



Full Length Article

Dynamic fluid interactions during CO₂-ECBM and CO₂ sequestration in coal seams. Part 2: CO₂-H₂O wettabilitySijian Zheng^{a,b,c}, Yanbin Yao^{a,b,*}, Derek Elsworth^d, Dameng Liu^{a,b}, Yidong Cai^{a,b}^a School of Energy Resource, China University of Geosciences, Beijing 100083, China^b Coal Reservoir Laboratory of National Engineering Research Center of CBM Development & Utilization, China University of Geosciences, Beijing 100083, China^c Beijing Key Laboratory of Unconventional Natural Gas Geological Evaluation and Development Engineering, China University of Geosciences, Beijing 100083, China^d Department of Energy and Mineral Engineering, Pennsylvania State University, University Park, PA 16802, USA

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ABSTRACT

In addition to CO₂-CH₄ interactions (Part 1), the success of CO₂ enhanced coalbed methane (CO₂-ECBM) and geological sequestration are significantly affected by the CO₂-H₂O wettability. Wettability controls both gas desorption and transport and is influenced by injection pressure, reservoir temperature and the state of water that is present – as either adsorbed- or free-water. Dynamic changes in wettability remains poorly constrained – due to the innate difficulty and invasive nature of conventional measurements (e.g., captive gas bubble and pendent drop tilted plate methods). In part 2, we use nuclear magnetic resonance (NMR) as a non-invasive method to explore the mechanisms of these factors (pressure, temperature, water-state) on CO₂-H₂O wettability during CO₂-ECBM. Results for contrasting subbituminous coal and anthracite show that the CO₂ wettability of coals significantly increases with increasing CO₂ injection pressure up to 5 MPa before stabilizing to a limiting value. This suggests that the most economically-suitable injection pressure is ~5 MPa. CO₂ wettability also increases with a decrease in temperature suggesting that shallower reservoirs may be marginally improved in this trend. Additionally, the presence of non-adsorbed water in coals significantly reduces both the sensitivity of CO₂ wettability to pressure and the absolute magnitude of wettability relative to the case where free-water is absent. Thus, draining free-water from the reservoir will serve the dual purposes of both increasing gas transport and the potential for desorption from the perspective of CO₂-H₂O wettability. The far-reaching results in this study, together with the companion paper (Part 1) are significant for evaluating CO₂-ECBM improvement both in enhancing methane recovery and CO₂ utilization in coals.

1. Introduction

Industrial emissions of CO₂ are of sufficient magnitude that they represent an important factor in modifying climate, promoting sea level rise and posing a serious threat to biodiversity and humankind [1–3]. Total global CO₂ emissions rose to ~37 billion tons in 2018 and if continued at this pace will contribute to a global average temperature increase of ~3.5 °C and sea level rise of ~15–95 cm by the end of the century [4–6]. CO₂ sequestration in geological formations is a potential mitigation strategy with long-term storage in abandoned hydrocarbon reservoirs, deep saline aquifers, the ocean and coal seams [7–10]. Of these methods, CO₂ injection into coal reservoirs not only has great potential for the geological sequestration of CO₂ but also offers the benefit of enhancing methane recovery.

Conventional methods of coalbed methane (CBM) recovery are by reservoir depressurization to enhance gas production [11,12].

Production enhancement techniques include hydraulic fracturing and gas injection (e.g., CO₂, N₂) technique. Hydraulic fracturing techniques mainly use high-pressure fluid injection, typically water, to create and connect fractures, successfully improving Chinese CBM production over the past few decades [13–15]. However, the presence of liquidous water in fractures/macropores may promote a sharp decline in methane production as a result of water blocking [16,17]. Alternatively, the sorption capacity of CO₂ in coals is ~2–10 times that of methane [18,19], establishing CO₂ injection into coal reservoirs as a feasible method to enhance methane recovery. This has been implemented in the field, based on the mechanism of competitive adsorption between CH₄ and CO₂ [20,21]. In April 2010, 233.6 t of CO₂ was injected into well SX-001 in the Qinshui Basin, resulting in a 2.5-fold increase in the post-injection methane production rate [22]. The estimated CO₂ sequestration capacity in the global unminable coal reserve could reach ~200 Gt [23], demonstrating the significant potential of CO₂ enhanced

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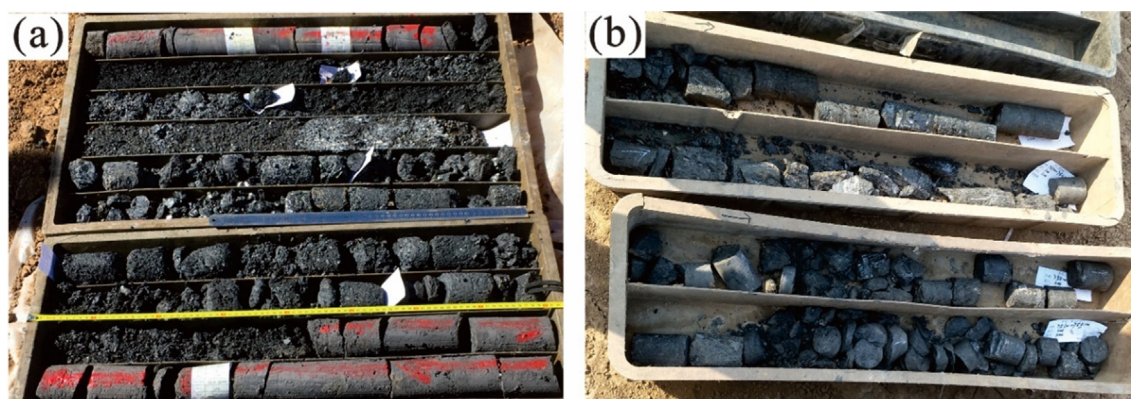


Fig. 1. Deep-Well core samples used in this study (a, subbituminous coal, 712 m, Southern Junngar Basin; b, anthracite coal, 557 m, Southern Qinshui Basin).

coalbed methane (CO₂-ECBM) recovery for the complimentary sequestration of CO₂.

Considering the presence of water in coal reservoirs, wettability in coal-H₂O-CO₂ mixtures is a fundamental factor controlling the interrelations among capillary pressure, CO₂ adsorption and fluid invasion mechanisms. This directly influences the rate of methane recovery and CO₂ geological sequestration capacity [24,25]. The most commonly used methods to characterize CO₂-H₂O wettability in coals are the captive gas bubble and pendent drop tilted plate methods [26–28]. The CO₂ gas bubble contact angle is positively correlated with injection pressure: a higher gas pressure is indicative of a greater CO₂ wettability [26]. The water contact angles measured by the pendent drop tilted plate method exhibit a positive relationship with CO₂ injection pressure, whereas negative related to experimental temperature [28]. However, enough time is much-required for CO₂ to sorb on coal surface, but the measurement needs to be performed quickly for these methods, that may result inaccurate of CO₂-H₂O wettability.

