

1 **Influence of surface chemistry on interfacial properties of low to high rank coal seams**

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16 **Abstract**

17 Wettability of CO<sub>2</sub>/water/coal systems is a fundamental petro-physical parameter, which  
18 governs the fluid flow and distribution in coal seams and thus directly affects CO<sub>2</sub>-storage and  
19 methane recovery from unmineable coal seams. The recognition of wettability of  
20 coal/CO<sub>2</sub>/brine systems help to de-risk CO<sub>2</sub>-storage and enhanced methane recovery projects  
21 in coal seams. To understand the factors influencing the wetting characteristics of coals, a  
22 detailed examination and characterization of coal surface chemistry is essential and literature  
23 data in this context is missing. We thus measured zeta potentials as a function of temperature  
24 (298 K-343 K), brine salinity (0 wt% NaCl – 5 wt% NaCl) and salt type (NaCl, CaCl<sub>2</sub> and  
25 MgCl<sub>2</sub>) for coals of low, medium and high ranks. Further, we measured water advancing and  
26 receding contact angles as a function of temperature and salinity for the same experimental  
27 matrix in order to associate wettability changes to the surface charge at the coal/brine interface.

28 Moreover, coal surfaces were investigated by Fourier transformed infrared (FTIR)  
29 spectroscopy and the surface functional groups responsible for a particular wetting behaviour

30 were identified. We found that zeta potential increased with temperature, salinity and cation  
31 valency. Both advancing and receding contact angles decreased with temperature, and  
32 increased with salinity and cation valency irrespective of the coal rank. Finally the XRD  
33 measurements and infrared spectra revealed that the presence of polar surface functional groups  
34 (e.g. Si-OH and carboxylic acid groups) which is responsible for the hydrophilic behaviour of  
35 low rank coals and the absence of these groups in high rank coal is responsible for their  
36 hydrophobic behaviour even at lower pressure. The high rank coal seams at high pressure are  
37 better for CO<sub>2</sub> storage and methane recovery.

38

## 39 **1. Introduction**

40 The injection of CO<sub>2</sub> in depleted oil and gas reservoirs or deep saline aquifers is capable of  
41 trapping tremendous amounts of CO<sub>2</sub> and thus reduce anthropogenic CO<sub>2</sub> emissions [1-3].  
42 Certain trapping mechanisms render CO<sub>2</sub> immobile in the porous medium, and these are  
43 structural trapping [4-7], residual or capillary trapping [8,9], dissolution or solubility trapping  
44 [10] and mineral trapping [11]. Coal seams, too, offer enormous potential for CO<sub>2</sub> storage and  
45 enhanced methane recovery by means of preferential adsorption of CO<sub>2</sub> [12,13]. Adsorption is  
46 the major CO<sub>2</sub> trapping mechanism in unminable coal seams and the wettability of the specific  
47 CO<sub>2</sub>/brine/coal system plays a significant role in this context [12,14]. Typically, the adsorption  
48 capacity of CO<sub>2</sub> is higher than that of methane, consequently, CO<sub>2</sub> displaces methane toward  
49 the production well and itself gets sorbed within the micropores of the coal seam and remains  
50 trapped [12]. Moreover, Arif et al. [12] pointed out that higher CO<sub>2</sub>-wettability would lead to  
51 higher CO<sub>2</sub>-adsorption and thus higher storage [12].

52 Although coal wettability has been characterized as a function of pressure, temperature, salinity  
53 and coal rank [12,15], the factors responsible for a particular wetting behaviour are so far  
54 unclear. Specifically, the knowledge and characterization of coal surface chemistry is essential  
55 to understand the factors that influence its wettability [16,17]. In this context, zeta potential is  
56 used to probe the double layer at the surface of the coal. The nature of the double layer affects  
57 the repulsion/attraction of system's components, and depends upon the physicochemical  
58 properties of all components in the overall system [18]. Thus, what occurs at the brine/mineral  
59 or brine/rock interface (at a particular temperature and brine salinity) is strongly affected by  
60 the electrical double layer and studies have shown that this double layer is closely related to  
61 wettability [19-21].

62 We thus examined the electrochemical behaviour of coal by measuring zeta potentials as a  
63 function of temperature (298 K-343 K), salinity (0 wt% NaCl-5 wt% NaCl), salt type (NaCl,  
64 CaCl<sub>2</sub> and MgCl<sub>2</sub>) and coal rank (low, medium and high rank) to allow surface characterization  
65 for broad range of conditions. In addition, following the same experimental matrix, we  
66 measured advancing and receding contact angles for air/coal/brine systems (at ambient  
67 pressure). The associated trends were analysed systematically and relationships were  
68 developed between zeta potential and wettability. We found that the zeta potential increased  
69 with increasing rank and increasing salinity and contact angles also increased with increasing  
70 rank and salinity, implying a positive correlation between zeta potential and wettability.  
71 However, with increasing temperature zeta potential increased but contact angle decreased,  
72 implying that correlation with respect to temperature is inconsistent. Moreover, the zeta  
73 potential results were also compared to our published contact angle data at high pressure, and  
74 we hypothesized that zeta potential at high pressure may follow similar trends as those at  
75 ambient pressure.

76 Further, in order to evaluate the impact of coal rank on wettability of the coal/CO<sub>2</sub>/brine  
77 systems, we conducted Fourier transformed infrared spectroscopy (FTIR) measurements on the  
78 three coal samples (low, medium and high rank) and thoroughly characterized the surface  
79 functional groups. The results demonstrated that the abundance of OH and carboxylic acid  
80 groups on the low rank coal is responsible for the hydrophilic nature of lignite and the lack of  
81 these groups explains the hydrophobic nature of high rank coal (semi-anthracite).

82

## 83 **2. Experimental Methodology**

### 84 *2.1. Fluid/sample preparation*

85 Three coal samples [high rank (semi anthracite; from Hazelton, Pennsylvania, USA), medium  
86 rank (medium volatile bituminous; from Morgantown, West Virginia, USA), and low rank  
87 (lignite; from North Dakota, USA; Table 1)] were used in this research. The samples were cut  
88 to cuboid shape (~1cm x 1cm x 0.5cm) or crushed into fine powder (particle size ~30 microns)  
89 using milling equipment (Labtechnics Adelaide, Model TP-4/5, and Oscillation: 50Hz). The  
90 powdered samples were then placed in an oven at 90°C for 12 hours until the weight became  
91 constant.

92 Coal/brine composite samples for all coal ranks were prepared by adding 2wt% coal powder  
93 to aqueous salt solutions composed of DI water (0M), 1wt% NaCl (0.17M), 5wt% NaCl  
94 (0.855M), 1wt% CaCl<sub>2</sub> (0.27M), and 1wt% MgCl<sub>2</sub> (0.305M). Note: the numbers in brackets  
95 represent the equivalent ionic strength of electrolyte which is typically preferred while  
96 comparing different types of salt of same strength. In this paper, we mainly used wt% to express  
97 salinity, however, for salts comparison we used ionic strength (Section 3.3). Moreover, the  
98 alternative common units to express salinity are ‘mg/L’ and ‘ppm’.

99 Materials used were de-ionized water (Conductivity: 0.02 mS/cm) and brine comprising of  
100 NaCl, CaCl<sub>2</sub> and MgCl<sub>2</sub> (Salts Source: Scharlab s.l., Spain, Purity: ≥ 0.995 mass%). The  
101 solutions were covered with parafilm and stirred for 5 hours using a magnetic stirrer at 40 °C  
102 to ensure homogenous dispersion of the solid powder within the base liquid. The dispersions  
103 were then used for the zeta potential measurements. For contact angle measurements, the  
104 cuboid samples (low, medium and high rank coal) were selected and for spectroscopic  
105 measurements samples were used in powdered form.

106

## 107 *2.2. Zeta potential measurements*

108 Zeta potential was measured on a Zetasizer Nano ZS (Malvern instrument). The coal dispersion  
109 was placed in a folded capillary cell and sealed at the top. The zeta potential was measured for  
110 coal/DI-water for high, medium and low rank coals at 298 K, 308 K, 323 K and 343 K to  
111 investigate the effect of temperature on zeta potential. Moreover, the effect of salinity and  
112 cation type was analysed for coal dispersed in 1 wt% NaCl, 5 wt% NaCl, 1 wt% CaCl<sub>2</sub> and 1  
113 wt% MgCl<sub>2</sub> brine. The measurements were repeated three times and the standard deviation of  
114 zeta potential measurements was 3 mV at 298 K, ~2.5 mV at 308 K and ~1.5 mV at 323 K and  
115 343 K. Moreover, for higher salinities (5wt% NaCl), standard deviation was also high (3 mV).  
116 We used error bars to graphically represent the standard deviation in our results. We observed  
117 that the sources of error in zeta potential measurements are evaporation, time lapse between  
118 sample preparations to actual measurement, degree of homogeneity of mixing, size of coal  
119 particle and electrolyte strength. If these factors are not properly addressed the Zetasizer Nano  
120 ZS may give different quality of measurements. We here reported the best three set of  
121 measurements which we observed.

