Implications of carbon dioxide sorption kinetics of low rank coal

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Abstract. This study appraises the dynamic of porosity and permeability measurement of the coal for reservoir modelling during gas production. Known as one of the main target areas for coalbed methane (CBM) production and potentially in integrating testing methodology, these measurements were carried out on low rank coals. During the testing, the pore pressure was varied at each pressure in stepwise with the adsorption equilibration. The gas content of the core sample was estimated until equilibration of the system and the sample of swelling in response to adsorption was measured. By employing newly achieved measurements, CT scan and acoustic emission wave methods, this study determines the porosity and permeability evolution which acts an important role in the dynamic changes in CO$_2$ sorption kinetics of coal. Permeability can be calculated by applying a pressure difference between both end sides of inlet-outlet of a certain direction according to Darcy’s law. While the Kozeny-Carman is an empirical equation influenced by several parameters such as total porosity, specific surface area, pore shape, tortuosity, and porosity to determine the permeability. By merging both approaches, empirical and laboratory method, the sorption kinetics of coals and other controlling factors are also counteracted.

1. Introduction
Coal is a highly heterogeneous porous medium comprises micropores (<2 nm), mesopores (between 2 and 50 nm), macropores (>50 nm) and natural fractures formed during coalification [1, 2]. In literature, coalbed is characterised by a dual-continuum system which comprised porous coal matrix and cleats (fractures) [3, 4]. Porous coal matrix is the primary medium for gas storage in coalbeds and accounts for up to 95-98% of gas storage [5]. Storage in the coal matrix is performed via two primary mechanisms. With natural gas production (CBM) and carbon dioxide (CO$_2$) or other gases storage in coalbeds, complex interactions with varying stress state and sorption phenomena are influenced and affect the transport and sorptive properties of coal. This consequently affects production and/or injectivity rates. Therefore, understanding the mechanisms of the dynamic evolution of sorption, flow, transportation, rock mechanics, porosity and permeability are of fundamental importance for CBM/ECBM recovery [3].
2. Methodology

2.1 CT Scan Tomography

Darcy’s law and the Kozeny-Carman equation are the most utilized calculations in valuing permeability. In order to find the correlation between the empirical calculations and laboratory measurements, digital image obtained by micro computed tomography (CT) scan is used to calculate the porosity and permeability of coal A2 and coal B1 samples in two conditions, before and after CO₂ saturations.

Cleat porosity reflects the number of pore, which size is bigger than one pixel. The image-based CT scan investigation (figure 1) shows that the cleat porosity of Coal A2 decreased dramatically from 6.7 % to 3.3 %, and for sample Coal B1 the reduction was very small, from 4 % to 3.6 %. While the cleat permeability of Coal A2 decreased affectedly from 369 mD to 91 mD, cleat permeability of Coal B1 decreased from 112 mD to 48 mD. Out of total 4 samples namely A1, A2, B1 and B2, only two samples were used in CT scan test due to samples limitation.

\[ k_{\text{cleat}} = 33.30(\phi_{\text{total}}) - 38.26 \] (1)

Figure 1. 3D image of coal A2 based CT image before and after CO₂ saturation.

2.2. Acoustic Emission Test

Acoustic emission is selected as an alternative tool to experiment the mechanism transpired between the coal structure between both conditions, in unsaturated and CO₂ saturated conditions, concerned primarily with processes associated with CO₂ transportation processes in microporous solids, that are governed by bulk diffusion, Knudsen diffusion, or surface diffusion subject to the feature size, shape and geometric arrangement of pores and matrix blocks [6, 7].

In order to consider the dual porosity of coal gas movement, three processes to be considered are: 1) gas desorption from internal micropore surfaces in coal matrix; 2) diffusion of gas through the coal matrix governed by concentration gradient; and 3) laminar Darcy’s flow through cleats that is provided by permeability [8]. Due to limitations of samples, cleat permeability calculations used equation 1.
where \( k_{\text{cleat}} \) is cleat permeability value and \( \phi_{\text{total}} \) is total porosity fraction. Cleat porosity (\( \phi_{\text{cleat}} \)) value was obtained by using inversion of equation 2 and the micro pore value was assumed by reducing total porosity with cleat porosity.

\[
k_{\text{cleat}} = 451.8 \ln(\phi_{\text{cleat}}) - 493.1
\]  

By comparing both before and after CO\(_2\) saturation, figure 2 shows the average values of cleat porosity, micro porosity and cleat permeability on each coalbed that are foreseeable to understand the sorption kinetics effects on the dynamic changes of rock physic of low rank coals (figure 2) [7].

