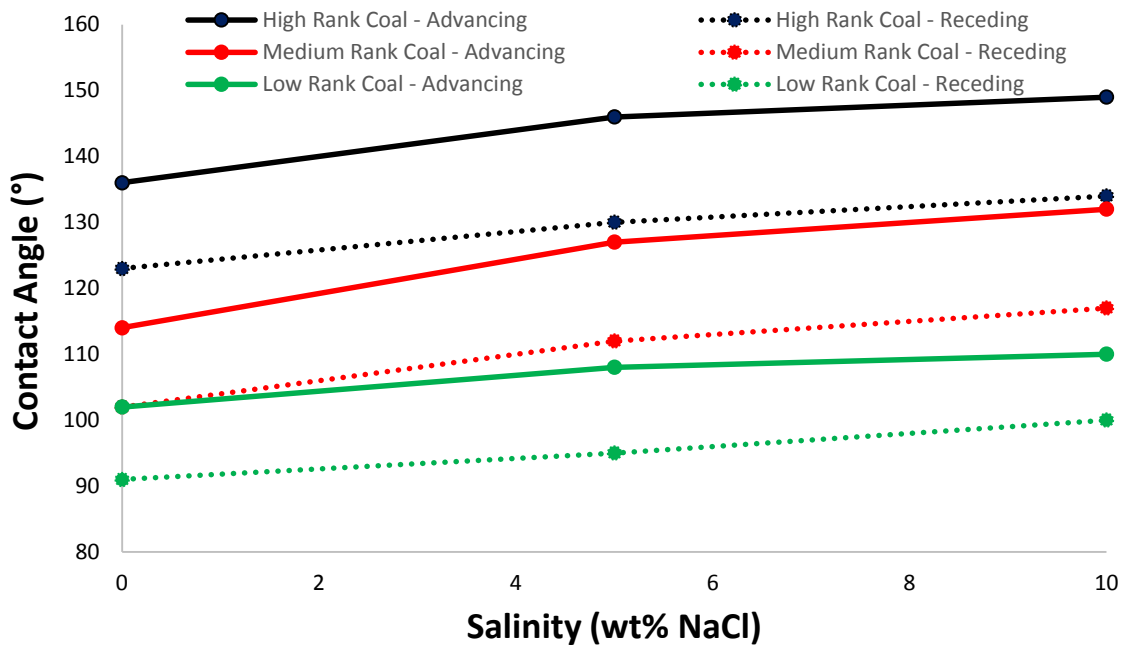
328 Water can exist in coals seams in the form of free water in cleats, chemically bound hydration
 329 water, and water adsorbed onto the surface of the matrix blocks [76,77]. The cleat system is
 330 initially filled with water and it provides the flow path for production by Darcy's law. We
 331 thus analysed the impact of brine salinity on CO₂-brine-coal wettability for various salinities
 332 (0wt% NaCl, 5wt%NaCl and 10wt% NaCl) at 15 MPa and 323K on all the coal samples
 333 studied in this work; as salinity is expected to vary in subsurface coal seams [78].

334 Both, θ_a and θ_r , increased with salinity for all coal samples (Figure 7). This increase was
 335 stronger for the brine salinity increase from 0wt% NaCl to 5wt% NaCl; e.g. for medium rank
 336 coal, θ_a increased from 114° to 127° and θ_r increased from 102° to 112° when salinity
 337 increased from 0wt% NaCl to 5wt% NaCl brine. For the salinity increase from 5wt% NaCl to
 338 10wt% NaCl, the increase in contact angle was very small; e.g. for medium rank coal, θ_a
 339 increased from 127° to 132° and θ_r increased from 112° to 116° when salinity increased from
 340 5wt% NaCl to 10wt% NaCl brine. Moreover, we found similar trends for low, medium and
 341 high rank coals (Figure 7). In the literature, there is a lack of data on the effect of salinity on
 342 CO₂-wettability of coal, yet our results are consistent with Ibrahim et al. [52], who analysed
 343 contact angles of CO₂-brine-coal systems for brine salinities varying between 0 g/L-15 g/L
 344 NaCl), and who reported that contact angles were highest for 15 g/L and lowest for DI water.