Water may exist in three states at typical in-situ coal reservoir conditions. This is as: (1) Adsorbed water, physically adsorbed to the microporous surface. (2) Capillary water, confined in the small pore capillaries. (3) Free water, saturating the macro-pores or fractures and distant from a gas-water interface [29–31]. The presence of adsorbed water directly decreases methane adsorption capacity, with free water potentially limiting gas access to the coal interior via water blocking and the Jamin effect [32]. During CO₂-ECBM, the injected CO₂ can exist as an adsorbed phase on the surface of the coal matrix, as a free phase in fractures and also dissolved within the interstitial water [33] – similar to the methane occurrences in coals. Nevertheless, the impact of the presence of multiphase water on CO₂ wettability, and its impact on CO₂-ECBM remain unresolved. This is due both to the reality that CO₂-ECBM is a new and evolving technique, but also since the challenges of non-invasive measurement of this response under in-situ conditions are particularly challenging. Non-invasive monitoring of this response is one approach that can yield high fidelity measurements and resolve this issue.

Nuclear magnetic resonance (NMR) is widely used to evaluate the petrophysical properties of hydrogen-bearing reservoir fluids (i.e., water and methane) [34–39]. Exist researches have proved that NMR measurement could serve as an accurate method to investigate the CO₂/

CH₄ interactions during CO₂-enhanced gas recovery (CO₂-EGR) process [40–44]. Xu et al. [40] found that the internal pore connectivity and methane migration pathway of coals were enhanced after CO₂ injection. Liu et al. [33] suggested that the methane sweep efficiency can achieve ~80% by injection of CO₂ in shale reservoir. Compared against measurements made by standard USBM or Amott index experiments, the geometric mean of the NMR transverse relaxation time (T_2) has been demonstrated as an accurate index to probe water wettability in conventional reservoirs (e.g., sandstones and carbonates) [45–47]. For a typical coal NMR spectrum, the change in the rightmost peak of the T_2 distribution provides a quantitative characterization of water wettability either with or without CO₂ injection [48]. However, prior studies have been limited to water-wetting of coal powder and neglect consideration of the influence of different water states on CO₂ wettability. In addition, the sensitivity of sortie mass and sorption rates to CO₂ wettability, and the impact of pressure and temperature are ill-defined – and present a unique opportunity for NMR as an exploration tool. The following explores the dynamic interaction between CO₂ and H₂O during staged CO₂-ECBM flooding at in situ reservoir. In particular, the response of subbituminous coal and anthracite are followed for variable injection pressures, temperatures and water occurrence states by using NMR. The effect of these conditions on wettability is vital in guiding CO₂-ECBM in recovery for both enhanced gas recovery (EGR) and for CO₂ geological sequestration.

2. Samples and experimental methods

2.1. Properties of samples

The experimental samples including subbituminous coal and subbituminous coal that were cored from exploration wells in the Southern Junngar Basin and Southern Qinshui Basin, respectively (Fig. 1). The sampling depth of the subbituminous coal is 712 m (Table 1), with an in-situ reservoir pressure of 4.2 MPa [49]; while that of the anthracite coal is 557 m, with an in-situ reservoir pressure of 3.5 MPa [49]. The maximum vitrinite reflectance ($R_{o,m}$) of the subbituminous coal is 0.54%, with 76.5% vitrinite content and 21.7% inertinite content. The Anthracite is characterized by high vitrinite maceral composition (87.9%), with an $R_{o,m}$ of 3.16% (Table 1). Contact angle was measured

Table 1

Basic petrophysical characteristics of the selected coal samples (from the companion paper [49]).

Sample	Coal basin	$R_{o,m}$ (%)	Depth (m)	Contact angle (°)	Maceral composition (%)			
					V	I	E	M
Subbituminous	Southern Junngar	0.54	712	67.5	76.5	21.7	1.1	0.7
Anthracite	Southern Qinshui	3.16	557	107.6	87.9	9.2	2.1	0.8

Notes: $R_{o,m}$ is maximum vitrinite reflectance, V- vitrinite; I- inertinite; E- exinite; M- minerals.

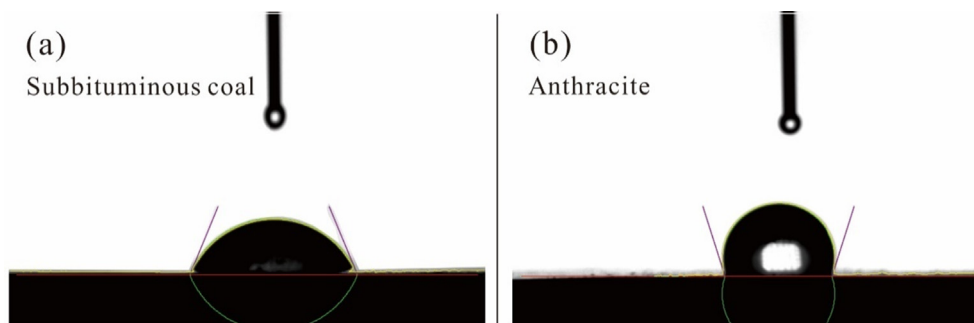


Fig. 2. Photographs of the contact angle measurement.

on the high-pressure compressed artificial surface of the disc, as noted in Fig. 2 and listed in Table 1. The subbituminous coal is water-wetting, with a contact angle of 67.5° , whereas the anthracite water-non-wetting, with a contact angle of 107.6° .

2.2. Low-field NMR

Low-field NMR methods are widely used to evaluate the petrophysical properties of hydrogen-bearing reservoir fluids (i.e., water and methane) including the evolution of fluid typing, methane adsorption capacity, and wettability [35–39,45–50]. The transverse relaxation time (T_2) is a preferable index parameter, relative to longitudinal relaxation time (T_1) – due to its fast and convenient application in NMR laboratory testing. According to the principle of low-field NMR, the hydrogen nuclei (^1H) in the reservoir fluids characterized by T_2 are affected by the bulk relaxation time (T_{2B}), surface relaxation time (T_{2S}) and diffuse relaxation time (T_{2D}). This is expressed as following [51–53]:

$$\frac{1}{T_2} = \frac{1}{T_{2B}} + \frac{1}{T_{2S}} + \frac{1}{T_{2D}} = \frac{3T_k}{298\eta} + \rho_2 \left(\frac{S}{V} \right) + \frac{D(\gamma GT_E)^2}{12} \quad (1)$$

where T_k is the laboratory temperature, K; η represents fluid viscosity, cp; ρ_2 represents surface relaxivity, $\mu\text{m}/\text{ms}$; S represents pore specific surface, μm^2 ; V represents pore volume, μm^3 , D represents molecular diffusion coefficient, $\mu\text{m}^2/\text{ms}$, γ represents proton gyromagnetic ratio, MHz/T; G represents field-strength gradient, Gs/cm; and T_E represents echo spacing time, ms. Typically, by applying a low-homogenous magnetic field intensity and the Carr-Purcell-Meiboom-Gill (CPMG) sequence, the parameters $1/T_{2B}$ and $1/T_{2D}$ in Eq. (1) can be neglected. Thus, Eq. (1) can be simply expressed as:

$$\frac{1}{T_2} = \frac{1}{T_{2S}} = \rho_2 \left(\frac{S}{V} \right) = F_S \left(\frac{\rho_2}{r} \right) \quad (2)$$

where F_S is the pore shape factor; and r is the pore size, μm . As seen in Eq. (2), T_2 is positive correlated with the pore size – a longer T_2 represents a larger pore size. The occurrence of water in different forms is apparent in the NMR spectrum as the left peak for adsorbed water ($T_2 < 10$ ms), the central peak for capillary water ($10 \text{ ms} < T_2 < 100$ ms) and the right peak for free water ($100 \text{ ms} < T_2$) [32,35].