122

123 2.3. Petrology, Ultimate and Proximate Analysis

124 The results of the proximate, ultimate and petrological analysis and the internal properties  
 125 (density and volume) of the coal samples are listed in Table 1. Note that coal samples of  
 126 different rank differ mainly in volatile matter, moisture, fixed carbon and vitrinite reflectance  
 127 [22]. Petrology was analysed in accordance with Australian Standard AS2856 and ISO7404;  
 128 proximate analysis was conducted using standards AS1038.3, ISO11722 and ASTM D3172-  
 129 07a, and ultimate analysis was performed using standards AS1038.6 and ISO 609.

130

131 **Table 1.** Properties of coal samples used.

Sample	Rank	Semi-Anthracite	Medium-volatile Bituminous	Lignite
	Geological Location	Hazleton, Pennsylvania	Morgantown, West Virginia	North Dakota
	Overall rank (used in this work)	High rank	Medium rank	Low rank
Petrology	Vitrinite Reflectance ( $R_o$ , % <sup>*</sup> )	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

132 \* All percentages in above table represent weight percent.

133

#### 134 2.4. pH measurements

135 The pH values of the solutions were measured at 298 K using a pH meter (model: Orion 420+  
136 and a Thermofisher pH probe, accuracy:  $\pm 0.005$  pH), the results of which are tabulated in Table  
137 2. These pH measurements are helpful for a) explanation of zeta potential results as a function  
138 of coal rank and brine salinity, and b) precise comparison with zeta potential literature data.

139

140 **Table 2.** Measured pH values of the solutions used.

Electrolyte	pH values		
	Anthracite*	Bituminous*	Lignite*
DI-water	7.09	6.78	6.78
1wt% NaCl	8.13	7.37	6.42
5wt% NaCl	7.97	7.05	6.03
1wt% CaCl <sub>2</sub>	7.57	6.96	5.48
1wt% MgCl <sub>2</sub>	8.21	8	5.86

141 \*All solutions contained 2 wt% coal powder.

142

#### 143 2.5. Infrared spectroscopy

144 Fourier Transformed Infrared spectroscopy was performed using a Nicolet iS50-FTIR  
145 instrument (from Thermo Scientific) at 4 cm<sup>-1</sup> resolution. The powdered sample was placed on  
146 a diamond attenuated total reflection (ATR) crystal and pressed into contact. A total of 64 scans  
147 were added to generate the final infrared spectrum and the internally available ATR correction  
148 was applied to each spectrum with the software (which was supplied by the manufacturer with  
149 the instrument).

150

#### 151 2.6. XRD analysis

152 XRD analysis was carried out on the three coal samples and minerals were detected in each  
153 sample (Table 3). It is evident that the coal mainly comprised of quartz and kaolinite, however,  
154 overall mineralogy of these coals is different.

155

156 **Table 3.** Mineral identified by XRD in the three coal samples investigated.

Mineral name	Chemical formula	High rank coal (semi-anthracite)	Medium rank coal (medium volatile bituminous)	Low rank coal (lignite)
Illite	$(K,H_3O)Al_2Si_3AlO_{10}(OH)_2$	34	17	–
Quartz	$SiO_2$	21	41	76
Kaolinite	$Al_2Si_2O_5(OH)_4$	24	30	24
Anatase	$TiO_2$	21	–	–
Montmorillonite	$HA_2CaO.5O_{12}Si_4$	–	6	–
Illite- montmorillonite	$KAl_4(Si,Al)_8O_{10}(OH)_4.4H_2O$	–	6	–

157

158 *2.7. Contact angle measurements*

159 Contact angles were measured using the pendant drop titled plate technique [23], the schematic  
160 of the experimental apparatus has been published previously [12]. The coal substrates were  
161 placed in the cell and temperature was set to a desired value (298 K, 308 K, 323 K or 343 K  
162 within  $\pm 1$  K). Coal surfaces were washed with acetone and then cleaned with air plasma for 2  
163 min (within this selected time the error in contact angle measurements was minimum) and this  
164 selected time was neither too short to compromise on the surface contaminants (which need to  
165 be removed, [24]) and neither too intense to allow the removal of natural particles from the  
166 coal surfaces [12]. A few studies, however, report different coal-surface cleaning methods, e.g.  
167 the use of wet polish with abrasive papers, which were then removed by ultrasonic cleaning  
168 [14,25].

169 Subsequently brine was pumped with a high precision syringe pump (ISCO Teledyne 500D)  
170 resulting in a droplet of de-gassed brine (vacuumed for 12 h) being dispensed onto the substrate  
171 (in air, at ambient pressure and the pre-set temperature) by means of a needle. At the leading  
172 edge of the droplet, just before the droplet started to move, the angle between coal surface and  
173 the brine interface was measured as the advancing contact angle ( $\theta_a$ ) whereas the receding  
174 contact angle ( $\theta_r$ ) was measured at the trailing edge of the droplet. A high performance video  
175 camera (Basler scA 640–70 fm, pixel size = 7.4  $\mu$ m; frame rate = 71 fps; Fujinon CCTV lens:  
176 HF35HA-1B; 1:1.6/35 mm) recorded the entire process, and contact angles were measured on  
177 images extracted from the movie files. The standard deviation of these measurements was  $\pm 4^\circ$

178 based on measurements repeated thrice and is shown by error bars in the results. The  
179 measurements were done on one sample each of low, medium and high rank. The coal samples  
180 may vary in terms of composition, thus the conclusions drawn in the study may vary depending  
181 upon the composition of the coal samples under investigation. In fact, our results revealed that  
182 difference in coal rank (e.g. low, medium and high rank, which are obviously different in  
183 composition) leads to different zeta potential (at the same operating conditions) which leads to  
184 different wettability (discussed in detail in section 3.4).

185

### 186 **3. Results and discussion**

187 In order to understand the factors influencing wettability of coal seams, we examined the  
188 surface properties of coals. The results lead to a broad understanding of the factors responsible  
189 for the distinct wetting characteristics of coals as a function of coal rank, pressure, temperature  
190 and brine salinity and thus the results help to precisely understand fluid flow and distribution  
191 in coal seams. This information can be used to optimize CO<sub>2</sub>-storage and (enhanced) methane  
192 recovery projects. Below the influence of each individual parameter is discussed in detail.

193

#### 194 *3.1. Effect of temperature on zeta potential and contact angle*

195 We found a clear and consistent temperature dependence trend of contact angle and zeta  
196 potential for coal/DI water systems. Zeta potentials of these systems increased with increasing  
197 temperature within the experimental error (at constant ambient pressure, Figure 1), irrespective  
198 of coal rank. Moreover, the advancing and receding water contact angles decreased with  
199 temperature for all coal ranks (Figure 2, consistent with [12]). The increase in zeta potential  
200 with increasing temperature implies a surface with more screening ions within the double layer  
201 at higher temperatures which in turn gives a more water-wet coal surface, i.e. the observed  
202 behaviour is different than previously reported behaviour [26].

203 Specifically, for the high rank coal (semi-anthracite), the zeta potential increased from -23.1  
204 mV to 2.63 mV when temperature increased from 298 K to 343 K (Figure 1). For the same  
205 temperature increase,  $\theta_a$  decreased from 59° to 32° and  $\theta_r$  decreased from 52° to 27° (Figure  
206 2). Similar trends were found for medium and low rank coals i.e. the zeta potentials of coal/DI  
207 water increased with temperature (Figure 1) and corresponding  $\theta_a$  and  $\theta_r$  decreased with  
208 temperature. For instance, for the medium rank coal (medium volatile bituminous), the zeta



209 potential increased from -24.8 mV to 0.236 mV when temperature increased from 298 K to  
210 343 K, and correspondingly,  $\theta_a$  decreased from 40° to 18° and  $\theta_r$  decreased from 33° to 12°  
211 (Figure 2).

212 On the coal surface, ionisable groups are present (e.g. phenolic and carboxylic groups, [27]),  
213 thus, as temperature increases and the pH decreases (pH decreases with temperature due to  
214 reduction in pK values of water and also due to a reduction in hydrogen bonding leading to  
215 increased number of protons ( $H^+$ ); [28]), the released protons ( $H^+$ ) interact with the surface  
216 functional groups and ionize them, e.g.  $C=O$  reacts to  $C-OH^+$  or  $C-OH^+$  reacts to  $C-OH_2^{2+}$  [27].  
217 Therefore the surface of the coal becomes more positive with an increase in temperature, and  
218 consequently the zeta potential increases. Moreover, it is also reported that with increase in  
219 temperature, surface oxidation is accelerated and hydrophilic groups are formed on the coal  
220 surface at high temperature [29-31] which may lead to lower water contact angles with  
221 increasing temperature. However, we believe that oxidation of coal surfaces require sufficient  
222 exposure time which is likely to be well beyond the timescale of surface exposure to high  
223 temperature during our contact angle measurements [32]. Thus, we point out that oxidation  
224 may not be a governing factor for the decrease in contact angle with temperature despite a  
225 corresponding increase in zeta potential. We believe that further research is required to explore  
226 this effect.