3. Result

Figure 2 shows that micro porosity of coal A1, coal A2 and coal B2 decreased after CO\(_2\) saturated. Meanwhile, Coal A2 had a significant reduction after CO\(_2\) injection from 5.3 % to 1.9 %. Swelling process occurred while some gases adsorb into the micropore. Configuration of porosity and permeability evolution describe that Coal A2 had the largest swelling capacity and it is proven with the highest CO\(_2\) adsorption volume based on adsorption test. In contrast, micropore for Coal B1 raised after CO\(_2\) injection. Perhaps limiting the swelling process that happened due to its brittleness, or semi – deformed body mass as once it has reached a limit of equilibrium adsorption pressure while some deformation (crack / damage) were created during the adsorption. Some gases might be released back and filled into cleat pore as a compressional free gas, consequently cleat permeability has a significant reduction [1].

By using the approach of pore pressure buildup during CO\(_2\) injection process, new equations were (Equation 1 and 2) proposed to calculate permeability changes based on experimental data obtained from this study. The recap of changes in permeability values based on the acoustic emission test can be seen in figure 2. The initial permeability condition (\( k_o \)) was taken based on the permeability value under unsaturated CO\(_2\) conditions in 1 atm (101 kPa), and the permeability change values (\( k \)) were taken under different CO\(_2\) injection pressure test at 2, 4, 6, 8 and 10 MPa.

Summary of average porosity and permeability change (figure 2) indicates Coal B1 has decreased the most and coal A2 is the least (figure 3). This explains that Coal B1 has the lowest compressibility factor upon the rising of pore pressure during the CO\(_2\) injection.
Figure 3. Changes of permeability due to increase in pore pressure.

4. Discussion

4.1 Volume change during CO$_2$ transport
 Schroeder et. al. [8] has proposed an expression, which incorporates the effect of swelling and shrinkage of the coal on the CO$_2$ adsorption isotherm. Its generalized form is given in Equation 3,

$$ n_{\text{exp}} = n_{\text{ads}} + k \left( \frac{p}{\varepsilon} \right) $$

where $n_{\text{exp}}$ is the amount of adsorbed gas calculated from the $\Delta P$ determined experimentally when the void volume of the sample chamber ($V_v$) is considered constant at the value estimated by the gases expansion method, $n_{\text{ads}}$ is the amount of gas actually adsorbed on the coal sample, and $k$ is a constant, which includes the effect of the volume change in the sample cell.

4.2 CO$_2$ sorption kinetics
 The CO$_2$ transportation of gas molecule in the coal by the repeated pre-exposure to high pressure (>7.5 MPa) as CO$_2$ will cause additional changes in coal structure as shown in table 1 and magnitude (%) of all three stages illustrated in figure 4.

| Pressure (Mpa) | Instant equilibrium | Initial relaxation | Final relaxation |
|----------------|---------------------|--------------------|-----------------|
|                | $\tau_0$ (h)        | Magnitude (%)      | Magnitude (%)   | Magnitude (%)   |
| 0.4            | 0.03                | 53                 | 0.08            | 45              | 12.2           | 2               |
| 1.2            | 0.03                | 11                 | 0.08            | 84              | 23.0           | 5               |
| 1.9            | 0.03                | 69                 | 0.09            | 64              | 3.4            | 33              |
| 2.8            | 0.03                | 65                 | 0.17            | 35              | 0              | 0               |
| 4.0            | 0.03                | 100                | 0.17            | 35              | 0              | 0               |
| 5.1            | 0                  | 0                  | 0.17            | 35              | 0              | 0               |