2.3. Experimental set-up and procedures

Fig. 3 shows a schematic diagram of the experimental set-up. It comprises five components: (1) a gas supply system for two different gases (He and CO_2) contained in cylinders and with a booster pump; (2) a gas exhaust system – used for waste gas recovery; (3) a sample cell system, including a thermostat (to maintain a designated experimental temperature) and a non-magnetic PEEK cell (to hold the coal samples); (4) a reference cell, designed to transport and sustain methane for the sample cell; and (5) a MiniMR-60 NMR measurement device.

Prior to all experiments, the air tightness is measured and any contaminating impurities are removed by injecting He gas into experimental set-up. The coals were powdered to 60–80 mesh (size of 0.18–0.25 mm) then dried at 374.15 K for 12 h to remove the internal moisture. To explore the effect of pressure, temperature, and water occurrence on CO_2 - H_2O wettability during the CO_2 -ECBM process, we performed three separate experimental series: A, B and C (Table 2). There procedures were:

Experimental Series A: a) Place 10 g of dried coal powder into a canister of oversaturated- K_2SO_4 solution, leave to reach an equilibrium water saturation before placing into the sample cell and vacuuming for 3 h. b) Set and maintain the temperature at 298 K for the full experimental series A. c) Inject CO_2 into reference cell at 6 MPa and open valve G8 (Fig. 3) to fill the sample cell with CO_2 to a pressure of 3 MPa. d) Measure the sample cell T_2 spectrum every 60 min until the difference between subsequent measurements is negligible. e) Increase the CO_2 pressure in the sample cell and repeat the experimental procedure (d) at each of four incremented pressures of 4, 5, 6 and 7 MPa.

The experimental procedures of Experimental Series B and C were identical to Series A, except for experimental conditions in Series B (different temperatures of 308, 318 and 328 K but at a constant CO_2 pressure of 5 MPa), and the different sample preparation in Series C (5 g of free water was added after the equilibrium water condition). For the Experimental Series B, the sample cell temperature was controlled and maintained by the temperature sensor (Fig. 3), that can be set to any temperature in the range of 298–333 K. In this study, the NMR measurement was performed using Suzhou Niumag MiniMR-60 analytical instrument, with a low constant magnetic field of 0.5 T. The parameters were set as 0.3 ms echo spacing, 6000 ms waiting time, and 10,000 echo numbers, same as companion paper [49].

3. Results and discussion

3.1. Quantitative NMR model for water

To characterize the CO_2 - H_2O wettability of coals, it is necessary to establish a quantitative model for water based on the NMR data. Fig. 4a shows the NMR T_2 distributions for different masses of free water – a clear peak with long relaxation time is apparent at 200–1000 ms. The NMR total amplitude shows a linearly relationship with water mass (Fig. 4b), that can be expressed as:

$$M_{\text{water}} = 0.0001A \quad (R^2 = 0.9933) \quad (3)$$

where M_{water} is the mass of water, g; and A is the NMR T_2 amplitude, dimensionless.

3.2. Effect of pressure on CO_2 - H_2O wettability

As shown in Fig. 5, at equilibrium water content, the powdered coal sample contains only adsorbed water (black line with open circles) – as indicated by the fast relaxation time at ~ 0.1 – 2 ms – this is a result of

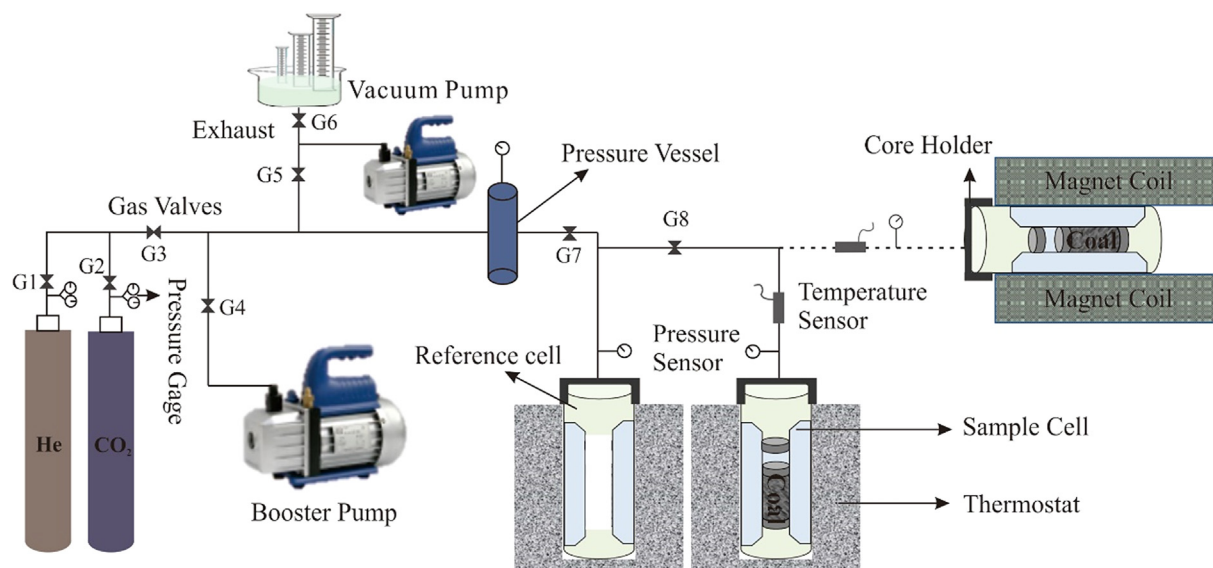


Fig. 3. Schematic diagram of the experimental set-up (modified from the companion paper [49]).

Table 2
Experimental series and sample preparation.

Experimental series	Sample preparation	Temperature (K)	CO ₂ pressure (MPa)
A	Equilibrium water condition	298	3, 4, 5, 6, and 7
B	Equilibrium water condition	308, 318, and 328	5
C	Added 5 g free water after equilibrium water	298	3, 4, 5, 6 and 7

the diffusion behavior of the evaporated water molecules. The amplitude of the T_2 peak for the subbituminous coal is much larger than that for anthracite for the equilibrium water content experiments, per unit mass of coal powder. The main reason for this is that the subbituminous coal has a higher water wettability than anthracite (Fig. 2), enabling more evaporated water to adsorb into micropores.

CO₂ injection pressure is a critical parameter defining improvement in methane recovery – higher injection pressures drive higher methane sweep efficiency. To assess the effect of pressure on CO₂-H₂O wettability during the progress of CO₂-ECBM, Experimental Series A was performed under five different pressures (3, 4, 5, 6 and 7 MPa) but at a constant temperature of 298 K.

Fig. 5 shows the real-time dynamic changes in the NMR T_2 distributions following CO₂ injection at 3 MPa in Experimental Series A.

With the injection of CO₂, the NMR spectrum changes from single-peaked to triple-peaked. The clear P1 peak ($T_2 = 0.01$ –6 ms), with a fast relaxation time, indicates the characteristics of adsorbed water in micropores. The in-conspicuous P2 peak ($T_2 = 10$ –30 ms) corresponds to the water in the small capillaries. The P3 peak ($T_2 > 100$ ms), with high T_2 relaxation times, references the free water in the sample. Considering the important distribution of adsorbed water to wettability, to simplify the interpretation, we used the P1 peak to represent the adsorbed water, the P2 and P3 peak to represent the non-adsorbed water.