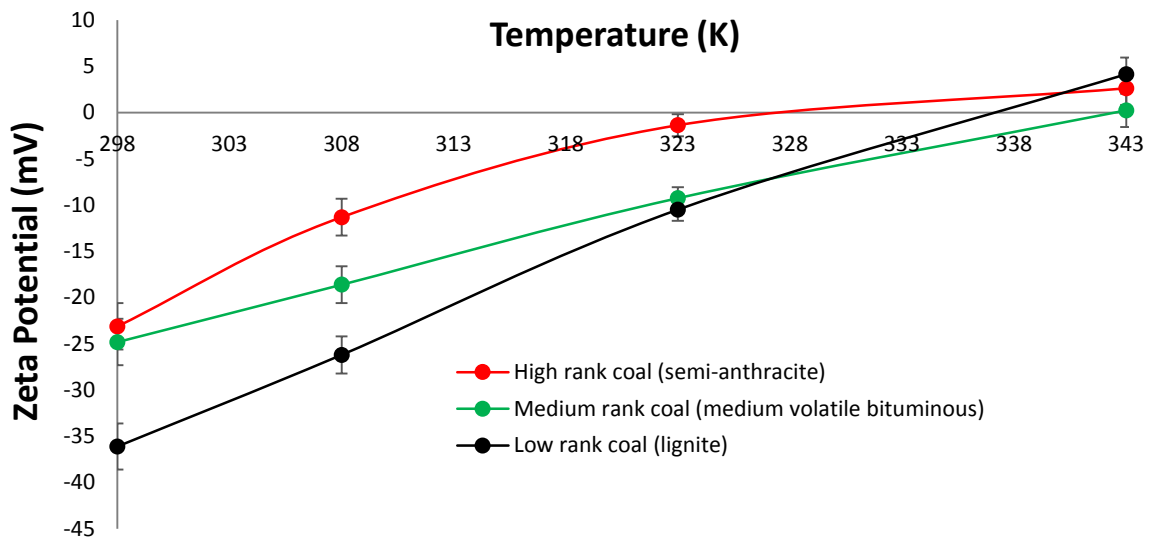
227 Somasundaran et al. [31] found that for high volatile bituminous coal (from Pennsylvania), the  
228 magnitude of zeta potential decreased with temperature (at a pH of 6.78, zeta potential  
229 measured -26 mV at 300 K and reduced to -20 mV at 363 K). At the same pH (6.78, Table 2),  
230 the zeta potential of our medium rank coal (medium volatile bituminous) measured -24.8 mV  
231 at 298 K in good agreement with Somasundaran et al. [31]. The slight difference is probably  
232 due to the slightly different coal and associated differences in coal surface chemistry. Because  
233 of the limited literature data on zeta potential of coals, we compared our data with coals of  
234 similar ranks (if not exactly the same) despite their origin from a different basin (e.g.  
235 Somasundaran's coal from Pennsylvania is compared to our coal sample from West Virginia).

236 The observed increase in zeta potential with increasing temperature is attributed to the  
237 reduction in pH (with increasing temperature), consistent with Vinogradov and Jackson [33],  
238 who reported that zeta potentials of sandstones decreased in magnitude with increasing  
239 temperature for low salinity brine (0.6 wt% NaCl to 3 wt% NaCl), and they concluded that pH  
240 reduction with increasing temperature was responsible for the zeta potential variation. Note:

241 The coals are compared with quartz (Vinogradov and Jackson's [33] work) because mineralogy  
242 of these coals revealed that quartz is a significant component of these coals (XRD results, Table  
243 3).

244 To further explain the charge reversal behaviour, we conducted pH measurements of the  
245 solutions at high temperatures and found that pH dropped only slightly (e.g. for lignite/water  
246 solution pH = 6.5 at 323 K and pH = 6.32 at 343 K), thus zeta potentials are only slightly  
247 impacted by pH changes. Therefore, divalent ions could possibly be acting as potential  
248 determining ions.

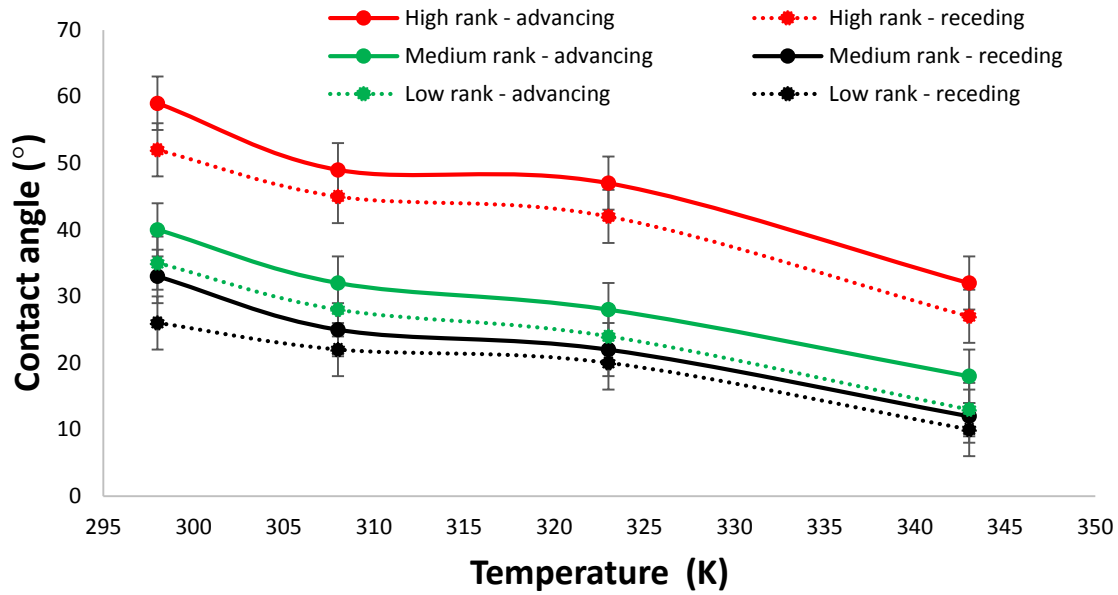
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250

251 **Figure 1.** Zeta potential as a function of temperature and coal rank (at ambient pressure).

252



253

254 **Figure 2.** Water contact angle as a function of temperature and coal rank (at ambient pressure).

255

256 We further found that at any given temperature, high rank coal exhibited higher values of zeta  
 257 potential and higher water contact angles than low rank coals. For instance, at 323 K, the zeta  
 258 potential measured -1.36 mV for the high rank coal, -9.25 mV for medium rank coal, and 10.5  
 259 mV for low rank coal (Figure 1), while the associated contact angles were ( $\theta_a = 47^\circ$ ,  $28^\circ$  and  
 260  $24^\circ$  and  $\theta_r = 42^\circ$ ,  $23^\circ$  and  $20^\circ$  for high, medium and low rank coals respectively). This  
 261 behaviour is attributed to the lack of hydrophilic function groups (OH groups) in high rank  
 262 coals (further discussed in Section 3.5).

263 Considering the above electrochemical behaviour of coals at ambient pressure, we now  
 264 consider CO<sub>2</sub>/brine/coal contact angle data at high pressure (15 MPa) from our previous work  
 265 (Arif et al., 2016c, [12]). It was found that at 15 MPa, for high rank coal, when temperature  
 266 increased from 308 K to 323 K,  $\theta_a$  decreased from  $146^\circ$  to  $119^\circ$ , implying a wettability  
 267 transformation from strongly CO<sub>2</sub>-wet to weakly CO<sub>2</sub>-wet. Similarly, for medium rank coal,  $\theta_a$   
 268 decreased from  $128^\circ$  to  $102^\circ$  when temperature increased from 308 K to 343K. However, for  
 269 low rank coal,  $\theta_a$  first decreased from  $112^\circ$  to  $102^\circ$  when temperature increased from 308 K to  
 270 323 K, and then became constant when temperature increased further (from 323 K to 343 K;  
 271 [12]). In summary, water-wettability of coal increased with increasing temperature irrespective  
 272 of the coal rank. Thus, the effect of temperature on wettability is similar at high pressure as  
 273 that found at ambient pressure (i.e. air/brine contact angles at low pressure and CO<sub>2</sub>/brine

274 contact angles at high pressure followed similar trend). It can therefore be concluded that the  
275 temperature dependence of CO<sub>2</sub>-wettability of coals is considerably controlled by  
276 electrochemical changes at the water/coal interface and that increase in temperature render the  
277 coal surface more water-wet due to formation of ionized surface functional groups.