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

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349

350 **Figure 7.** Effect of salinity on CO₂-wettability of coals at 323K and 15 MPa.

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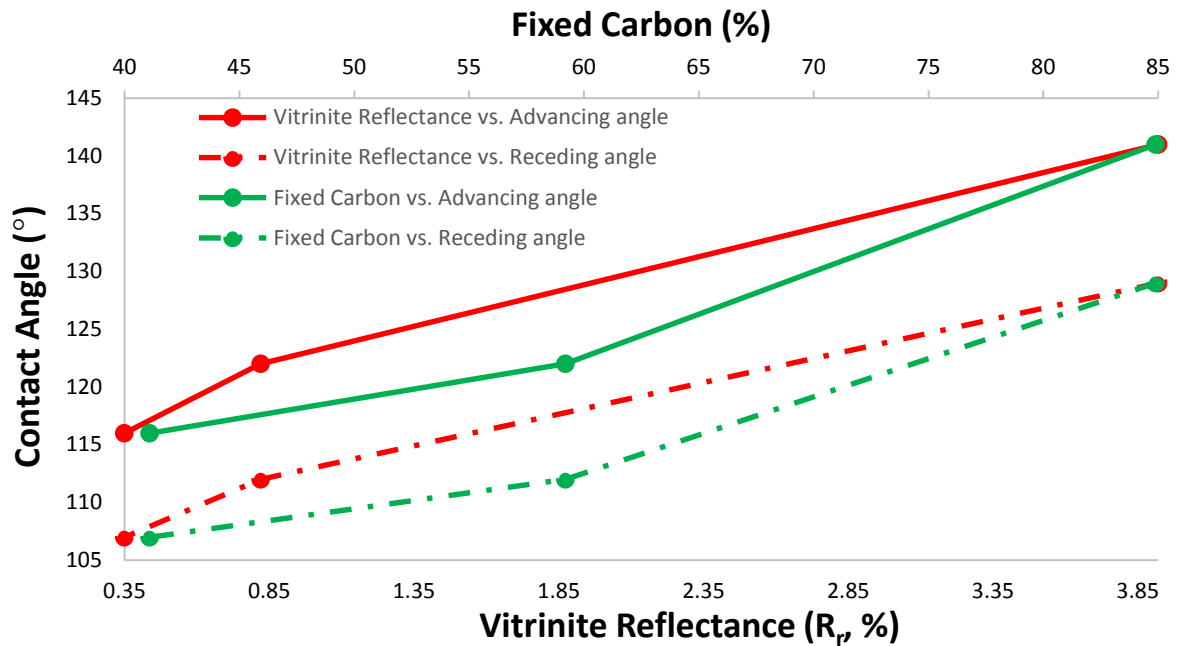
353 3.5. Relation between vitrinite reflectance, fixed carbon and coal wettability

354

355 There is a strong positive correlation between vitrinite reflectance and water contact angle.
356 Similarly, fixed carbon (which is the solid combustible residue that remains after coal is
357 heated and volatile matter is expelled) strongly correlates with the water contact angle
358 (Figure 8). Practically, coals with higher vitrinite reflectance are more CO₂-wet and thus will
359 store more CO₂ by means of adsorption; coals with higher fixed carbon content also have
360 better CO₂-wetting characteristics. At 20 MPa and 323K, coal with a vitrinite reflectance (R_r ,
361 %) of 3.8 is strongly CO₂-wet ($\theta_a = 140^\circ$), whereas at the same reservoir conditions medium
362 rank coal ($R_r = 0.82$) is weakly CO₂-wet ($\theta_a = 122^\circ$) and low rank coal ($R_r = 0.35$) is
363 intermediate-wet ($\theta_a = 116^\circ$); thus CO₂ injection into low rank coals will require higher
364 injection pressures to completely wet the surface in comparison to medium and high rank
365 coals. Thus we conclude that coals of higher vitrinite reflectance and fixed carbon exhibit
366 better CO₂ adsorption storage capacity, because of their better CO₂-wettability. This effect

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

369



370

371 **Figure 8.** Variation of CO₂-wettability with vitrinite reflectance and fixed carbon content.

