Pore structure change due to mineral reaction in CO₂ enhanced coal bed methane recovery

Shasha Gao 1* & Yanbin Wang 2

1 School of Earth Science and Resources, Chang’an University, Xi’an 710064, Shaanxi, China
2 College of Geoscience and Surveying Engineering, China University of Mining and Technology (Beijing), Beijing 100083, China

*E.mail: gs8636@126.com

Received 13 October 2016; revised 13 December 2016

In order to study pore structure change formed by mineral reaction, the reaction between CO₂, H₂O and coal was tested, and change of permeability and porosity of samples was carried out. The change of pore structure which make from mineral reaction is controlled by the content of minerals, the contact relationship between mineral and pores, and the pore structure itself. It shows that the permeability and porosity of coal beds are mainly changed after the reaction because of the dissolution reaction and forming precipitations. Carbonate minerals can react with CO₂ solution and dissolve in it, but Chlorite and orthoclase react with CO₂ solution, and the reaction create new mineral. According to the experimental results, three different models were established. The result shows that type L-L pore structure should not be used to inject CO₂ to enhance the recovery, and the type H-H which has high content of carbonate minerals are the best choice.

Keywords: Pore Structure, Mineral reaction, CO₂-ECBM, Coal, Permeability

Introduction

Coal bed methane has become an important energy resource in recent years, but porosity and permeability of coal bed is usually small. It found that the adsorption capacity of CO₂ in coal is bigger than CH₄, and it leads to a new techniquenamed CO₂ enhanced coal bed methane recovery (CO₂-ECBM). This methodhas potential to reduce the emission of CO₂ and increase the coal bed methane production.

CO₂-ECBM projects are developed all over the world with a main focus on countries like Australia, Canada, China and the United States, and many research and exploration is carry out in many further regions like Japan, Europe, Ukraine, or Indonesia. The earliest exploration of injected CO₂ enhanced coal bed methane was in the San Juan basin since 1995 that is the only large-scale ECBM field pilot using CO₂ injection. The result shows that the production of methane was enhanced about 15 percent. In addition, multi-well ECBM pilot with the Ardley coal was set up at Alders Flat, Alberta, Canada. The micro-pilot test with a single well and multi-well CO₂ injection tests at Yubari in northern Japan. CO₂-ECBM pilot in the Upper Silesian basin in Poland. A two-well demonstration test was performed in the Upper Silesian Basin, Poland within the RECPOL and MOVECBM projects funded by the European Union. A single well CO₂-micro-pilot test was carried out at south Qinshui, Shanxi, China. And then a multi-well pilot was performed, with design of an inverted 5-spot pattern around the injection well. Research about effective CO₂ storage capacity and model of enhanced coalbed methane was carried out in many countries, like New Zealand, Scotlandand India. The difficult degree of coal bed methane recovery mostly depends on the permeability of coal bed. During CO₂ injected into coal bed, the permeability of coal bed will be changed which is controlled by the pore structure change. In addition, the change of pore structure after CO₂ injected into coal bed should be studied.

The main component in coal inorganic materials, and the other small part are crystallization mineral phase, amorphous mineral phases. Mineral matter is composed by clay minerals, oxide, carbonate minerals and sulphate mineral mainly. Clay minerals are most frequent minerals in coal, and the main types are kaolinite, illite, chlorite and montmorillonite. It also contains different content of quartz, feldspar, calcite, dolomite in coal. These minerals occur as discrete flakes, grains or aggregates in a number of modes, and these minerals often interbedded with organic matter or filling in fracture frequently.
Carbonate minerals can react with CO₂ solution and dissolve in it, like Calcite (Eq.1), Magnesite, Siderite and Dolomite (Eq.2), etc. On the basis of this reaction, calcium ion and magnesium ion in solution will increase, and the content of carbonate minerals in coal will decrease. The pore structure will change after the reaction, and it turns out that the pores and fractures became larger after the dissolution reaction.

