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Influence of temperature on coal sorption characteristics and the theory of coal surface free energy

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Abstract

An experimental study was undertaken to examine the sorption and desorption characteristics of coal at temperatures of 35 °C, 45 °C and 55 °C. The study focused on the effect of changes in temperature and coal particle sizes on gas sorption and desorption characteristics. The coal size used ranged from fragmented coals, 16 mm, 8 mm, 2.4 mm, powdered coal of 150 μm and 54 mm core samples. The samples were tested in pressure vessels, known as “bombs”, charged with CO 2 gas at different pressure levels up to a maximum of 4000 kPa. It was found that temperature has a significant influence on the sorption and desorption behaviour of gas in coal. The degree of hysteresis phenomenon was found to be influenced by the coal surface area as well as temperature. Based on the principle of surface chemistry, the method of calculating coal surface energy with sorption parameters was used and the main parameter of surface tension was analysed. The calculation result showed that reduced value of surface tension parameter decreased with increasing temperature. Also the reduced value of surface tension parameter of adsorption is smaller than the desorption. The theory of coal surface free energy can be used to explain the coal sorption characteristics with CO 2 at higher temperatures. Results from this study have useful implication for enhanced CBM and gas drainage in coal mines.

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Keywords: Coal; Sorption; Desorption; Temperature influence; Surface free energy; Surface tension

1. Introduction

Gas sorption in coal has been studied over the years by many researchers [1, 2, 3], and in recent years, the coal sorption characteristics at high temperatures, beyond the normal temperature of 20 ~ 29 °C, have been identified as an attractive option which can shed light on the behaviour of gas.
sorption in and desorption from coal *in situ*, especially when mining is taking place at increasing depth.

Lama and Bodziony [4] reported that the term “sorption” consists of two parts: adsorption and absorption. Adsorption refers to the accumulation of gas on the surfaces of pores and cracks and absorption means the penetration of gas into the internal structure of coal. Sorption is an exothermic process and is opposite to desorption, which is endothermic. Studies reported by Moffat and Weale [5]; Yang and Saunders [6]; Stevenson et al. [7], cited by Lama and Bodziony [4], indicated that the heat of sorption is less than two or three times the heat of desorption/vaporisation.

Siemons and Busch [8] measured CO₂ sorption isotherms on both dry and moist coals of various ranks from coal basins from around the world and these measurements were made in temperature of 45 °C. Day et al. [9] carried out experiments on supercritical gas sorption of carbon dioxide on moist coals at temperatures of 21 °C and 55 °C and pressures up to 20 MPa. The differences of gas content due to different temperatures were not compared and the samples for the experiment were prepared by crushing and screening fresh air-dried lumps of coal to a particle size range of 0.5 ~ 1.0 mm.

Jun [10] reported that the changes of surface free energy of coal was the most important reason when different rank of coal sorbed different quantity of gas. Based on the principle of surface chemistry, coal surface free energy which indicates the interaction capacity between the coal surface and gases can be calculated. In his study, Jun found that the coal surface free energy is related to the rank of coal.

2. Experimental

2.1. Apparatus

The indirect gravimetric method was used to calculate the volume of gas adsorbed and desorbed from coal. The gas sorption apparatus shown in [11] and Lei et al. [12]. In this apparatus, each vessel, known as “bomb”, has its own pressure transducer so that the sorption process and changes in bomb pressure can be readily determined. The equipment has since been further modified to accommodate increases in temperature up to 100 °C. The addition of a heat isolation jacket outside the water bath as well as the insulation cover enabled the coal bombs to maintain the desired experimental temperature with an accuracy of 0.1 °C.
2.2. Coal sample preparation

The coal samples used in the study were collected from longwall panel 520, Area 5, West Cliff Colliery. Details of the coal samples are shown in Table 1 and Table 2 [13]. The coal core samples were prepared according to the International standard of rock core sample preparation [14]. In addition to coal cores, larger coal lumps were freshly dug out of the development headings. They were wrapped in plastic sheets and taken to the laboratory where they were immersed in water tanks to minimise oxidation and adverse environmental effects. Samples of the collected coals were then crushed and sieved to obtain the desired particle sizes for the test. In addition to 54 mm core samples, coal fragments of 16 mm, 8 mm, 2.4 mm and coal powder, 150 μm were used in this study.