278

### 279 *3.2. Effect of salinity on zeta potential and contact angle*

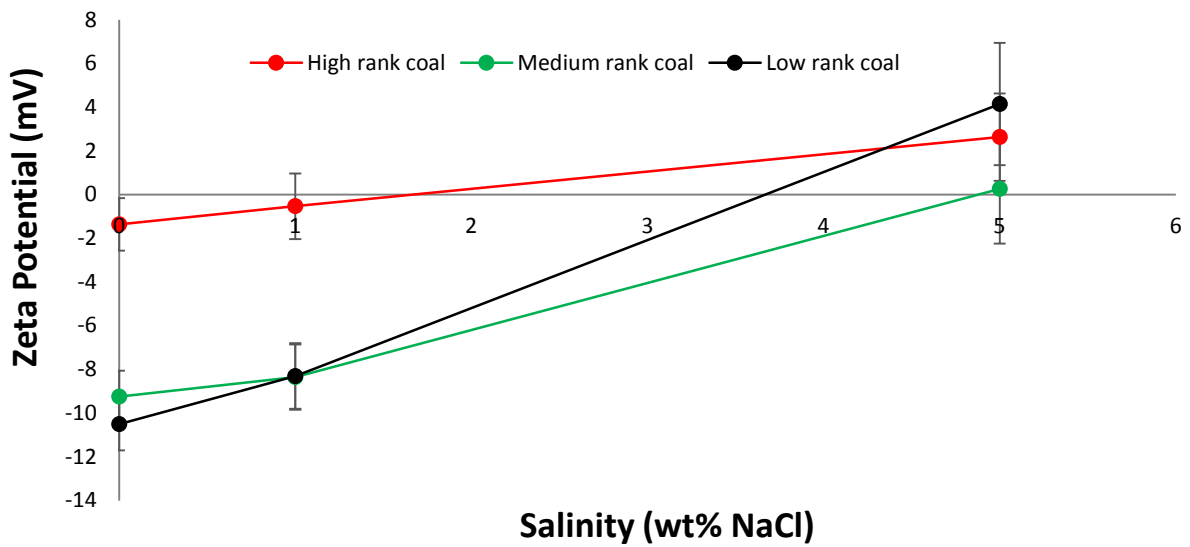
280 The effect of salinity on zeta potential and contact angle was studied as a function of brine  
281 salinity (0 wt% NaCl, 1 wt% NaCl and 5 wt% NaCl) at constant temperature (323 K). It was  
282 found that zeta potential increased with an increase in salinity for all coal ranks (Figure 3).  
283 Moreover, both  $\theta_a$  and  $\theta_r$  increased with salinity for all coal samples (Figure 4). Specifically,  
284 for the high rank coal, when salinity increased from 0 wt% NaCl to 5 wt% NaCl (or  
285 equivalently from 0M to 0.855M), zeta potential increased from -1.63 mV to 2.63 mV. For the  
286 same salinity increase,  $\theta_a$  increased from 47° to 60° and  $\theta_r$  increased from 42° to 53° (Figure  
287 4). Similarly, for medium rank coal, the zeta potential increased from -9.25 mV to 0.263 mV  
288 when salinity increased from 0 wt% NaCl to 5 wt% NaCl, indicating a clear increase in zeta  
289 potentials with increasing salinity, and the corresponding values of  $\theta_a$  increased from 28° to  
290 41° and  $\theta_r$  increased from 22° to 35° (Figure 4). Generally, for any solid/brine system, the  
291 composition of solid and the concentration and valency of ions in the solution are responsible  
292 for the sign and value of the zeta potential [34]. Physically, the coal surface exhibits negative  
293 charges due to the presence of polar functional entities, which partially dissociate, e.g.  
294 carboxylic or phenolic groups [35]; the concentration of these functional groups depends on  
295 the coal rank ([36] see also FTIR discussion in Section 3.5). The results found here are  
296 consistent with Ibrahim and Nasr-El-Din [37] who reported that both zeta potentials and contact  
297 angles on coals increased with salinity. Fuerstenau et al. [38] reported that for low ash  
298 anthracite coal, the zeta potential was measured to be -25 mV at 0.01 M NaCl (pH = 7) at room  
299 temperature. We found that for high rank coal (semi-anthracite) at (almost) the same pH (7.09,  
300 Table 2), the zeta potential was measured to be -23 mV (Figure 1) indicating consistent results.  
301 Harvey et al. [39] also found an increase in zeta potential of coal with salinity. They reported  
302 that for sub-bituminous (medium rank) coal, at a pH of 8, zeta potential increased from -32 mV  
303 to -25 mV when salinity changed from 0 wt% NaCl (DI-water) to 0.5 wt% NaCl at room  
304 temperature. For a similar bituminous coal we also measured an increase in zeta potential at  
305 323K (-9.25 mV for DI-water decreased to -8.5 mV for 0.5 wt% NaCl brine, Figure 3). Roshan

306 et al. [40] recently introduced a model to describe the physical processes for wettability  
307 variation as a function of salinity and they related the contact angle to the electric potential at  
308 the mineral surface. According to their explanation, the dielectric constant of the fluid  
309 decreases with increasing salinity, which leads to an increased contact angle. The decrease in  
310 zeta potential correlates with the charge on the surface being more screened as more ions are  
311 present in the double layer, this leads to an increased water contact angle [41].

312

313

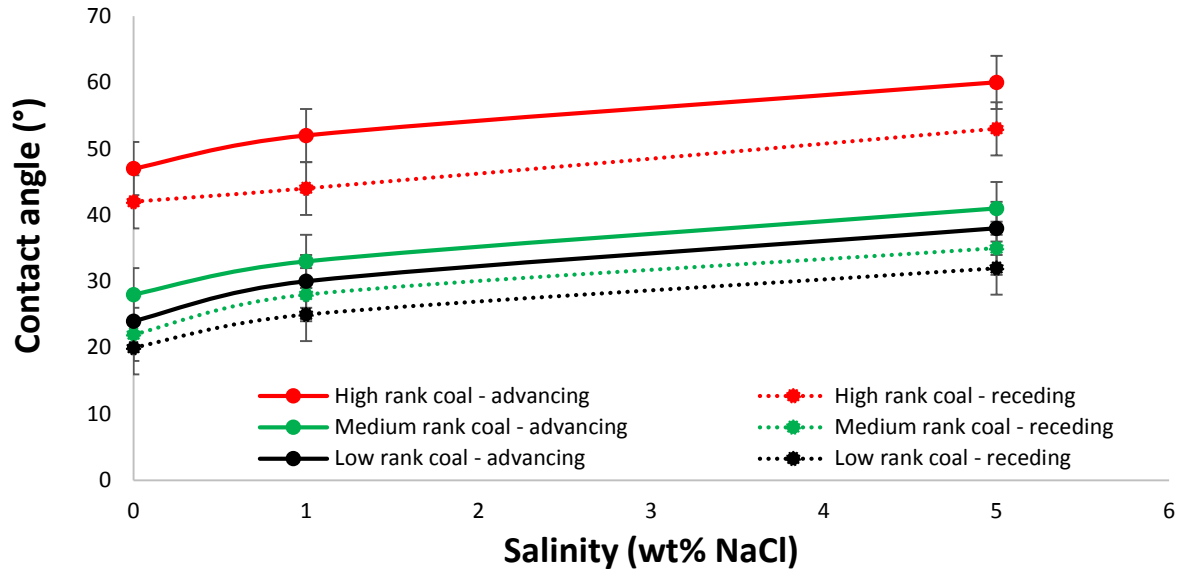
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315

316 **Figure 3.** Effect of salinity on zeta potential at 323 K (and ambient pressure) as a function of  
317 coal rank.

318



319

320 **Figure 4.** Water contact angle as a function of salinity and coal rank at 323 K (and ambient  
321 pressure).

322

323 Mechanistically, with the increase in ionic strength, the number of counter ions on the surface  
324 increases, which screens the surface charge (and thus results in a reduction of the thickness of  
325 the Debye layer). This means that the zeta potential decreases with increasing salt  
326 concentration. It is also notable that for the high rank coal, at a salinity of approximately 1.8  
327 wt% NaCl the zeta potential is zero, while for low rank coal 3.7 wt% NaCl (Figure 3) is required  
328 to reach the point of zero zeta potential. The shift in salinity at which a zero charge is obtained  
329 varies between high, medium and low rank coal and is associated with the relative affinity of  
330 the respective coal surface for  $H^+$  and  $OH^-$  ions (which varies with coal rank [23], and again is  
331 related to the concentration of surface functional groups, see FTIR discussion in Section 3.5).  
332 The salt content for achieving a zero charge as reported here is also of important consideration  
333 for processes that involve colloidal dispersion and coagulation [35], e.g. in coal processing  
334 [42].

335 Further, we compared zeta potentials to advancing and receding contact angles measured at  
336 high pressure (15 MPa and 323 K, Arif et al. [12]). For all coal ranks, both,  $\theta_a$  and  $\theta_r$ , increased  
337 with salinity at high pressures (Arif et al. [12]). For medium rank coal, at 15 MPa and 323 K,  
338  $\theta_a$  increased from  $114^\circ$  to  $127^\circ$  and  $\theta_r$  increased from  $102^\circ$  to  $112^\circ$  when salinity increased from  
339 0 wt% NaCl to 5 wt% NaCl brine. For a salinity increase from 5 wt% NaCl to 10 wt% NaCl,  
340  $\theta_a$  increased from  $127^\circ$  to  $132^\circ$  and  $\theta_r$  increased from  $112^\circ$  to  $116^\circ$ . Moreover, we found similar

341 trends for low and high rank coals. Considering the fact that the trends of contact angle  
342 variation with temperature, salinity, and rank at high pressures were same as those at ambient  
343 conditions, it can be hypothesized that zeta potentials might also follow similar trends at high  
344 pressures (in a coal/CO<sub>2</sub>/brine system) as we showed in this work at ambient pressure (in a  
345 coal/air/brine system).

