Suitability of Victorian brown coal for CO_2 sequestration: An experimental overview on effect of moisture on CO_2/CH_4 exchange

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ABSTRACT

Brown coal seams located in Victoria, Australia are possible sinks for CO_2 storage. However, the higher moisture contents (55-60%) present in these coal seams may affect the CO_2/CH_4 exchange capacities and was investigated in this study as the main objective. A series of isothermal (40^{0}C) sorption tests were carried out on brown coal specimens for different moisture contents (dry, 20%, 40% and 60%) and both CO_2 and CH_4 was flooded up to 10.5 MPa. The data was then evaluated by fitting to the modified Dubinin–Radushkevich (DR) model. The CO_2 and CH_4 capacities of the brown coal was affected by the presence of moisture. However, both sorbates displayed some critical moisture levels and afterward, sorption capacity was not affected. The net heat of adsorption pronounced a marginal decrease on addition of moisture for both sorbates. The current findings permit further investigations on swelling effect on wet brown coal for long-term CO_2 sorption capacities.

Keywords: adsorption, brown coal, carbon dioxide, enhanced methane recovery, moisture

1 INTRODUCTION

To adhere the Paris Protocol, Australia is targeting for a 26 to 28% reduction in cumulative emission of CO_2 by 2030 (Australia's Emission Projections, 2017). Carbon capture and storage is one potential method to achieve this target. It helps by reducing the anthropogenic CO_2 released to the atmosphere. CO_2 sequestration in deep unmineable coal seams with the recovery of natural coal bed methane (CBM) is an attractive way of addressing the rise in atmospheric concentrations of anthropogenic CO_2. This technology has the potential to off-set the costs for CO_2, capture, compression, transportation and storage by producing a comparatively eco-friendly fuel, CBM. Of the other options for the possible storage of CO_2, deep unmineable coal beds are more feasible basins as they are widespread located near large coal power plants. Further, around 98% of CO_2 is in its adsorbed phase of the coal micropores which enables the stable storage of CO_2 for a geologically significant period (White et al., 2005).

2 BACKGROUND

Australia's potential capacity for the geological storage of CO_2 in deep coal seams, was identified as 417 Gt (Carbon Storage Taskforce, 2009). Among these locations, the offshore Gippsland low rank coal basin in Victoria, Australia, has the greatest capacity from the eastern basins (Durie, 1991). It is also very close to the Latrobe Valley hub (150 km) which reduces the cost of CO_2 transport. Therefore, it is worthwhile to investigate the applicability of Victorian brown coal for CO_2-ECBM. Ranathunga et al. (2017) conducted a series of core flooding tests for brown coal (Carbon content – 69.3%) from the Hazelwood coal mine, located at Morwell in South Gippsland, Victoria, Australia as a preliminary study to check the applicability of Victorian brown coal for CO_2 enhanced CH_4 recovery.

Testing was conducted on CH_4 saturated (5 MPa) meso-scale (38 mm in diameter and 80 mm in height) dry samples in isothermal conditions (40 ^{0}C). A confining pressure of 11 MPa (an approximate depth of 400 m) was used for this study. Upon reaching to the equilibrium state, the brown coal samples were subjected CO_2 flooding of: 5,6 and 7 MPa (sub-critical CO_2) and 8 and 9 MPa (super-critical CO_2) to observe the CO_2/CH_4 exchange patterns in brown coal (critical point of CO_2 is 7.38 MPa and 31.8 ^{0}C).

According to the core flooding results, CO_2 flooding can considerably enhance coal seam CH_4 production compared to natural recovery methods. Additionally, higher CO_2 pressures can drive the CH_4 towards the production wells with nearly 100% sweep efficiency (refer to Table 1). Furthermore, injection of higher CO_2 pressures exchange CH_4 to CO_2 rapidly, resulting a larger transition zone from CH_4-saturated to CO_2-saturated coal mass in the field. This will facilitate higher recovery of CH_4 from the production wells.

Hence, Victorian brown coal can be used for CO_2-ECBM.

However, Victorian brown coal consists of higher moisture contents around 55-60% (on dry ash free basis – d.a.f.) (Jasinge, 2010). Further, a study done on high rank coal by Wolf et al. (2001), observed higher reductions in sweep efficiencies in wet coal for both sub- and super-critical CO_2 floods. Therefore, the effect of moisture on CH_4 to CO_2 exchange on Victorian brown coal should be further analysed to confirm its feasibility for CO_2-ECBM and was the main objective of this study.