Prior to testing the moisture content of the samples was determined in accordance with the Australian Standard [15] for the determination of the moisture content of coal. All samples were then enclosed in pressure bombs and subjected systematically to CO2 gas pressurisation at various temperatures of 35 °C, 45 °C and 55 °C respectively. The level of gas pressurisation of the samples was carried out initially in 500 kPa steps until reaching 1000 kPa and subsequently increased in steps of 1000 kPa until reaching the maximum of 4000 kPa.
Table 1. Coal density and proximate analysis

| Sample Code | Depth (m) | Moisture (%) | Volatile Matter (%) | Fixed Carbon (%) | Ash Yield (%) | Volatile Matter (%), daf | Coal Density |
|-------------|----------|--------------|---------------------|------------------|---------------|-------------------------|--------------|
| 520         | 450      | 1.3          | 21.7                | 71.4             | 5.6           | 23.3                    | 1.43         |

Table 2. Coal petrography

| Sample Code | Vitrinite Reflectance (%) | Maceral (%) | Maceral (%), mineral free |
|-------------|---------------------------|--------------|---------------------------|
|             | Vitrinite | Liptinite | Inertinite | Mineral | Vitrinite | Liptinite | Inertinite |
| 520         | 1.28      | 41.6       | 0.1          | 55.3    | 3.0        | 42.9      | 0.1        | 57.0       |

3. Results and analysis

Sorption test of coal samples at 35 °C, 45 °C and 55 °C shows the variation in the CO₂ pressure decrease with time from the initially charged pressure level of 900 kPa at different temperatures of 35 °C. The variation in the rate of pressure drop, during the first 6 000 s is different for different coal particle sizes. The rate of pressure drop appears to be affected by the particle size particularly during the first 1 000 s of the sorption process. The sharpest drop in gas pressure is in 150 μm samples and the slowest being in 54 mm core sample. However, the consistency of the pressure does not hold well over longer periods of time. And the 150 μm particle size easily achieves pressure equilibrium in a relatively shorter time in comparison with larger coal particle sizes. The 35 °C sorption rate result is shown as an example, the general same trend happens with 45 °C and 55 °C sorption test. It is concluded that the coal particle size has an important bearing on CO₂ sorption rate in coal.

Fig. 2 shows that the adsorption isotherm at three temperatures for different particle sizes. For each coal particle size and at every pressure step from 0 to 4 MPa, the adsorbed volume of CO₂ is decreased with increasing temperature step. The sorbed volume achieved the highest level at 35 °C and the lowest at 55 °C.

With the exception of the 54 mm diameter core sample, there is no common trend of variation between sorbed volume of CO₂ gas and particle size, and increased temperature reduces or minimises the influence of particle size on gas sorption and it was found that high temperature helped to reduce sorption duration.

There is no clear relationship between the CO₂ adsorption volume and coal sample particle size.
Fig. 1. 900 kPa pressure drop of CO₂ at 35 °C.

Fig. 2. CO₂ adsorption isotherms at selected temperatures (a) 54 mm, (b) 16 mm, (c) 8 mm, (d) 150 μm.
3.1. Desorption test of coal samples at 35 °C, 45 °C and 55 °C

Fig. 4 represents the desorption isotherms of five particle size coal samples at 35 °C, 45 °C and 55 °C respectively. The desorption hysteresis of CO₂ sorption in coals at each temperature is clear and the desorption isotherms lie above the adsorption isotherms. The desorption isotherm is inconsistent with coal particle size. However, it is clear that at each temperature level, the desorption hysteresis of the 150 μm size in Bomb 1G was relatively smaller than that of the other larger particle sizes. This is because powdered coal has a smaller amount of coal matrix. Also, higher temperatures caused a reduction in the degree of desorption hysteresis.

According to Harpalani et al. [2], the desorption hysteresis on coal or any adsorbent may occur due to two different reasons, which are the changes in the adsorbent properties/structures and/or the capillary condensation in the adsorbent micropores. Busch et al. [1] observed significantly positive deviations for CO₂ desorption curves, attributed to a metastable sorbent-sorbate system, which prevents the release of gas to the extent corresponding to the thermodynamically equilibrium value with decrease in pressure during desorption. This was also confirmed by Ozdemir et al. [16], where the positive deviation of CO₂ desorption was attributed to the swelling of the coal matrix. Shrinkage/swelling of coal matrix is believed to be associated with the desorption/adsorption process.

Fig. 3. CO₂ adsorption isotherm in different coal particle sizes, (a) 35 °C, (b) 45 °C, (c) 55 °C.
4. Application of coal surface free energy

4.1. Theory of coal surface free energy

The theory of coal surface free energy has been studied for years by several researchers [10, 17], and according to surface chemistry theory, when CO$_2$ is adsorbed on the coal surface, the concentration of CO$_2$ gas on the surface area of coal is larger than the concentration in the coal structure, this difference is called the surface excess $\Gamma$:

$$\Gamma = \frac{V}{V_0S}$$  \hspace{1cm} (1)

Where $\Gamma$ is the surface excess (mol/m$^2$), $V$ is adsorbed volume (L), $V_0$ is molar volume of gas, 22.4 L/mol at standard condition and $S$ is the specific surface area. When the coal adsorbs the gas, the coal surface tension ($\gamma$) will decrease. $\gamma$ can be calculated from Gibbs equation:

$$-d\gamma = RT\Gamma d(ln p)$$  \hspace{1cm} (2)
Where $\gamma$ is surface tension (J/m$^2$), $R$ is the universal gas constant (8.3143 J/mol·K), $T$ is the absolute temperature (K) and $p$ is gas pressure (kPa). So combining Eq. (3) and Eq. (4) and by integrating the pressure from 0 to $p$, then the reduced value of surface tension can be calculated:

$$\Delta \gamma = \gamma_0 - \gamma = \frac{RT}{V_0 S} \int_0^p \frac{pV}{p} dp$$  \hspace{1cm} (5)