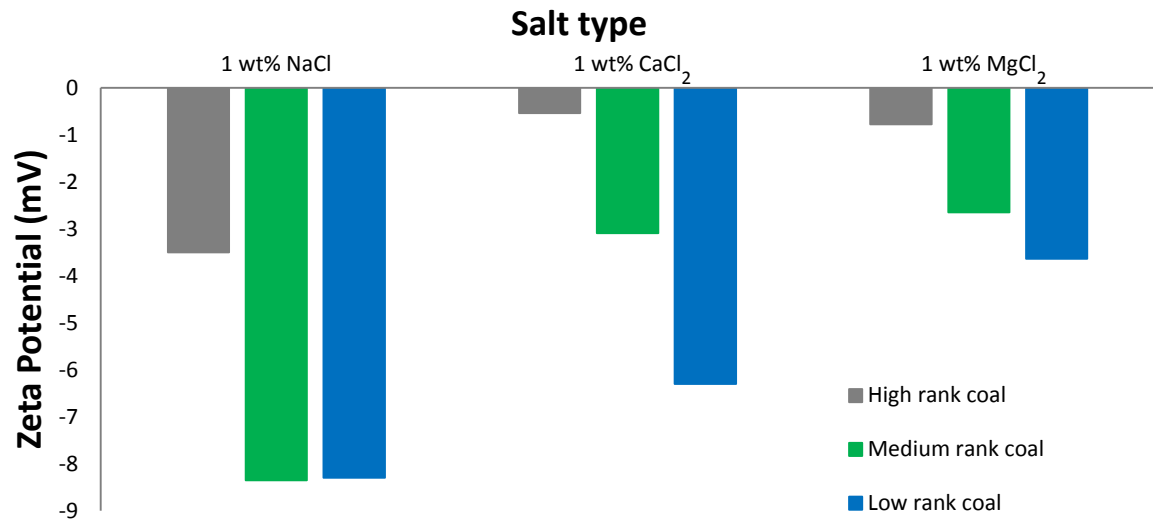
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### 347 *3.3. Effect of brine composition on zeta potential and contact angle*

348 The effect of salt type on zeta potential and contact angles was analysed by measuring zeta  
349 potentials and contact angles for coal/brine systems at 323 K and ambient pressure for three  
350 brines 1 wt% NaCl (0.17M), 1 wt% CaCl<sub>2</sub> (0.27M) and 1 wt% MgCl<sub>2</sub> (0.305M) for all coal  
351 ranks investigated. To facilitate the comparison of salt types, we have plotted zeta potential as  
352 a function of salt type in two formats: a) in terms of salt concentration in wt%, and b) in terms  
353 of the ionic strength of the solution (Figure 5 a, and b). We found that from Na to Ca to Mg  
354 brine types, at the same salinity and temperature, the zeta potential increased (Figure 5a) and  
355 contact angle also increased for all coal ranks (Figure 6). Specifically, for instance, for medium  
356 rank coal the zeta potential at the interface of coal/1 wt% NaCl-brine measured -8.3 mV, while  
357 at the coal/1 wt% CaCl<sub>2</sub>-brine interface it measured -3.09 mV, and at coal/MgCl<sub>2</sub>-brine  
358 interface it measured -2.65 mV indicating an increase in zeta potential with increasing cation  
359 charge-to-volume ratio (which is  $2.61 \times 10^{-7} \text{ C}\cdot\text{pm}^{-3}$  for Na<sup>+</sup>,  $4.92 \times 10^{-7} \text{ C}\cdot\text{pm}^{-3}$  for Ca<sup>+</sup> and  
360  $1.66 \times 10^{-6} \text{ C}\cdot\text{pm}^{-3}$  for Mg<sup>+</sup>, [43]). At the ionic strength of 0.27M (1.58 wt%) NaCl, the zeta  
361 potential can be interpolated from Figure 3 (corresponding to 1.58 wt% NaCl) to facilitate  
362 comparison at exactly the same ionic strength as that of Ca and Mg based salts.

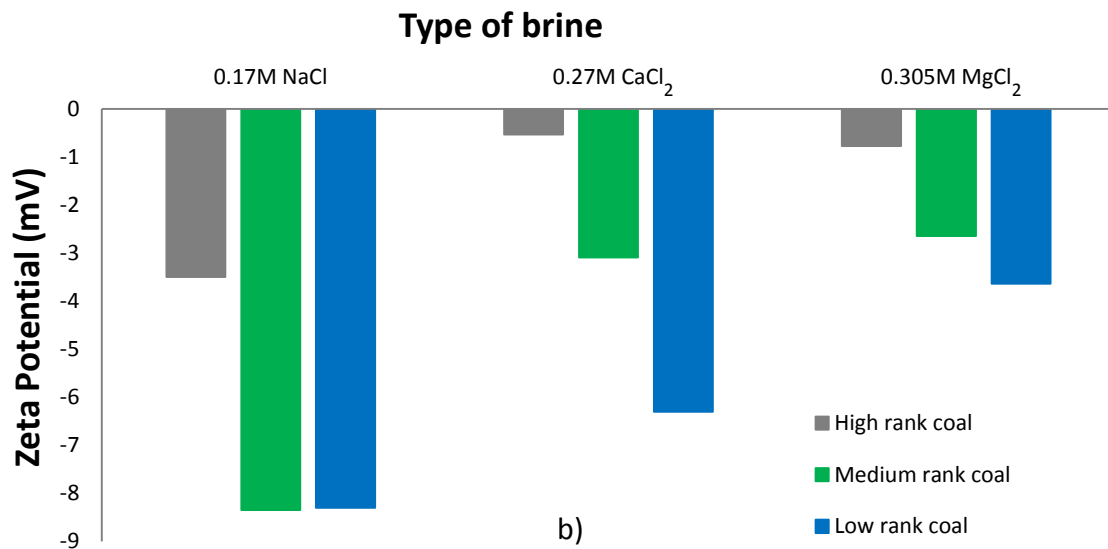
363 The negative values of the coal zeta potentials can be attributed to dissociation of surface  
364 functional groups (e.g. -COOH) [44]. The positive zeta potential values obtained are attributed  
365 to the surface charge screening effect due to counter ions provided by the cations of the salt as  
366 discussed above. Moreover,  $\theta_a$  increased from 52° to 60° and  $\theta_r$  increased from 44° to 53° when  
367 brine composition changed from 1 wt% NaCl to 1 wt% MgCl<sub>2</sub> (Figure 6). The results are  
368 consistent with [37] who also reported that coal/brine zeta potentials increased for divalent  
369 cations (Ca<sup>2+</sup> and Mg<sup>2+</sup>). Harvey et al. [39] also found that MgCl<sub>2</sub> brine resulted in an increase  
370 in zeta potential.

371



372

a)



373

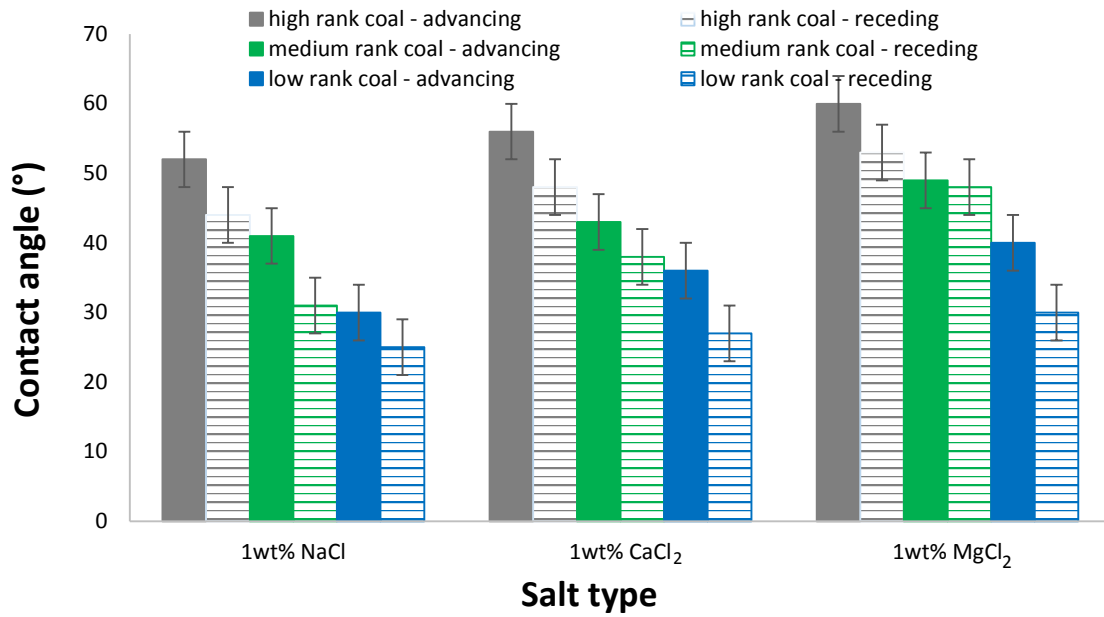
b)

374 **Figure 5.** Zeta potential as a function of salt type (NaCl, CaCl<sub>2</sub>, MgCl<sub>2</sub>) and coal rank (at 323  
 375 K and ambient pressure). Data is shown in two formats: a) In terms of concentration in wt%,  
 376 b) In terms of ionic strength of brine

377

378





379

380 **Figure 6.** Water contact angle as a function of salt type (NaCl, CaCl<sub>2</sub>, MgCl<sub>2</sub>) and coal rank  
 381 (at 323 K and ambient pressure).