\[
\begin{align*}
\text{CO}_2 + \text{H}_2\text{O} + \text{CaCO}_3 & \rightleftharpoons \text{Ca}^{2+} + 2\text{HCO}_3^- & \ldots (1) \\
2\text{CO}_2 + 2\text{H}_2\text{O} + \text{CaMg(CO}_3)_2 & \rightleftharpoons \text{Ca}^{2+} + \text{Mg}^{2+} + 4\text{HCO}_3^- & \ldots (2)
\end{align*}
\]

Most clay minerals have high stability in acid solution, like kaolinite, illite and montmorillonite. But chlorite (Eq.3) can react with CO₂ solution, and the reaction creates new minerals like kaolinite and quartz. The minerals are consumed in this reaction, and new pores will be created in coal beds. Otherwise, some new precipitations, which are created by the reaction, will block the pores and fractures. Permeability and porosity are affected by two factors: The tiny precipitations, which can move out of the micro pores, will make the pores bigger; and if the precipitations block in the channels that will decrease the porosity.

\[
[\text{Fe/Mg}]_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8 + 5\text{CaCO}_3 + 5\text{CO}_2 \rightleftharpoons 5\text{Ca}^{2+} + 5[\text{Fe/Mg}]^{2+} + 10\text{CO}_3^{2-} + \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + \text{SiO}_2 + 2\text{H}_2\text{O} \ldots (3)
\]

Another mineral which can react with CO₂ solution is orthoclase (Eq.4). In this reaction, potassium matters resolve in the solution and become ions, and the salic matters turn to precipitations as kaolinite. This reaction is similar to chlorite which has two different effects to porosity. And it depends on the position where the minerals are. This problem will be analyzed in the next chapter.

\[
2\text{KalSi}_3\text{O}_8 + 2\text{CO}_2 + 3\text{H}_2\text{O} \rightleftharpoons 2\text{K}^+ + 2\text{HCO}_3^- + 4\text{SiO}_2 + \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \ldots (4)
\]

### Materials and Methods

In order to find out the change of pore structure in different coal beds, the reaction between CO₂, H₂O and coal samples was tested. In this experiment, CO₂ solution reacted with different coal samples, and the change of permeability and porosity was observed. The method is that the property and permeability was tested before reaction, by contrast with the values after reaction, and the differences and outcomes were found out. By analysis, the relationship between mineral composition and pore structure change will be established.

The experiment procedure was divided into four steps. Step 1, make the coal samples into column with size of 25mm*(25-50) mm, dry the coal samples, preparation of CO₂ solution with dry ice and groundwater. Step 2, test the initial permeability and porosity by using AP-608, and observe the pore structure using SEM. Step 3, put the coal samples CO₂ solution into respectively under room temperature and atmospheric pressure for one month. Step 4, dry the coal samples, test the change of permeability and porosity, and observe the pore structure change by using SEM.

Coal samples were collected from five different places, Sihe, Yuwu, Changcun, Shaqu, Tunliu (Table 1). The initial porosity and permeability of these samples were tested by percolation apparatus under overburden pressure, and the coal samples were
divided into three types (Table 2). The samples that have higher than 2% porosity and $1 \times 10^{-3} \mu m^2$ permeability were classified into type H-H. Moreover, the samples that have less than 2% porosity and $1 \times 10^{-3} \mu m^2$ permeability were type L-L. In addition, the residual samples were type H-L.

In order to find out the pore structure change formed by mineral reaction, the mineral composition of different samples came from different place was tested by X-ray diffraction analysis (Table 3). Because of the heterogeneity of coal beds, several samples were tested at the same time, and the average value were used.

**Results**

The results show that the porosity and permeability of different type coal samples show different change characters, and the change of same type samples were presented as different laws. These changes are affected by pore structure of themselves as important as reaction of minerals in coal.

**Type H-H**

Type H-H samples came from three different place, and the mineral composition is different from each other. Coal samples of type H-H exhibit a good pore structure, which have high porosity and good connectivity. After reaction, the change of permeability divided into two different forms (Figure 1).