Table 1. Sweep efficiency for different CO_2 flooding (Ranathunga et al., 2017)

CO_2 pressure	Representative phase	Sweep efficiency (%)
-	-	46.4
5	Sub-critical	93.1
6	Sub-critical	96.4
7	Sub-critical	96.6
8	Super-critical	100.0
9	Super-critical	100.0

3 METHODOLOGY

3.1 Adsorption tests

A series of sorption capacity tests were carried out on brown coal samples obtained from the same Hazelwood coal mine. The brown coal samples used for this study consisted a moisture content of 58% dry-ash-free (d.a.f.) basis. Hence, a series of sorption capacity testing was conducted under different moisture contents of 0% (dry), 20%, 40% and 60% for both CO_2 and CH_4 (up to 10.5 MPa). Temperature was kept constant at 40^0C similar to the core-flooding study done by Ranathunga et. al. (2017). Fresh air-dried lumps of coal (particle size from 0.5-1.0 mm) was prepared by crushing and screening for the sorption tests. The adsorption isotherms were measured using a volumetric system available at Commonwealth Scientific and Industrial Research Organisation (CSIRO), Clayton, Australia which has been described in detail by Sander et al., (2016). A schematic of the experimental rig is shown in Fig 1.

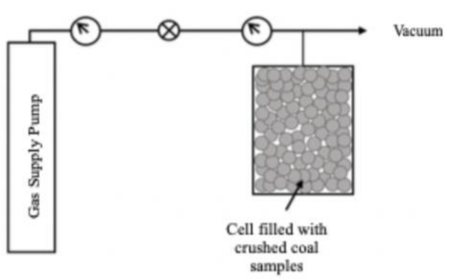


Fig. 1. Schematic diagram of the experimental measurement unit used for adsorption and desorption measurements of moist brown coal (modified after Sander et al., 2016)

Procedure for adsorption tests was as follows: 1). gas was injected into the sample cell to the intended pore pressure, 2). the sample was shut-in when the desired pore pressure reached, 3). the pressure decay in the cell over time was recorded including the pump pressure, volume, and temperature and 4). When equilibrium was achieved, the pore pressure was constant, i.e. adsorption had ended. This procedure was continued in steps until 10.5 MPa for both CO_2 and CH_4. Same methodology was adopted for the desorption tests. However, the pump pressure was set to a lower pressure than the current sample pressure to result a gas flows from the sample to the pump.

3.2 Evaluation of Sorption Isotherms

The experimental sorption isotherm data was then evaluated by fitting to the modified Dubinin–Radushkevich (DR) sorption isotherm (Eq. (1)). According to Day et. al. (2008), this model can represent sorption data for a wide range of pressures and temperatures accurately.

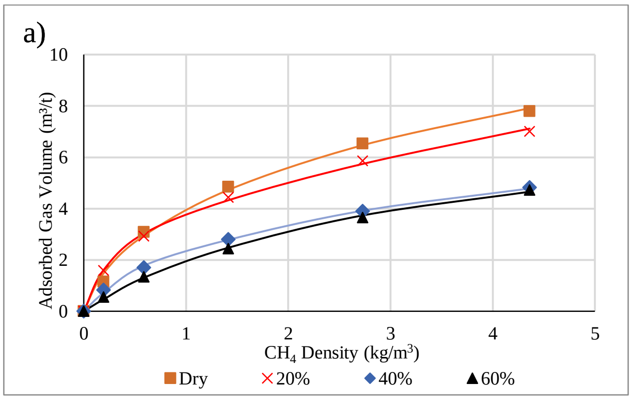
$$W_{ads} = W_o\left(1-\frac{\rho_g}{\rho_a}\right) exp\left\{-D\left[\ln\left(\frac{\rho_a}{\rho_g}\right)\right]^2\right\} \tag{1}$$

where, W_{ads} is adsorbed volume, W_o is surface adsorption capacity of the substrate, ρ_g is the gas density, ρ_a is the density of the adsorbed phase and D is a constant related to the affinity of the sorbent of the gas. The density of the adsorbed phase (ρ_a) was taken as 1000 kg/m^3 for CO_2 and 420 kg/m^3 for CH_4 (Sakurovs et al., 2010). Note that all the adsorption calculations have been done on dry-ash-free (d.a.f.) basis.

4 RESULTS AND DISCUSSIONS

4.1 Sorption Isotherms

The CO_2 and CH_4 sorption isotherms for brown coal at different moisture contents versus gas density are illustrated in Fig. 2.