382

### 383 3.4 Zeta potential and contact angles as a function of coal rank

384 To investigate the impact of coal rank on zeta potential and wettability, the results shown in  
 385 Figures 1-6 are reconsidered briefly. At any temperature (except 343 K), the zeta potential of  
 386 the coal/water system increased with increasing rank (Figure 1). For instance, at 308 K, the  
 387 zeta potential was -26.2 mV for low rank coal (lignite,  $R_o = 0.35\%$ ), -18.6 mV for medium rank  
 388 coal (medium volatile bituminous,  $R_o = 0.82\%$ ) and -11.3 mV for high rank coal (semi-  
 389 anthracite,  $R_o = 3.92\%$ ). This is consistent with Abotsi et al. [45] who found that at a pH > 5.5  
 390 low rank coal had more negative zeta potential values in DI water at room temperature. For  
 391 instance, they reported that at a pH = 6.5, zeta potentials of lignite (North Dakota) were -40  
 392 mV, ~ -30 mV for sub-bituminous and ~ -20 mV for bituminous coals which is quite  
 393 comparable to our results (at 298 K, zeta potentials measured -36 mV and -25 mV for low and  
 394 medium rank coals, respectively).

395 As the coal rank increases, the zeta potential increases, indicating a diminishing number of  
 396 polar surface sites (a proportion of which are negatively charged due to dissociation), [42].  
 397 This results in a strong dependence of the isoelectric point (the pH at which the surface carries  
 398 no net charge) and the sign of the zeta potential on the carbon content (i.e. the coal rank, [46]).

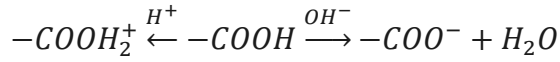
399 In addition, aqueous cationic ion concentrations increase due to dissociation of groups capable  
400 of forming ions or decrease by re-adsorption of some dissolved ions on the solid particle surface  
401 [47]. Consequently the electrical double layer on the particle becomes thinner or thicker, which  
402 induces a change in zeta potential. In the case of coal, the high mineral content and dissociation  
403 of ionogenic groups on the (complex) coal surface [48] leads to different charges on coals of  
404 different ranks (low zeta potentials for low rank coal and high zeta potentials for high rank  
405 coal).

406 We relate the variation in zeta potential as a function of coal rank to the mineralogy of coal. In  
407 this context, we note that the major components of the coals are quartz and kaolinite (XRD  
408 results, Table 3). The low rank coal contains 76% quartz and 24% kaolinite. At room  
409 temperature, we find from Kaya and Yukselen [49] that zeta potential of quartz/water and  
410 kaolinite/water were both negative for a wide range of tested pH and that quartz/water zeta  
411 potential was much lower than that of the kaolinite/water (e.g. at pH of 6.8, zeta potentials were  
412 -52 mV for quartz and -34 mV for kaolinite). Thus our measured value of zeta potential of  
413 lignite which was -36.1 mV at room temperature is in accordance to the mineralogy of lignite  
414 i.e. the zeta potential of lignite is comparable to individual mineral's zeta potentials. Moreover  
415 the percentages of quartz and kaolinite were 41 wt% and 30 wt% in medium rank coals, and  
416 21 wt% and 24 wt% in high rank coals (Table 3). The measured values of zeta potential of  
417 medium and high rank coal at 298 K were -24.8 mV and -23.1 mV. The impact of mineralogy  
418 is thus clear in the sense that the increase in percentage of quartz and kaolinite in coal leads to  
419 a reduction in zeta potential (low rank coal has lower zeta potential because of higher quartz  
420 and kaolinite content).

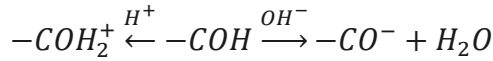
421 The decrease in negative charge density on the coal surface with increasing coal rank is  
422 attributed to the increase in fixed carbon (%) and a decrease in oxygen content with rank [50],  
423 Table 1. We note that high and medium rank coal demonstrated similar trend of zeta potential  
424 variation as a function of salinity but low rank coal showed slightly inconsistent behaviour as  
425 a function of salinity at higher salinity (5wt% NaCl) which can be attributed to the presence of  
426 more hydrophilic groups (OH groups) in low rank coals, Figure 3).

427 The surface charge on coal in the presence of electrolytes is induced by ionization or  
428 protonation of the surface carboxylic and hydroxyl groups; note that the dissociation of  
429 carboxylic groups is enhanced in the presence of  $\text{OH}^-$  [51].

430



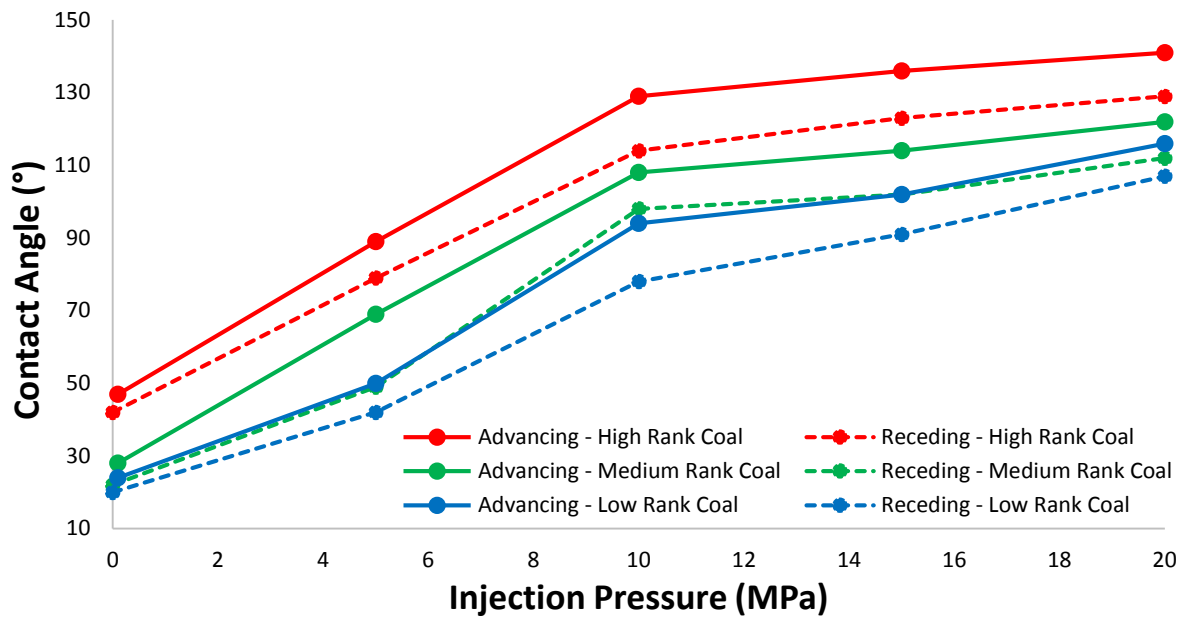
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432

### 433 3.5. Surface functional group characterization and associated hydrophobicity of coals

434 In order to assess the factors responsible for the wetting behaviour of the coal/CO<sub>2</sub>/brine  
 435 systems, we consider experimental data for water advancing and receding contact angle from  
 436 our previous work (Arif et al. [12]), Figure 7. It can be seen that water wettability of coals  
 437 decreases with increasing pressure and increasing rank. At any given CO<sub>2</sub> pressure, the high  
 438 rank coal had the highest water contact angle which means that these coals are less water-wet.  
 439 Low rank coals (e.g. lignite) are more water-wet and medium rank coal (e.g. bituminous) are  
 440 intermediate-wet. These results are in agreement with Shojai Kaveh et al. [15] who compared  
 441 CO<sub>2</sub>-wettability of semi-anthracite and high volatile bituminous coals, and they measured  
 442 higher contact angles for semi-anthracite coals, and thus they concluded that hydrophobicity  
 443 of coals increases with coal rank. However, the surface functional groups responsible for such  
 444 wetting behaviour were unclear. We thus conducted FTIR (Fourier transformed infrared)  
 445 spectroscopy measurements on the three coal samples, the results are presented in Figure 8.



446

447 **Figure 7.** Water contact angle as a function of pressure and coal rank at 323 K (experimental  
 448 data from Arif et al. [12]).