In Experiment Series A, the coal powder at equilibrium water content was flooded by CO₂ at 3 MPa with an NMR measurement performed every 1 h. As shown in Fig. 5, with an increase in the CO₂ exposure time, the adsorbed water T_2 amplitude decreases (P1 peak) and

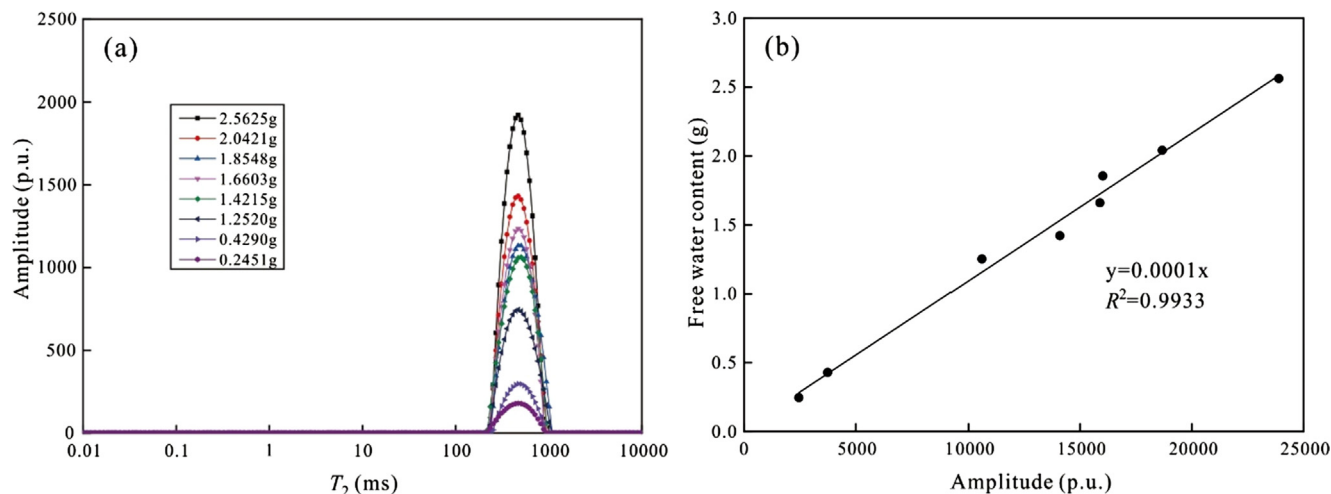


Fig. 4. NMR T_2 distributions for different masses of water (a) and relationship between the NMR T_2 amplitude relative to water mass (b).

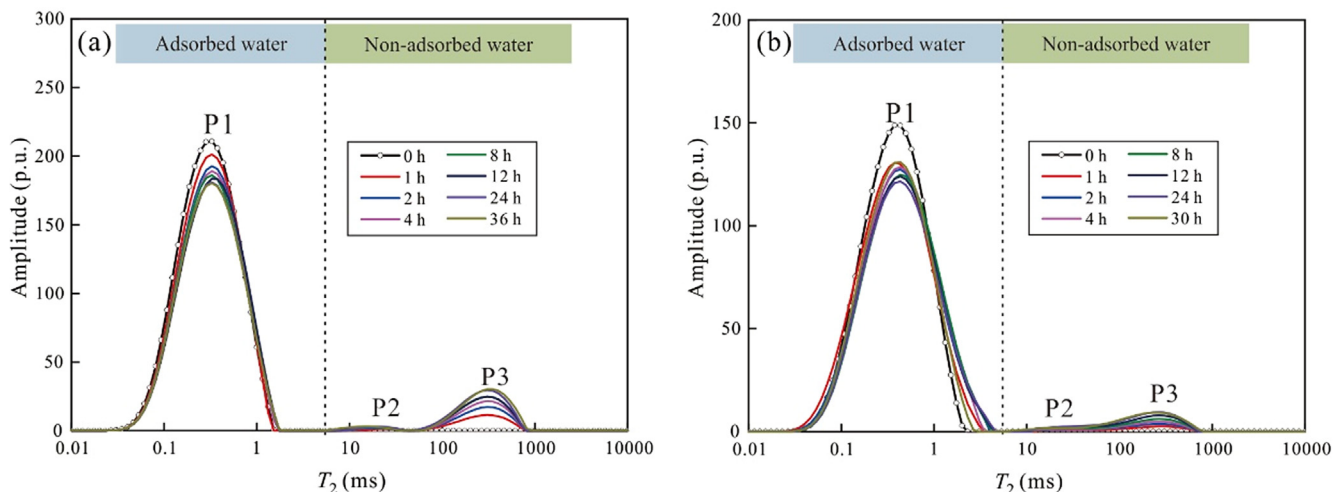


Fig. 5. Changes in NMR T_2 spectrum of water with time following CO_2 injection at 3 MPa (a, subbituminous coal; b, anthracite).

the non-adsorbed water amplitude increases significantly (P3 peak). Since the system is closed, this suggests the transformation of adsorbed water into non-adsorbed water as a result of CO_2 injection. It should be noted that the P3 peak gradually shifts rightward over time – indicating that the free water spreads to larger pores.

The geometric mean of the T_2 relaxation time (T_{2gm}) is an accurate index to probe water wettability in porous media (e.g., sandstones, carbonates and coals) [45–48]. The geometric mean is defined as:

$$T_{2gm} = \exp \left[\sum \frac{\ln(T_{2i})A_i}{A_{total}} \right] \quad (4)$$

where T_{2i} are the individual values of T_2 , ms; A_i their amplitude at T_{2i} , dimensionless; and A_{total} is the total amplitude of the NMR spectrum, dimensionless. Generally, a reduction in the T_{2gm} value represents the movement of fluid into smaller pores – an indication of a weaker water wettability [45,46].

Fig. 6 shows the real-time dynamic changes in T_{2gm} resulting from CO_2 flooding at 3 MPa for both subbituminous coal (Fig. 6a) and anthracite (Fig. 6b). During the CO_2 soaking process (3 MPa), the subbituminous coal reestablished an equilibrium in CO_2 - H_2O interaction after ~36 h where the T_{2gm} increases from 0.41 ms to 0.69 ms. Equilibrium in T_{2gm} is reestablished for anthracite after ~30 h where T_{2gm} increases from 0.36 ms to 0.65 ms. Again, these results suggest that the adsorbed water spreads into the larger pores – due to the decrease in

water wettability in coals following CO_2 injection. During this process, T_{2gm} first increases rapidly before asymptote to an ultimate value, similar in form a Langmuir-like sorption isotherm.

As shown in Fig. 7, the adsorbed water (P1 peak) amplitude decreases significantly with an increase in CO_2 injection pressure, whereas the non-adsorbed water (P2 and P3 peak) amplitude increases. In order to exclude the effect of evaporative water loss, we compared the change in relative water mass rather than absolute water mass in quantifying water migration – i.e., its exchange from adsorbed to non-adsorbed state following an increase in CO_2 pressure (Fig. 8). The relative mass of adsorbed water for the subbituminous coal fell from 100% to 65% as CO_2 pressure increased from 0 MPa to 7 MPa, liberating ~35% of the originally adsorbed water to the non-adsorbed state. For the anthracite, the increase in relative mass of non-adsorbed water was both smaller and slower, rising from 0% to 19% as CO_2 pressure was raised to 7 MPa. The reduction in relative mass of adsorbed water (i.e., increase in mass of non-adsorbed water) during the CO_2 - H_2O interaction, represents a transformation from water-wet to CO_2 -wet during the CO_2 -ECBM process.