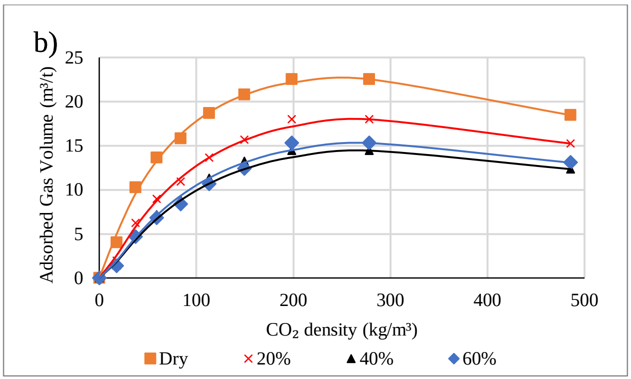


Fig. 2. Adsorption Isotherms for (a) CH_4 and (b) CO_2 during different moisture contents. Line plots represents the fits calculated by modified DR model

According to Fig. 2, the maximum sorption capacity of the coal specimens was obtained for dry samples for both CO_2 and CH_4 sorption. However, this sorption capacity for both CH_4 and CO_2 were reduced in the presence of moisture. Interestingly, reduction in the sorption capacity for both CH_4 and CO_2 were decreased at higher moisture contents.

4.2 Effect of moisture on sorption capacity (W_o)

The effect of moisture content on sorption capacity is shown in Fig. 3. Here, the maximum sorption capacity, W_o versus moisture content for the CH_4 and CO_2 sorption was used.

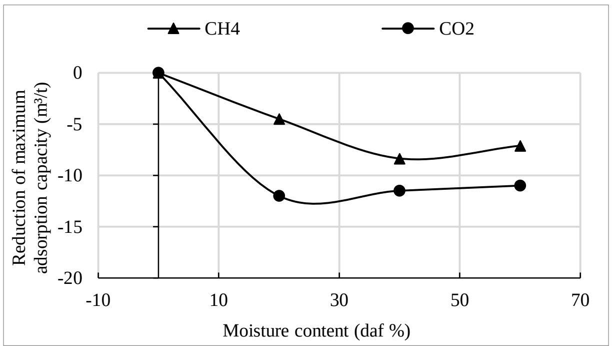


Fig. 3. Reduction in maximum adsorption capacity compared to dry coal for CH_4 and CO_2.

The initial sections of the curves where the sorption capacity is affected by the moisture (in Fig. 3) were approximately linear for both CH_4 and CO_2. Further, around 0.2 m^3/t of CH_4 is displaced by 1% of moisture in brown coal and it is around 0.5 m^3/t for CO_2. Interestingly, the sorption capacities of sorbates were unaffected when the moisture content of the coal specimens are above the critical moisture level. Here, this critical moisture content is around 40% for CH_4 while it is around 30% for CO_2.

According to Li (2004), Victorian brown coal comprises wide range of pore structures namely: macro (>50 nm), meso (2-50 nm), micro (0.4-2 nm) and sub-micro (<0.4 nm) pores. Among these various pores, water molecules attach to hydroxyl groups (polar sites), on the coal surface (large or interparticle voids) and hence by physical displacement, it reduces the sorption capacity for CH_4 and CO_2 (Day et al. 2008). Since water only attracts to the hydrophilic sites on coal, the remained hydrophobic sites are available for adsorption of sorbates (Arif et al., 2016). Therefore, after the critical moisture content, sorption capacity will be increased by the sorption of sorbates in to hydrophobic sites of coal.

However, the effect of moisture on gas adsorption is less pronounced for CO_2 compared to CH_4 though the trend of capacity reduction was similar. For example, the CO_2 capacity was reduced by about 29% while it was reduced by 36% for CH_4, for the critical moisture content. This might be due to the higher affinity of CO_2 adsorbed into the coal matrix compared to CH_4. CO_2 has a van der Waals volume of 4.28E-5 m^3/mol and the volume for CH_4 is 4.31E-5 m^3/mol (Day et. al., 2010). This comparatively smaller molecular size of CO_2 facilitates higher adsorption in micro pores than for CH_4 with stronger van der Waals bonds (van der Waals density for CO_2 = 1028 kg/m^3 and for CH_4 = 372 kg/m^3 (Day et. al., 2010)). This is further confirmed by the sorption capacity of dry and moist coal samples in Fig. 2, which illustrates about 3 to 5 times higher capacity for CO_2 (Fig. 1(b)) than for CH_4 (Fig. 2(a)) over the range of different moisture contents.

4.3 Effect of moisture on Net heat of sorption (*D*)

Term *D* in Eq. (1) is a constant related to the affinity of the sorbent of the gas and can be expressed as:

$$D = [RT/\beta E]^2 \qquad (2)$$

Where R is the universal gas constant, T is the temperature, β is an affinity constant for the gas onto the coal and E is the heat of adsorption (Sakurovs et al., 2010).

Using Eq. (2), the net heats of adsorption, βE, were evaluated for CO_2 and CH_4 sorption at each moisture content. The βE values versus the moisture content is illustrated in Fig. 4 for both sorbates.