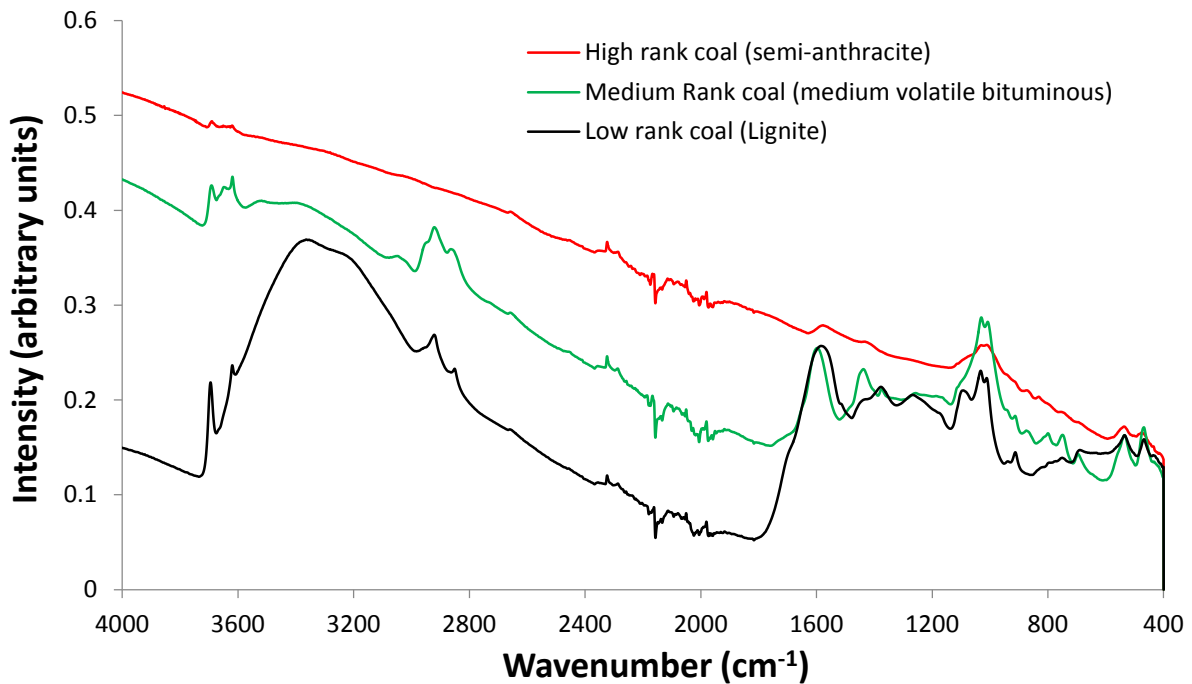
450 High rank coal (semi-anthracite) demonstrated a rather smooth FTIR intensity response  
451 throughout the observed wavenumber spectrum, with only small bands observed at a  
452 wavenumber range of at 600-800  $\text{cm}^{-1}$  due to a possible C-S stretching vibration, the 1000-  
453 1100  $\text{cm}^{-1}$  due to C-H out of plane bending and Si-O-H asymmetric stretch vibrations and a  
454 minute band at  $\sim 3800 \text{ cm}^{-1}$  due to -OH and N-H bond stretching vibrations [52,53];  
455 considering the fact that XRD confirmed the presence of Si (Table 3) and elemental analysis  
456 confirmed the presence of sulphur and nitrogen (Table 1). The rough part of the spectra for  
457 2000-2400  $\text{cm}^{-1}$  should be ignored as this is where the ATR crystal is absorbing itself  
458 (diamond) and the bands don't always perfectly cancel out. From the stand point of surface  
459 functional groups and associated wetting behaviour, the absence (or only minute presence) of  
460 hydrophilic sites e.g. OH groups in high rank coal is responsible for its hydrophobic behaviour  
461 ( $\theta > 130^\circ$ , Figure 7).

462 On the contrary, medium rank coal (medium volatile bituminous) exhibited significantly  
463 stronger bands (in comparison to high rank coal) at wave numbers from 600-800  $\text{cm}^{-1}$  and 1000-  
464 1100  $\text{cm}^{-1}$  indicating the presence of more C-S stretching vibrations and C-H out of plane  
465 bending. Moreover, medium rank coal also exhibited larger bands at  $\sim 3600\text{-}3700 \text{ cm}^{-1}$  which  
466 is attributed to O-H and N-H stretch vibrations. Furthermore, distinct bands were observed at  
467 2800-2900, and 1500-1700  $\text{cm}^{-1}$  which are due to C=C and C=O stretch vibrations respectively  
468 [53]. Thus, the presence of more hydrophilic sites (OH groups) in medium rank coal renders it  
469 relatively less  $\text{CO}_2$ -wet in comparison to high rank coal (e.g. for instance at 10 MPa,  $\theta_a = 108^\circ$   
470 for medium rank coal in comparison to  $129^\circ$  for high rank coal, Figure 7).

471 Low rank coal demonstrated the largest peak beginning at about 2800  $\text{cm}^{-1}$  and ending at 3800  
472  $\text{cm}^{-1}$  which is attributed to the O-H and N-H stretch vibrations and this largest peak is  
473 responsible for the hydrophilic nature of lignite coal even at high pressures (Figure 7). The  
474 band at  $\sim 2900 \text{ cm}^{-1}$  observed for low rank coal is due to the presence of aliphatic C-H stretching  
475 vibrations [36]; however, its absence in high rank coal is unusual and is perhaps due to C-H  
476 stretching where the carbon is in a C=C bond. Moreover, the sharp band observed at 1500-  
477 1800  $\text{cm}^{-1}$  for low rank coal is attributed to aromatic ring vibrations, which are enhanced by  
478 oxygen groups [35]. The corresponding shoulder peaks at 1600  $\text{cm}^{-1}$  is attributed to C=O  
479 stretching vibrations and these represent all C=O functionalities, e.g. carboxylic acids or  
480 phenolic esters [54,55]. Chemically, the presence of such polar functional groups leads to an

481 increase in hydrophilicity of the coals' surface and that is evident from the contact angle data  
482 (e.g. lignite is relatively more water-wet as compared to bituminous and anthracite coals,  
483 Figure 7).

484



485

486 **Figure 8.** ATR-infrared spectroscopy measurements on low, medium and high rank coals

487

488 In summary, the much lower number of Si-OH, hydroxyl, ester, and carboxylic groups in high  
489 rank coal is responsible for its hydrophobic behaviour. On the contrary, the abundance of these  
490 groups (especially OH) is responsible for the hydrophilic nature of low rank coal. Medium rank  
491 coal stands somewhere in the middle (consistent with contact angle data; Figure 8). Thus the  
492 increase in contact angle (at typical operating conditions) with coal rank (Figure 7, Arif et al.  
493 [12]) is adequately explained by surface functional groups.

### 494 *3.6 Correlation between zeta potential and coal-wettability*

495 Our results showed that zeta potential increased with increasing rank and salinity, and contact  
496 angle also increased with increasing rank and salinity, implying a positive correlation between  
497 zeta potential and coal-wettability, i.e. higher zeta potential correspond to a less water-wet  
498 surface (= higher  $\theta$ ). In order to demonstrate this relation, we developed a cross plot between

499 water advancing contact angle and zeta potential as a function of rank (Figure 9a) and as a  
500 function of salinity (Figure 9b).

501 Specifically, for any given temperature (298 K-343 K), advancing contact angle increased with  
502 the increase in zeta potential (all solid coloured trend lines in Figure 9a) for all coals. Moreover,  
503 as salinity increased, zeta potential increased and contact angle also increased (Figure 9b). The  
504 overall correlation between zeta potential and wettability is also positive (Figure 9b).

505 However, with respect to temperature, a contradictory trend is found such that as temperature  
506 increased zeta potential increased but contact angle decreased (this can be visualized by joining  
507 the points of the same symbol in Figure 9a by means of a trend line). The reason for this  
508 contradiction is not clearly known yet, however, the possible factors responsible for this  
509 deviation could be evaporation at high temperature, and/or the experimental error associated  
510 with equipment at high temperatures (which we found was relatively high).