Table 1. CO$_2$ sorption kinetics on coal (modified after [7])
Figure 4. CO$_2$ sorption kinetics/ swelling by final relaxation magnitude (modified by Romanov and Soong [7])

Swelling at 1.5 – 3 MPa is shown by negative increment [7]. The negative slope of cumulative excess sorption as a function of CO$_2$, relaxation during the first 1–2 min of every pressure, shows that unreachable volume of the coal core curty increased by 2% at 4 MPa (figure 5). An alternative approach is proposed to estimate the swelling region of CO$_2$ adsorption isotherm following [8] ideas. By referring to table 1 and figure 4, CO$_2$ adsorption isotherm of the low rank coals are calculated based on AE experimental value.

Coal A2 and Coal B1 that are set with two conditions, unsaturated (term used before CO$_2$) and CO$_2$ saturated (term used after CO$_2$) are aimed to identify the acoustic emission (AE) changes in relation with uniaxial stress. Expression formulas are generated to estimate the AE value at CO$_2$ adsorption pressure measurement, which is expressed below based on the AE data.

\[ AE = 762.1 \ln(P) - 859.8 \]  \hspace{1cm} (4) \text{ for unsaturated coal A2}
\[ AE = 600.3 \ln(P) + 301.5 \]  \hspace{1cm} (5) \text{ for saturated coal A2}
\[ AE = 638.3 \ln(P) + 1034 \]  \hspace{1cm} (6) \text{ for unsaturated B1}
\[ AE = 621.8 \ln(P) - 218.6 \]  \hspace{1cm} (7) \text{ for saturated B1}

where AE is the acoustic emission count and $P$ is adsorption pressure test. Figure 5 is the CO$_2$ transportation by AE counting.

The relationship between AE value and CO$_2$ adsorption capacity for unsaturated samples is shown in figure 6. Equation 8 and 9 below are used to calculate the CO$_2$ adsorption capacity value for coal A2 and B1.

\[ V_{ads} = 9E - 22 \text{ AE}^{5.603} \]  \hspace{1cm} (8)
\[ V_{ads} = 8E - 28 \text{ AE}^{7.037} \]  \hspace{1cm} (9)

where $V_{ads}$ is the CO$_2$ adsorption volume and AE is acoustic emission count.
By using equations 5, 7, 8, and equation 9, the calculation results of CO\textsubscript{2} adsorption capacity for saturated coal A2 and coal B1 is shown in figure 8. It demonstrates that Coal A2 larger swelling and CO\textsubscript{2} volume capacity than Coal B1, following isotherm interval between blue line and yellow line.

In addition, Coal A2 has higher accessible volume of excess sorption capacity than coal B1. It is noted that CO\textsubscript{2} injection treatment in coal A2 is not fully saturated. Meanwhile, during CO\textsubscript{2} injection, swelling occurred with increment in matrix volume dramatically even at low injection pressure. Based on the isotherm proposed in figure 5, there is a peak swelling region at low coal rank represented by Coal A2 that is shown by the negative increment of delta adsorption volume (blue transparent block). Peak of matrix swelling of coal A2 sample occurred at 1.8 – 3.3 MPa. This result is closely with swelling at 1.5 – 3 MPa seen as negative increments in excess sorption [7] in table 2 and figure 4 above.
During the CO₂ injection, swelling occurred with very low reduction in matrix volume of coal B1. Coal B1 has a limit of adsorption capacity after CO₂ saturated, proven by previous experiment that coal B1 has the lowest CO₂ Langmuir isotherm (table 1, figure 7).

![Adsorption Isotherm Change of Coal A2](image1)

![Adsorption Isotherm Change of Coal B1](image2)

**Figure 7.** CO₂ adsorption due to volume change and swelling.

5. Conclusion
The sorption kinetics affecting changes in the rock physics of coal. The evolution of matrix porosity has controlled primarily by compressional stress during deposition and the coal content, portion of inorganic volatile matter. Meanwhile, the permeability evolution has been controlled by complex procedure such as swelling that is derived by two cementation factors such as ash content and coal moisture themselves.

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