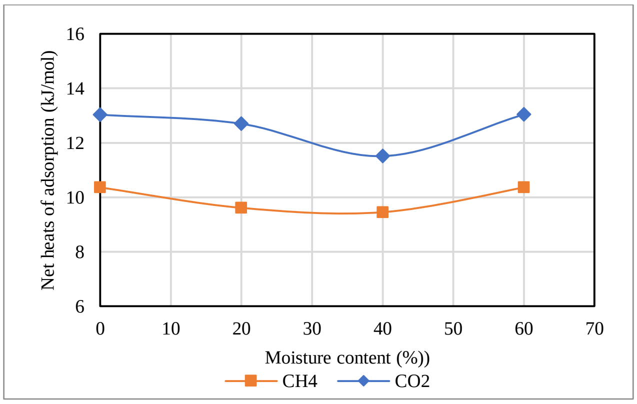


Fig. 4. Net heat of adsorption (βE) for CH_4 and CO_2 sorption in brown coal at 40^0C

The βE of CH_4 was marginally less than for CO_2. For the brown coal, average βE for CH_4 is around 9.9 kJ/mol, and around 12.6 kJ/mol for CO_2. In addition, there was a slighter decrease in βE with increasing moisture content for both sorbates. However, this reduction is lesser in CH_4 than witnessed for CO_2. Similar behaviours of CO_2 and CH_4 sorption on different ranked wet coals have been recorded in previous literature confirming these observations (Clarkson and Bustin, 2000; Day et al., 2008).

5 IMPLICATIONS FOR FIELD APPLICATION

This study was conducted to investigate the effect of moisture on Victorian brown coal to thorough the understanding of applicability of CO_2-ECBM. According to the results, both CO_2 and CH_4 sorption are affected by the presence of moisture up to a critical moisture level. There onwards, the sorption capacity is unaffected. This critical moisture level is less than the natural moisture content (58%) of the brown coal sample for both CO_2 (~30%) and CH_4 (~40%). Hence, in the field application, the effect of moisture on the CO_2/CH_4 exchange would be lesser.

Further, βE for dry coal is higher than the βE for moist coal during adsorption of both sorbates. For example, around 7% and 2.5% reduction of βE is observed from dry to 20% moist coals when CH_4 and CO_2 are flooded respectively. Water molecules create hydrogen bonds with coal, occupying the higher energy adsorption sites. This will restrict gas sorption to less energetic sites causing reduction on βE in moist coals (Day et. al., 2011). Hence, in field application, higher injection pressures should be injected to wet brown coal in order to fully saturate the coal matrix with CO_2.

At the same time, previous researchers (Day et. Al., 2010; White et al., 2005) have identified that CO_2 causes coal mass swelling and it reduces the sorption capacity of any coal type. Further, Ranathunga et. al. (2017) also observed a higher volumetric strain on dry brown coal samples during CO_2/CH_4 exchange. Hence, it is important to find the effect of moisture on this regard. Day et. al. (2011) conducted a series of sorption tests on dry and moist coals (carbon content from 79.3 to 88.9%) to study the coal swelling. They found that swelling of dry coals is higher than wet samples. Because, the moist in wet coal samples have already swollen the sample, partly. If this pre-swelling due to water is also considered for the calculations, the total swelling (swelling created by moist + swelling created by CO_2) of the wet coals is higher than the swelling created by dry coal. Therefore, the presence of moisture can affect the long-term sorption capacity of CO_2 in coal seams and warrants future studies using Victorian brown coals (carbon content ~ 69.3%) to check the suitability for CO_2-ECBM.

6 CONCLUSIONS

CO_2 and CH_4 sorption isotherms were measured on dry and wet Victorian brown coal at 40 °C and pressures up to 10.5 MPa. The isotherms were fitted to modified Dubinin–Radushkevich model and was analyzed obtaining the effect of moisture on CO_2/CH_4 exchange. Following conclusions were drawn after the study.

- Presence of moisture affects the sorption capacity of both CO_2 and CH_4.
- However, both CO_2 and CH_4 displayed some critical moisture content of which the sorption capacity was unaffected. Because, water prefers the hydrophilic sites, the gas sorbates will have more provision to be adsorbed to hydrophobic sites.
- This critical moisture content was higher for CH_4 (around 40%) than for CO_2 (around 30%). It may be due to the higher affinity of CO_2 for adsorption than for CH_4.
- The net heat of adsorption of CO_2 was marginally higher than for CH_4. In addition, there was a smaller decrease in net heat of adsorption with increasing moisture content for both sorbates and this reduction is lesser for CH_4 than for CO_2.

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