In increasing CO_2 pressure from 0 to 7 MPa, the T_{2gm} increases from 0.39 ms to 1.79 ms for subbituminous coal, and 0.36 ms to 1.12 ms for anthracite (Fig. 9). This suggests the reduction in water wettability and growth in CO_2 wettability with pressure – consistent with prior observations on coals [26,48]. This change in wettability may result from

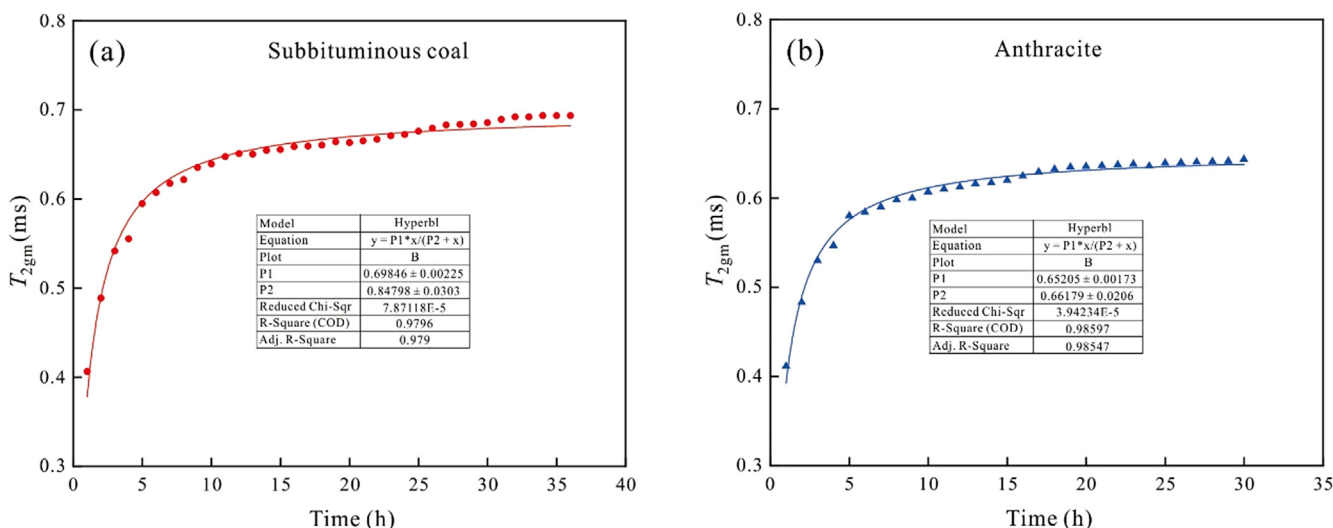


Fig. 6. Changes in T_{2gm} as a function of time for CO_2 present at 3 MPa for (a) subbituminous coal and (b) anthracite.

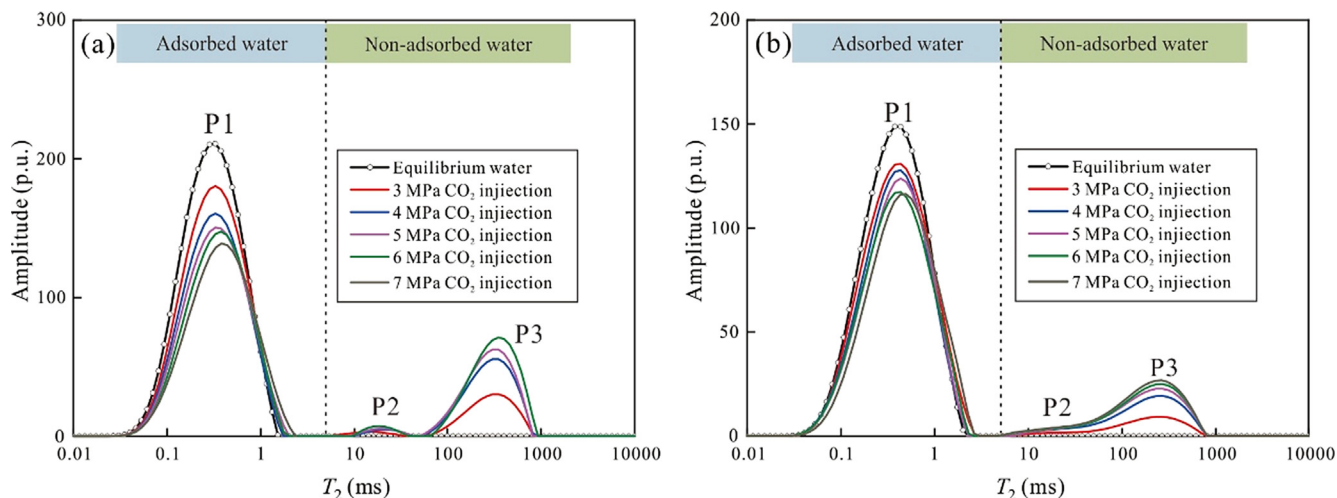


Fig. 7. Changes in water T_2 spectrum for different CO_2 injection pressures (a, subbituminous coal; b, anthracite).

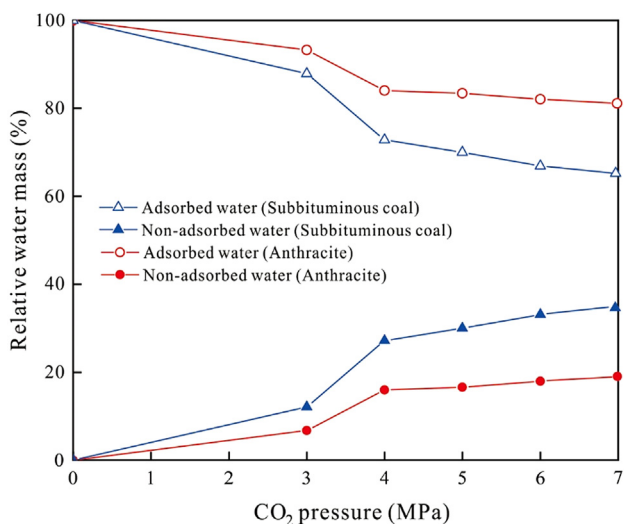


Fig. 8. Relative changes in water mass changes as a function of CO_2 pressure.