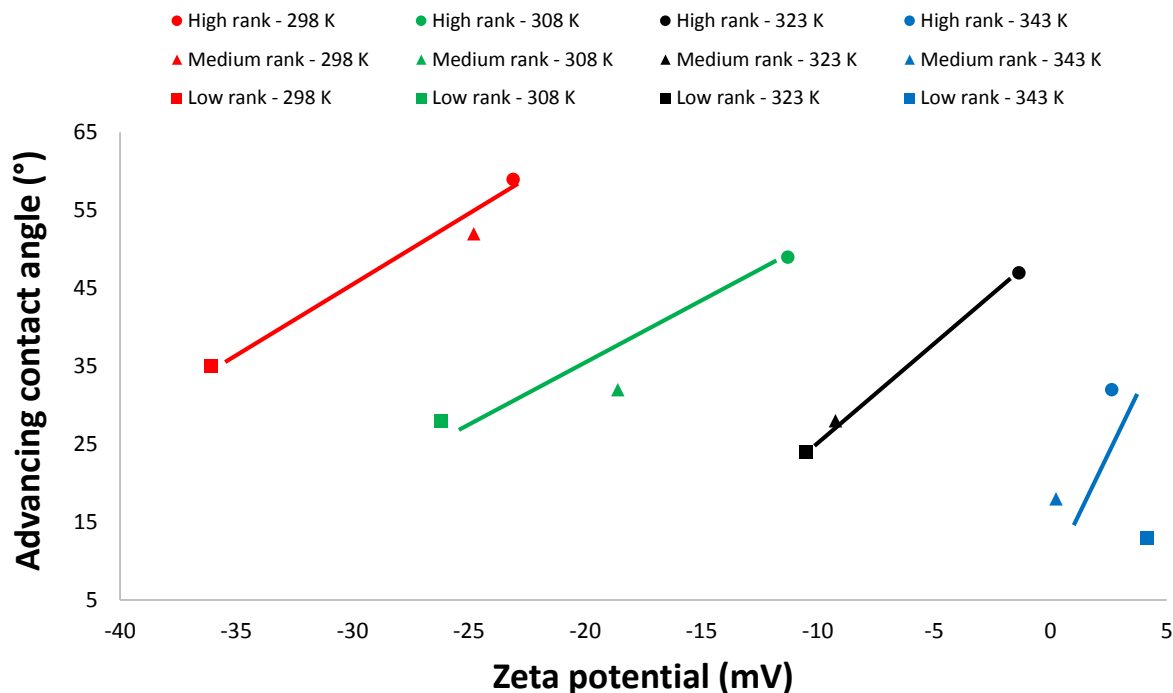
511 On a whole, it appears as if zeta potential is not the primary driver of coal-wettability despite  
512 clear positive correlation with respect to salinity and coal rank. Thus it can be established that  
513 zeta potential is a secondary factor which controls the coal-wettability variation to some extent.  
514 The primary control of wettability is governed by the interfacial interactions of fluids with  
515 surface [56] as a function of pressure, temperature and salinity.

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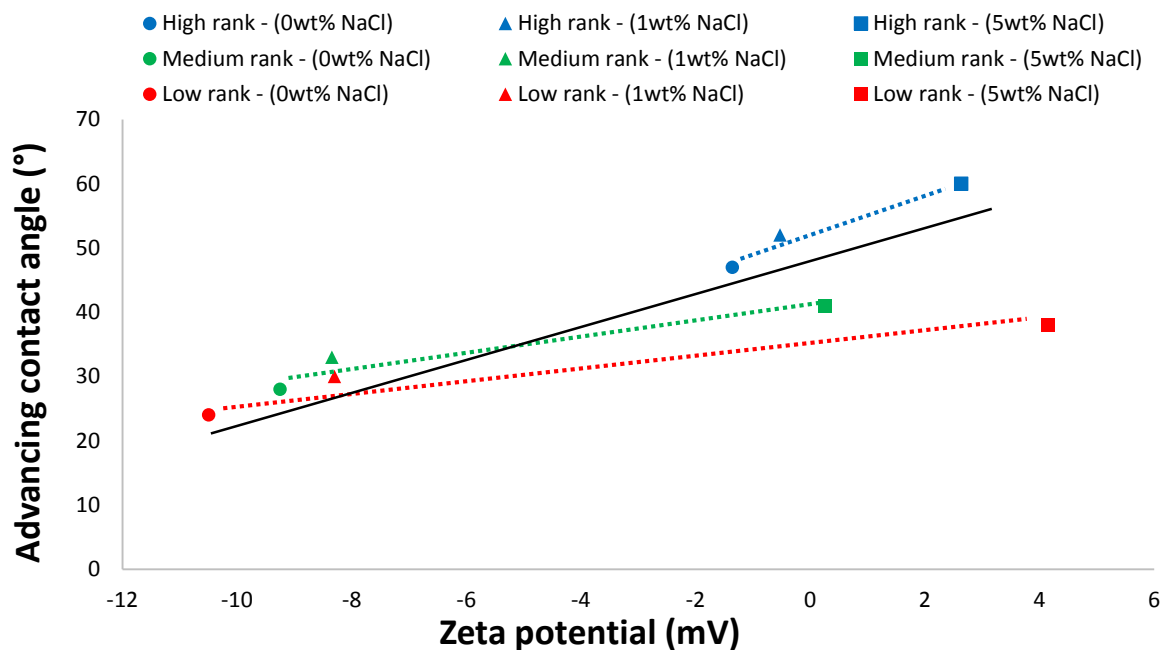
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520

521 **Figure 9a.** Contact angle-zeta potential cross plot at all temperatures as a function of coal rank.  
 522 Circle = high rank, triangle = medium rank, square = low rank coal. The colour differentiates  
 523 the measurements as a function of temperature (red, green, black and blue). The solid lines are  
 524 the trend lines for relation between zeta potential and wettability as a function of coal rank at  
 525 isothermal and iso-saline conditions.



526

527 **Figure 9b.** Contact angle-zeta potential cross plot as a function of salinity for all coal ranks at  
 528 323 K. The symbol differentiates the measurements as a function of salinity (Circle: DI-water,

529 triangle: 1wt% NaCl, square: 5wt% NaCl). The dotted lines are the trend lines for relation  
530 between zeta potential and wettability as a function of salinity for all ranks at isothermal  
531 conditions. The solid black line represent the overall trend.

532

#### 533 *4. Implications*

534 In order to assess the factors affecting wetting behaviour of coals, which is of immense  
535 importance in terms of understanding micro- and nano-scale fluid dynamics in coal seams, we  
536 provided insight into the fluid interactions at the coal/brine interface and their relation with  
537 wetting behaviour as a function of temperature, salinity and coal rank. The measured data  
538 essentially leads to a better understanding of the mechanism occurring at the pore scale and is,  
539 therefore, useful for understanding CO<sub>2</sub> storage and (enhanced) methane recovery in coal beds.  
540 Zeta potential measurements provide a better understanding of the effect of salinity and rank  
541 on wettability, however trend of zeta potential with temperature when correlated with contact  
542 angle data was contradictory which needs further investigation. Moreover, the presence of  
543 typical surface functional groups (e.g. OH and carboxylic groups) is responsible for the specific  
544 wettability of coals (Figure 7), and this data can thus be used to assess the storage potential of  
545 coal seams.

546 Specifically, we observed that high rank coal was CO<sub>2</sub>-wet (at reservoir conditions), and thus  
547 once injected, CO<sub>2</sub> occupies the smallest pores (nano- and micropores in the coal seams) due  
548 to its larger affinity to adsorb onto the coal surface [57,58]. As a result, methane is displaced  
549 towards the production wells and thus leads to improved methane production. However, the  
550 lower coal ranks are relatively less suitable for enhanced methane recovery and CO<sub>2</sub>-storage  
551 due to their more water-wet characteristics, which implies poorer adsorption of CO<sub>2</sub> onto the  
552 coal micro surface [59]. We also point out that with the increase in pressure coal swelling  
553 occurs which leads to a reduction in permeability; and this effect limits CO<sub>2</sub> injection into coal  
554 seams [60].

555

556

#### 557 **5. Conclusions**



558 We measured zeta potentials as a function of temperature and salinity for low, medium and  
559 high rank coals. It was found that zeta potential increased with temperature and the water  
560 contact angle decreased with temperature. Zeta potentials increased with increasing salinity  
561 due to reduction in the thickness of the Debye layer, which occurred because of the surface  
562 charge screening by the counter ions. The coal/brine/CO<sub>2</sub> water contact angle also increased  
563 with increasing salinity. Furthermore Mg<sup>2+</sup> brine demonstrated higher contact angles and  
564 higher zeta potentials than those of Ca<sup>2+</sup> and Na<sup>+</sup> brines, and, at any temperature or salinity,  
565 high rank coals exhibited high zeta potentials, which is due to their higher carbon content and  
566 associated lower surface charge (due to absence of polar functional groups). Zeta potential  
567 increased with salinity and rank, and contact angles also increased with salinity and rank,  
568 implying a positive relation between zeta potential and wettability. However, the effect of  
569 temperature was not conclusive in that the zeta potential increased with temperature but the  
570 contact angles decreased with temperature. Thus, despite zeta potential appears to have  
571 significant relation with contact angles, yet, it may not be considered as a primary driver of  
572 wettability and that further investigation is required to explore this effect.

573 The contact angle trends with temperature and salinity at ambient conditions were similar to  
574 those at high pressures and thus we hypothesized that zeta potential measurements at ambient  
575 conditions should follow similar trends at high pressure conditions. Furthermore, we conducted  
576 ATR-FTIR spectroscopy measurements on the coal substrates, and we measured an abundance  
577 of OH groups on the low rank coal, which is responsible for their hydrophilic nature, while  
578 high rank coals exhibited minimal OH peaks (and thus absence of OH groups), which explains  
579 their hydrophobic nature.

580 We furthermore provided implications of the measured data for CO<sub>2</sub>-storage and enhanced  
581 methane recovery and it can be concluded that high rank coal seams (at low temperature and  
582 high pressure) are most feasible for CO<sub>2</sub>-storage and enhanced methane recovery due to better  
583 CO<sub>2</sub>-wettability and thus improved CO<sub>2</sub>-adsorption capacity.

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