Permeability value of HH1, HH2 and HH3 increases in different degree, which means the mineral reaction make many pores connected to each other. The total mineral content of coal samples are different, and the value is about 2-14% (Table 1). The minerals in coal samples that can react with solution are calcite, dolomite and orthoclase. The content of these minerals in HH1’s total mineral content is about 11%, and in HH2 and HH3 is about 13% (Table 3). Two value of sample HH4 are decreased, which because of the mineral reaction. The mineral composition of HH4 shows that content of carbonate minerals is about 3.4%, the mineral precipitation reaction is bigger than dissolution reaction. It means that the precipitation occupy the original pores and fractures. The result shows that the improvement of permeability value in type H-H is controlled by the mineral composition.

---

<table>
<thead>
<tr>
<th>Sample number†</th>
<th>Porosity (%)</th>
<th>Permeability ($\times 10^{-3} \mu m^2$)</th>
<th>Classification</th>
<th>Serial number</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>3.40</td>
<td>9.83</td>
<td>H-H</td>
<td>HH1</td>
</tr>
<tr>
<td>S2</td>
<td>2.00</td>
<td>1.30</td>
<td>HH2</td>
<td></td>
</tr>
<tr>
<td>S3</td>
<td>3.90</td>
<td>1.42</td>
<td>HH3</td>
<td></td>
</tr>
<tr>
<td>Y4</td>
<td>3.95</td>
<td>3.20</td>
<td>HH4</td>
<td></td>
</tr>
<tr>
<td>S5</td>
<td>3.20</td>
<td>0.35</td>
<td>HL1</td>
<td></td>
</tr>
<tr>
<td>Y6</td>
<td>3.10</td>
<td>0.17</td>
<td>HL2</td>
<td></td>
</tr>
<tr>
<td>C7</td>
<td>2.70</td>
<td>0.0066</td>
<td>H-L</td>
<td></td>
</tr>
<tr>
<td>C8</td>
<td>3.10</td>
<td>0.0073</td>
<td>HL3</td>
<td></td>
</tr>
<tr>
<td>C9</td>
<td>2.20</td>
<td>0.0042</td>
<td>HL4</td>
<td></td>
</tr>
<tr>
<td>Q10</td>
<td>0.11</td>
<td>0.90</td>
<td>HL5</td>
<td></td>
</tr>
<tr>
<td>Q11</td>
<td>0.08</td>
<td>0.45</td>
<td>LL1</td>
<td></td>
</tr>
<tr>
<td>Q12</td>
<td>0.03</td>
<td>0.70</td>
<td>LL2</td>
<td></td>
</tr>
</tbody>
</table>

†Sample T1 from Tunliu; S2, S3 and S5 from Sihe; Y4, Y6 from Yuwu; C7, C8 and C9 from Changcun, Q10, Q11 and Q12 from Shaqu.

---

<table>
<thead>
<tr>
<th>Number</th>
<th>Clay</th>
<th>Quartz</th>
<th>Orthoclase</th>
<th>Calcite</th>
<th>Dolomite</th>
<th>Hematite</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>85.8</td>
<td>3.2</td>
<td>3.5</td>
<td>4.0</td>
<td>3.5</td>
<td>0.0</td>
</tr>
<tr>
<td>S</td>
<td>78</td>
<td>9</td>
<td>1</td>
<td>5.0</td>
<td>7</td>
<td>0.0</td>
</tr>
<tr>
<td>Y</td>
<td>87.3</td>
<td>4.1</td>
<td>5.2</td>
<td>2</td>
<td>1.4</td>
<td>0.0</td>
</tr>
<tr>
<td>C</td>
<td>97.4</td>
<td>1.6</td>
<td>1.6</td>
<td>0.4</td>
<td>0.4</td>
<td>4</td>
</tr>
<tr>
<td>Q</td>
<td>85</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>4</td>
</tr>
</tbody>
</table>