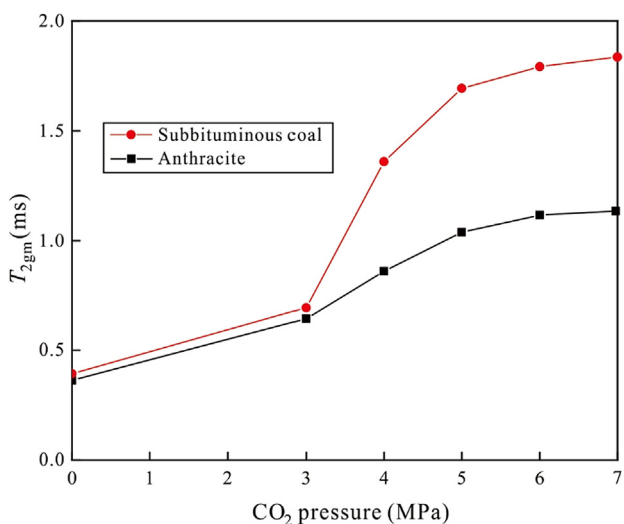


Fig. 9. Changes in T_{2gm} with CO_2 injection pressure.

the increase in CO_2 pressure due to a pressure induced: (1) increase the CO_2 adsorption capacity of coals [54], (2) increase in dissolved CO_2 content in water, resulting in an increase in H^+ concentrations, which

further improves CO_2 wettability [55], (3) increase in CO_2 density, increasing the interfacial tension by strengthening the intermolecular attraction between both the CO_2 - H_2O and H_2O - H_2O bonds [56].

The H_2O wettability change with CO_2 injection pressure – the change is gradual below 3 MPa with a rapid rise from 3 to 5 MPa before stabilizing at ~ 7 MPa. For the subbituminous coal, the average net increase of T_{2gm} is 0.65 ms in the range 3–5 MPa, compared to only 0.07 ms above 5 MPa, per unit pressure of CO_2 injected. A similar trend in T_{2gm} as a function of CO_2 pressure is also found for anthracite, indicating only a minor increase in CO_2 wettability when CO_2 pressure is > 5 MPa.

3.3. Effect of temperature on CO_2 - H_2O wettability

Fig. 10 shows the T_2 spectra for both subbituminous coal and anthracite at temperatures of 298 K, 308 K, 318 K and 328 K, but at a fixed CO_2 pressure of 5 MPa (Experimental Series B). With increasing of temperature, T_2 amplitude representing the adsorbed water increases and that for the non-adsorbed water declines. This indicates that increasing temperature increases the water wettability and correspondingly decreases the CO_2 wettability.

The change in relative mass of water, sequestered in either adsorbed or non-adsorbed state, is shown as a function of temperature in Fig. 11. When temperature rises from 298 K to 328 K in Experimental Series B (constant pressure), the relative mass of adsorbed water increased from 70% to 83% for subbituminous coal and increased from 83% to 94% for anthracite. As shown in Fig. 12, the T_{2gm} decreases with an increase in temperature for both subbituminous coal and anthracite. As temperature is raised to 328 K, the T_{2gm} falls from 1.69 ms to 0.65 ms for the subbituminous coal. For anthracite, the T_{2gm} decreases more slowly with temperature, falling from 1.04 ms to 0.55 ms. The variation with temperature of both T_{2gm} and the relative mass of adsorbed/non-adsorbed water both indicate the decrease in CO_2 wettability with increasing temperature in coals.

Two principal factors may be responsible for this CO_2 wettability decrease with increasing temperature. First, CO_2 adsorption capacity is known to gradually decrease with an increase in temperature – due to the increase in kinetic energy and rate of diffusion of CO_2 [48]. Second, the intermolecular attractive forces between in CO_2 - H_2O and H_2O - H_2O decrease with rising temperature, and result in the reduction of CO_2 - H_2O surface tension [56].

3.4. Effect of water content on CO_2 - H_2O wettability

The form of water occurrence (adsorbed versus non-adsorbed) on

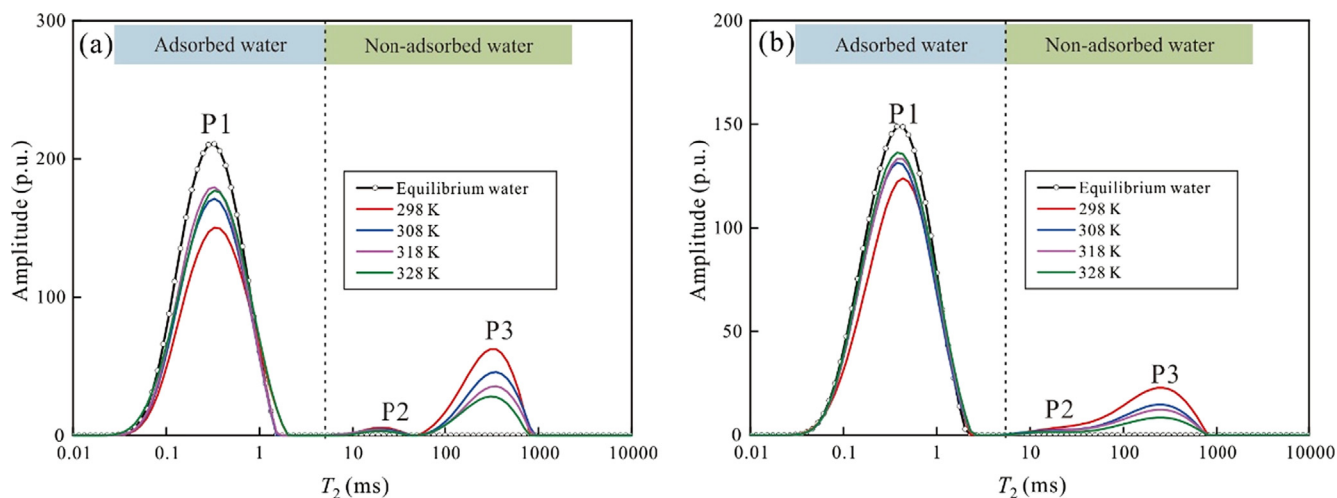


Fig. 10. Changes in water T_2 spectrum with temperature (a, subbituminous coal; b, anthracite).

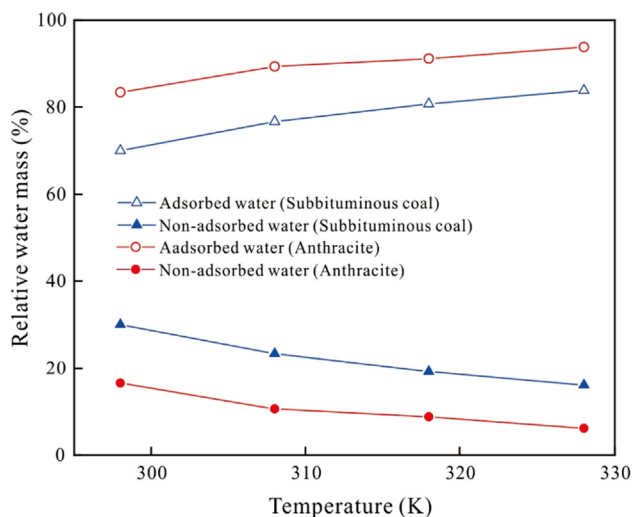


Fig. 11. Changes in relative water mass with temperature for CO_2 injection at 5 MPa.