Where $\Delta \gamma$ is the reduced value of surface tension (J/m$^2$), $\gamma_0$ is surface tension at vacuumed condition (J/m$^2$) and $\gamma$ is surface tension after coal adsorbed gas (J/m$^2$). The Langmuir module used to calculate the adsorbed volume $V$ is given by:

$$V = \frac{pV_L}{p + P_L}$$ \hspace{1cm} (6)

Where $V_L$ is Langmuir volume (cc/g) and $P_L$ is Langmuir pressure (kPa). Then subtitling for adsorbed volume $V$ from Eq. (7) into Eq. (8), the reduced value of surface tension ($\Delta \gamma$) can be simplified as:

$$\Delta \gamma = \frac{RT}{V_0 S} \int_0^p \frac{V_L}{p + P_L} dp = \frac{V_L RT}{V_0 S} \ln(1 + \frac{P}{P_L})$$ \hspace{1cm} (9)

From Eq. (10), it can be concluded that the reduced value of surface tension ($\Delta \gamma$) can be determined from the gas adsorbed volume, coal surface structure, sorption system temperature and gas pressure. According to surface chemistry theory, the sorption capacity is determined by the reduced value of surface tension, the larger the reduced value of surface tension, the stronger will be the sorption capacity.

4.2. Analysis of the reduced value of surface tension

In order to calculate the reduced value of surface tension ($\Delta \gamma$), the Langmuir volume $V_L$ and Langmuir pressure $P_L$ need to be calculated first. As shown in the Langmuir equation (Eq. (11)), the inverse of the slope of the Langmuir plot provided the Langmuir volume ($V_L$). The product of the Langmuir volume within the Y-intercept gave the Langmuir pressure ($P_L$). $V_L$ is the maximum monolayer capacity and when the adsorbed volume is half of the Langmuir volume, the pressure value is referred to as the Langmuir pressure $P_L$.

$$\frac{P}{V} = \frac{1}{V_L} \times \frac{1}{P + \frac{P_L}{V_L}}$$ \hspace{1cm} (12)

With calculation result of Langmuir volume ($V_L$) and Langmuir pressure ($P_L$) for each of the isotherm, the reduced value of surface tension ($\Delta \gamma$) can be calculated by Eq. (13).

In this study, the 54 mm core sample is taken as an example, Fig. 5 (a) shows the CO$_2$ surface free energy calculation result in terms of different temperature in the adsorption process, for each temperature, the reduced value of surface tension increases with the increasing pressure steps, according to the surface chemistry theory, it indicates that the coal adsorption capacity should also increase with the increasing pressure step, and this is confirmed by the experimental adsorption isotherm results. At the same pressure point, the reduced value of surface tension is decreased with
increasing temperature steps of 35 °C, 45 °C and 55 °C, which is confirmed by the adsorption isotherm shown in Fig. 5 (b).

Fig. 5. CO$_2$ surface free energy in terms of different temperature, (a) surface free energy calculation, (b) adsorption isotherm.

Fig. 6 (a) shows the CO$_2$ surface free energy calculation results in terms of adsorption and desorption for the 54 mm core sample at 35 °C, the same trend shown as adsorption surface tension curve, in the desorption process, the reduced value of surface tension also keep increasing with the increasing pressure steps, another finding is that at the same pressure point, the reduced value of surface tension of adsorption is relatively smaller than that of desorption which is also confirmed by the experiment adsorption isotherm result shown in Fig. 6 (b).

Fig. 6. CO$_2$ surface free energy in terms of adsorption and desorption, (a) surface free energy, (b) adsorption isotherm.

5. Conclusion

Higher temperatures reduce the CO$_2$ sorption capacity of coal for different particle sizes, and for each temperature level of 35 °C, 45 °C and 55 °C, there is no clear relationship between the CO$_2$ sorption capacity and coal particle size.

The CO$_2$ sorption rate for all the five samples is consistent with their particle size, particularly during the early stage of sorption, that is the finest sample size achieves the quickest sorption rate
and hence reduces the sorption duration for all the temperature conditions. This clearly indicates that larger coal surface area attracts faster CO$_2$ adsorption.

The adsorbed volume of CO$_2$ decreases with increasing temperature. Also it was found that increased temperature reduces or minimises the influence of particle size on gas sorption.

At each temperature level the desorption hysteresis of the 150 μm size was found to be smaller than the larger particle sizes. The degree of desorption hysteresis is reduced at higher temperatures.

Based on the principle of surface chemistry, the method of calculating coal surface energy with sorption parameters was used and it is found that the theory of coal surface free energy can be used to explain the coal sorption characteristics with CO$_2$ at higher temperatures.

The calculation results showed that the reduced value of surface tension parameter decreased with increasing temperature. Also the reduced value of surface tension parameter of adsorption is relatively smaller than desorption.

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