---

Figure 1 — Porosity and permeability change of type H-H coal samples
Type H-L

The samples came from different places which have similar initial physical properties value and different minerals composition. Different mineral reaction makes the change of pore structure shows different. Because of the bed pore connectivity of sample HL1, the initial porosity value of sample HL1 is 3.2%, but the permeability is $0.35 \times 10^{-3} \mu m^2$. After reaction, the permeability value became $3.06 \times 10^{-3} \mu m^2$. The permeability improvement is the best in all samples, which due to the mineral reaction make pore connects to each other. The initial value of sample HL2 is similar with HL1. But the result shows that porosity and permeability values were respectively increased by 0.1% and $0.04 \times 10^{-3} \mu m^2$. (Figure 2)

The initial character of HL3, HL4 and HL5 is that the porosity lies between 2-3.5% and permeability is less than $0.001 \times 10^{-3} \mu m^2$. It means that the connectivity of pores is bed which can hinder the circulation of fluid. The value after the reaction shows that the change of porosity is less than 0.3%, and permeability didn’t change basically. That is mainly due to the bed connectivity of pore structure.

Type L-L

The initial porosity and permeability of these samples is very small, and the change after reaction is little, and the change without rules. Change value of porosity is little than 0.1%, and permeability is little than $0.05 \times 10^{-3} \mu m^2$ (Table 4). That means the change of pore structure formed by mineral reaction is very small, and it was attributed to the pore structure.

Discussions

The amount of minerals which react with solution and the amount of solution which can enter into pore are controlled by initial porosity and permeability of coal bed. The reaction between minerals in coal and the CO$_2$ solution can change the pore structure. The dissolution reaction can enlarge the initial pores, and the precipitation reaction and clay mineral’s expansion can block the pores. According to the result of experiment, the relationship between pore structure and mineral reaction is analyzed.

Type H-H pore structure

There are many pores and fractures in coal beds of type H-H, and the connectivity is better than other types (Figure 3). On one hand, the types and content of minerals in coal beds is different from each other. On the other hand, the reaction between minerals and CO$_2$ solution is different. The reaction products will change the size and forms of pores or throats. Therefore, after reacting with CO$_2$ solution, the size and forms of pore structure will be reformed to two different shapes. If the coal beds have high content of carbonate minerals, and these minerals are filled in main fracture, the porosity and permeability will be improved after the reaction (Figure 3. A). But if there are little content of carbonate minerals, the precipitation created by reaction will reduce the porosity (Figure 3. B), and which can explain the permeability value increase of sample HH4.

Table 4 — Change of porosity and permeability of type L-L coal samples

<table>
<thead>
<tr>
<th>Sample number</th>
<th>LL1</th>
<th>LL2</th>
<th>LL3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity (%)</td>
<td>Initial value</td>
<td>0.11</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>After reaction</td>
<td>0.19</td>
<td>0.14</td>
</tr>
<tr>
<td>Permeability</td>
<td>Initial value</td>
<td>$0.90 \times 10^{-3}$</td>
<td>$0.45 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>After reaction</td>
<td>$0.95 \times 10^{-3}$</td>
<td>$0.40 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
H-L are not connected. Therefore, this coal bed has the characteristics that high porosity and low permeability (Figure 4.). Two different shapes will turned up after reaction. Just like type H-H, if carbonate minerals are filled in main fracture, the pores and fractures will be communicated. The permeability will be improved after the reaction (Figure 4. A). But if precipitation created by minerals reaction stay on the pores and the channels, the porosity and permeability will decreased (Figure 4. B).

**Type L-L pore structure**

The initial value of porosity and permeability is very small in this type. In type L-L coal beds, there are little pores and fractures, and the connectivity of pores is bed. Solution is difficult to enter into fractures, and reaction between minerals and solution is rarely. In addition, it difficult to change the pore structure by mineral structure (Figure 5).

**Acknowledgments**

This research is supported by Natural Science Foundation of China, which named Kinetics of CO₂-H₂O-Coal Reaction and Quantitative Mineral Sequestration Research of Carbon Dioxide Storage in Deep Coal bed (41502153). In addition, the paper supported by the Fundamental Research Funds for the Central Universities (300102278101, 300102278114, 300102278202).

**References**

23 Yang, Y., Study on early warning system of coal and gas outburst driving face in coal road in sihe mine. Liaoning technical university, China, 2009, pp. 38.