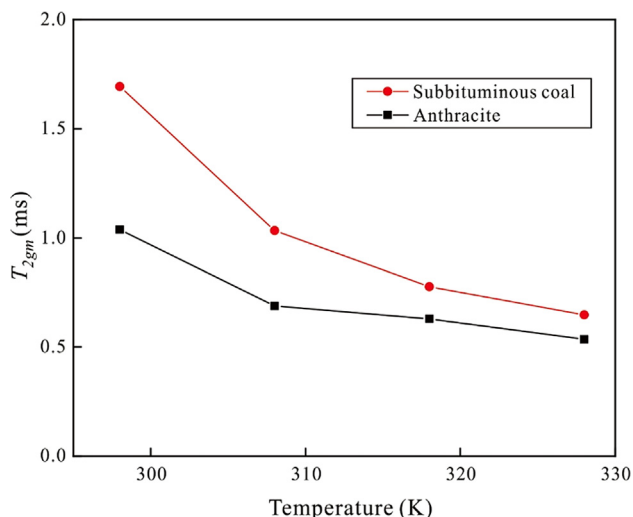


Fig. 12. Changes in T_{2gm} with temperature for CO_2 injection at 5 MPa.

potential impacts CO_2 - H_2O wettability for both subbituminous coal and anthracite. As shown in Fig. 5, when the coal contains only adsorbed water in the initial equilibrium water condition, the T_2 distribution is unimodal with the only of P1 peak. After addition of free water in the coal sample, the T_2 distribution changes to multiple peaks that represents both the adsorbed water and added non-adsorbed free water (Fig. 13). Changes in the water T_2 spectra with injection pressure CO_2 are shown in Fig. 13 (Experimental Series C). Similar to the variations for the equilibrium water content condition (Experimental Series A), the adsorbed water T_2 amplitude decreases and non-adsorbed amplitude increases with increased pressure for both two coals. The features of the change in adsorbed water mass with pressure (Experimental Series C) are clarified in Fig. 14a. At the conclusion of the Experimental Series C, the adsorbed water content falls from 0.32 g to 0.24 g for the subbituminous coal and from 0.31 g to 0.19 g for the anthracite. This indicates the transformation of adsorbed water into non-adsorbed states. Again, two different CO_2 - H_2O wettability change rates are apparent after raising CO_2 pressure: an initial rapid increase at < 5 MPa followed by stabilization (Fig. 14b), similar to the changes in where no free water is present (Experimental Series A), at least in terms of the T_{2gm} proxy.

CO_2 - H_2O wettability is typically presumed to be a fixed physical parameter for a typical coal sample, regardless of whether it is treated under equilibrium water condition or with free water added. Thus, to investigate the influence of the various phase of water occurrence on CO_2 - H_2O wettability of coals, we use the normalized T_{2gm} rather than absolute T_{2gm} . As shown in Fig. 15, for both subbituminous coal and anthracite, the normalized T_{2gm} increases significantly with an increase in pressure both for equilibrium water (Experimental Series A) and free water added conditions (Experimental Series C). This indicates that CO_2 injection pressure has fixed impact in decreasing water wettability with pressure independent of the form of water that is present. However, this impact on wettability is much reduced in the presence of free water (Fig. 15). The principal reason is likely that the non-adsorbed water occupies pore throat and renders these sorption sites unavailable for CO_2 .

3.5. Potential applications of this study

This study has used a novel NMR relaxation method to probe changes in CO_2 - H_2O wettability that result from CO_2 flooding, as an analog to CO_2 -ECBM. The experimental observations suggest that CO_2 - H_2O wettability of coals, are mainly affected by injection pressure, reservoir temperature and the state of water occurrence.

Experimental observations revealed that the sorption capacity of

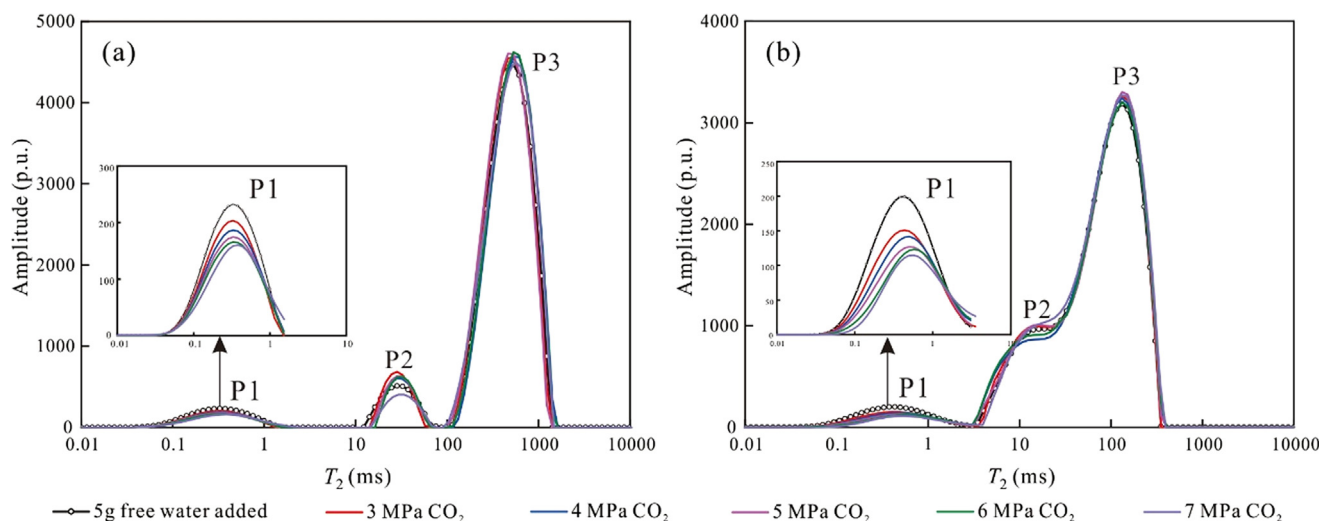


Fig. 13. Changes in water T_2 spectrum with increasing CO_2 injection pressure – 5 g free water added after equilibrium water condition is reached (a, subbituminous coal; b, anthracite).

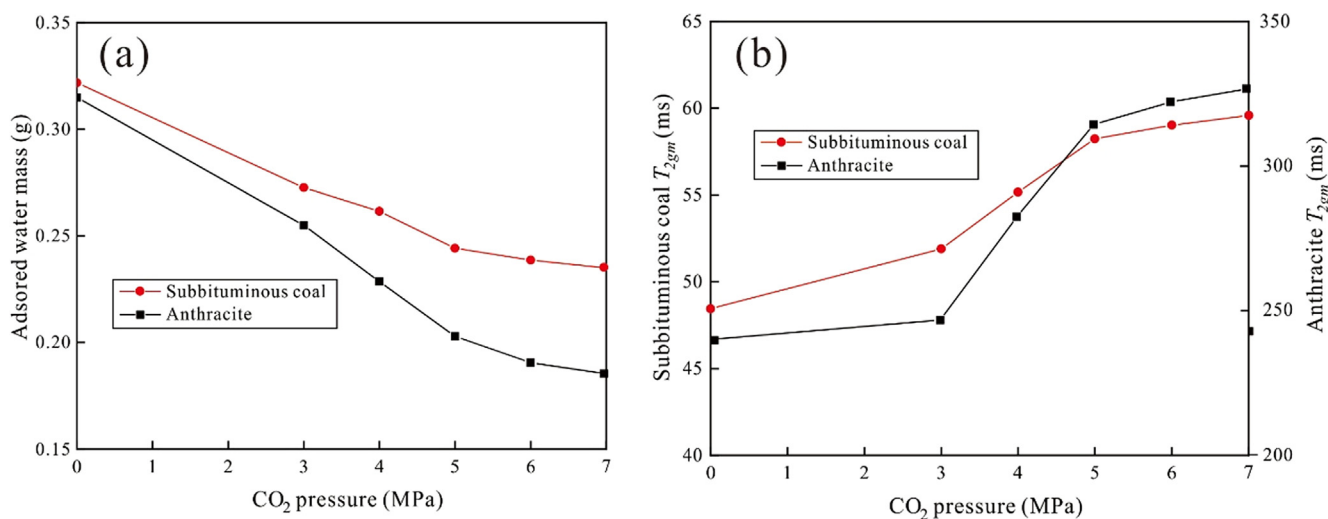


Fig. 14. Changes in adsorbed water amplitude (a) and T_{2gm} (b) with CO_2 injection pressure.