372

373 4. Implications

374

375 We measured CO₂-wettability of coals of varying ranks; which is essential to assess the CO₂
376 storage potential of coal seams, and also to assess enhanced hydrocarbon gas production from
377 unmineable coal seams. The measured data implies that CO₂ storage in coal seams is strongly
378 influenced by pressure, seam temperature, brine salinity, rank of the coal, vitrinite reflectance
379 and fixed carbon. As an example, consider three potential candidate coal bed methane
380 formations of different ranks (high, medium and low) at a depth of 1km and at temperature of
381 323K. The required CO₂ injection pressure will be approximately 10 MPa (estimated using
382 formation pressure gradient ~ 10 MPa/km). We note that at 10 MPa and 323K, the values of
383 the receding water contact angles for high, medium and low rank coals are 114°, 95° and 77°,
384 respectively, implying that high rank coal is weakly CO₂-wet, medium rank coal is
385 intermediate-wet and low rank coal is weakly water-wet at storage conditions (note: θ_r is
386 considered here owing to the advancement of the CO₂ phase, which displaces brine; or
387 alternatively 'drainage', Broseta et al. [54]). Consequently, the adsorption trapping capacities
388 will be higher for high rank coal seams and least for low rank coal. Thus high rank coal will

389 be more suitable for CO₂ storage considering that adsorption of CO₂ is the dominant trapping
390 mechanism [12,63]. Moreover, CO₂ injection into high rank coal at 10 MPa and 323K will
391 wet the surfaces of coal with CO₂ better as compared to medium and low rank coals.
392 Consequently, CO₂ will be distributed more uniformly into the micropores and thus recovery
393 efficiency of methane will improve. It is also important to mention that with the increase in
394 pressure and thus CO₂-wettability, coal will swell inducing a permeability reduction [64-66]
395 and this effect limits CO₂ storage in coal seams.

396

397 In summary, once injected, CO₂ will occupy the smallest pores (micropores of coal matrix)
398 and brine will occupy larger pores (cleats), and as a result brine will be watered-out. In
399 addition, it is experimentally proven that methane wettability of coal is lower than that of
400 CO₂ [34], and the sorption capacities of CO₂ relative to CH₄ on the coal surface are 1.1 – 9.1
401 times higher depending upon the coal rank [31,79-81]. Thus methane, which was adsorbed on
402 the coal surfaces, will be displaced rather easily by CO₂.

403

404

405 **5. Conclusions**

406

407 We measured water contact angles to characterize CO₂-wettability of coals of low, medium
408 and high rank as a function of reservoir pressure (0.1 MPa - 20MPa), temperature (308K-
409 343K) and brine salinity (0wt% - 20wt%NaCl). The results demonstrate that both, θ_a and θ_r ,
410 increase with pressure, consistent with [34-37] and the increase is quite rapid up to 10 MPa
411 and it flattens if pressure is increased further (10 MPa-20MPa, Figure 2-4), implying that
412 injection pressures must be optimized to ensure economic feasibility. The increase in contact
413 angles with pressure is attributed to a) increased CO₂-mineral intermolecular interactions due
414 to increased CO₂ density [53,58], and b) increased CO₂ adsorption at high pressures [33,59-
415 62]. Further we found that θ_a and θ_r decrease with temperature which is consistent with
416 independent experimental CO₂-adsorption data [69-74]. The influence of salinity was not
417 significant, and θ_a and θ_r increased only slightly with elevated salt content. Moreover, and
418 importantly, the CO₂-wettability increased with the increase in coal rank, which is in
419 agreement with other studies [35,36]. Specifically, we found that high rank coals (e.g. semi-
420 anthracite) are strongly CO₂-wet at typical storage conditions, while medium rank coals (e.g.
421 medium volatile bituminous) are weakly CO₂-wet and low rank coals (e.g. Lignite) are
422 intermediate wet, i.e. CO₂-wettability showed a positive correlation with vitrinite reflectance

423 and fixed carbon content. Finally, we predict that high rank coal seams existing at high
424 temperatures and high pressures are more feasible for CO₂ storage due to increased CO₂-
425 wettability.

426

427

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429

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