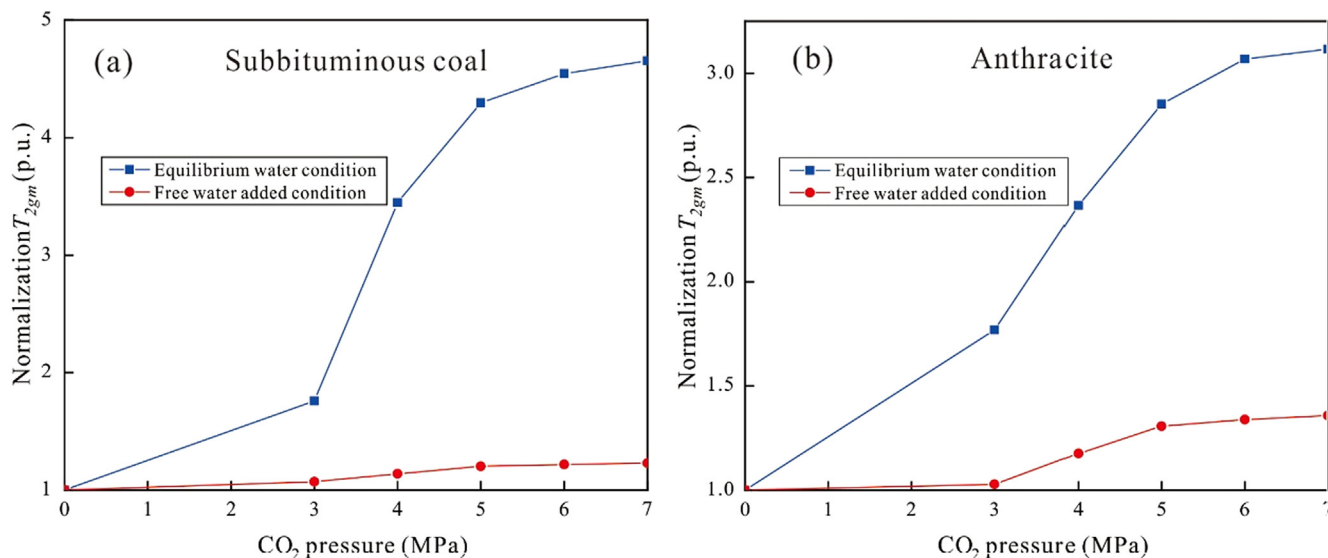


Fig. 15. Change in normalized T_{2gm} both at the equilibrium water condition and with free water then added as a function of CO_2 injection pressure (a, subbituminous coal; b, anthracite).

CO₂ is ~2–10 times that of methane in coals [21,22]. The injection of CO₂ into coal reservoirs, both in laboratory and field experiments, has been successful in enhancing methane recovery. As discussed in Sections 3.2 and 3.4, increasing the injection pressure increases the CO₂ wettability in coals with and without the presence of free water. However, a higher injection pressure often corresponds to a greater economic expense. Considering the rate change in wettability with pressure either absent (Experimental Series A) or with free water (Experimental Series C), the optimal injection pressure suggested in this study is ~5 MPa for elevating methane recovery. This is because wettability changes little above the pressure and therefore there is little increase in methane recovery even for an increased injection cost. The CO₂ wettability of coals declines with the increasing temperature (Experimental Series B), indicating that lower temperature is more suitable in enhancing methane recovery from the perspective of wettability in coals. Thus, shallower and cooler seams would be more productive, from this standpoint. But this remains a parameter – changing the temperature – that would be intractable to change for a coalbed reservoir.

In current field applications, the presence of large quantities of water in fractures/macropores usually inhibits and sometimes largely eliminates methane production – the water blocking problem – present both in hydraulic fracturing and for CO₂-ECBM. As discussed in Section 3.4, the presence of non-adsorbed water reduces the sensitivity of CO₂ wettability to pressure, potentially resulting in a reduction in CBM production. Thus, it is necessary to drain the free water, overcoming the negative impacts of non-adsorbed water in improving the CO₂ wettability, further enhancing the production rate of CBM.

In addition to enhancing methane recovery, injecting CO₂ into coal reservoirs also has a potentially significant impact in CO₂ geological sequestration and storage. CO₂ sequestration and storage in coal reservoirs are primarily influenced by the CO₂ adsorption capacity [24,48]. Since increasing CO₂ wettability in coals increases CO₂ adsorption capacity – this will further increase the potential mass of CO₂ sequestered and stored. Regardless of the different modes of water occurrences in coals, adsorbed versus free, elevated pressures and low temperatures favor increased mass of CO₂ sequestered.

4. Conclusion

We evaluated the effect of CO₂ injection pressure and temperature, together with different states of occurrence of water (adsorbed- versus free-water) on CO₂-H₂O wettability of subbituminous coal and anthracite using NMR. Conclusions are drawn as follows:

- (1) The principal forms of water in coals are as: adsorbed water (P1 peak, $T_2 < 6$ ms); and non-adsorbed water (including P2 peak and P3 peak, $T_2 > 6$ ms). Coal powder under an equilibrium water state contains only adsorbed water. Conversely, any subsequently added water contributes a non-adsorbed phase that supplement the pre-existing adsorbed phase in the micro-pores.
- (2) CO₂ wettability of coals increases with an increasing in the CO₂ injection pressure. This change in CO₂ wettability increases with increase in pressure to < 5 MPa before stabilizing at an asymptotic maximum magnitude. Absent a significant increase in wettability above 5 MPa suggest the optimal injection pressure is 5 MPa for both enhancing methane recovery and CO₂ sequestration – from the single perspective of wettability.
- (3) CO₂ wettability increases with a decrease in temperature and thus sequestered mass will be increased in lower-temperature coal reservoirs, all other factors being equal. Thus, shallow seams would benefit from this behavior, although changing reservoir temperature to benefit from this response is unlikely viable.
- (4) The presence of non-adsorbed water in coals significant decreases the rate of change in CO₂ wettability with pressure and reduces the maximum magnitude of the impact at elevated temperature. Thus,

the presence of free-water further results in the reduction in CBM production as a result of desorption, in addition to any impacts due to the occluding of pore and fractures and impeding transport. Thus, water drainage to improve methane transport in a dewatered pore/fracture network will additively aid in increasing the potential for methane drainage and CO₂ storage.

CRediT authorship contribution statement

Sijian Zheng: Validation, Writing - original draft, Investigation. **Yanbin Yao:** Conceptualization, Methodology, Supervision, Writing - review & editing, Project administration, Funding acquisition. **Derek Elsworth:** Writing - review & editing, Validation. **Dameng Liu:** Resources. **Yidong Cai:** Visualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fuel.2020.118560>.

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