Changes in pore structure of shale associated with supercritical carbon dioxide exposure

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Abstract: Pore structure changing of shale under the effect of supercritical carbon dioxide (\textit{ScCO}_2) is one of the key issues that affect the long-term production of shale gas and CO\textsubscript{2} storage significantly. Two type shale samples from Fuling and Changning area of Sichuan basin were exposed to carbon dioxide at a condition of 16MPa and 40°C for 5 days, low temperature nitrogen adsorption-desorption method and FHH(Frenkel-Halsey-Hill) model were used to characterize the pore structure of shale before and after \textit{ScCO}_2 treatment. The fractal dimension D based on the nitrogen adsorption data was used to represent the irregular pore surface and complexity pore structure in shale. The experimental results indicate that \textit{ScCO}_2-shale reaction mainly affects the micro- and mesopores, which led to decrease of micro- and mesopores in the \textit{ScCO}_2 treated sample. As a result, the surface area, pore volume, pore size distribution and average pore size are changed largely. Fractal analysis is observed. The \textit{ScCO}_2-shale reaction led to decrease fractal dimensions in the \textit{ScCO}_2 treated shale samples. It is to say that the pore surface wall of \textit{ScCO}_2 treated shale become smoother than before.

Keywords: shale gas; supercritical carbon dioxide; pore structure; fractal analysis

1 Introduction

Data from U.S. Energy Information Administration(EIA) in 2014 show that North American shale gas production up to 350×10\textsuperscript{9}m\textsuperscript{3} by 2013, which the United States more than 320×10\textsuperscript{9}m\textsuperscript{3}, and Canada is 30×10\textsuperscript{9}m\textsuperscript{3}(EIA, 2014). China’s natural gas demand growing increasingly and external dependence is also growing, which threat energy structural safety of China seriously. China has abundant shale gas resources, Ministry of Land and Resources’ forecast report in 2014 shows geological reserves of shale gas is 134.4×10\textsuperscript{12}m\textsuperscript{3}, technically recoverable resource is 25.08×10\textsuperscript{12}m\textsuperscript{3}(Zhang Da-wei et al., 2012). At present, the use of hydraulic fracturing technology in reservoir stimulation, because shale gas reservoir’s low porosity and permeability. Previous study indicated that hydraulic fracturing requires large amounts of water, and also cause some environment issues, in addition, hydraulic fracturing would induce irreversible harm on oil & gas reservoir, which directly related to the ultimate recovery of oil and gas field (Qian Bozhang et al., 2013). Vermont is the only state in US which prohibit hydraulic
fracturing technology to develop shale gas, in addition to related report shows that hydraulic fracturing will be prohibited in New York since 2015. Thus, we urgently need to find a new fracturing technology to replace hydraulic fracturing and mitigate environmental damage.

It has been reported, when temperature and pressure of CO₂ was more than 7.38 Mpa and 31.1℃, respectively, CO₂ will reach supercritical state(ScCO₂). ScCO₂ has special properties between gas and liquid, possessing low viscosity, easy to spread of gas and high density, high solubility characteristics of liquid. ScCO₂ fracturing shale gas formation shows a good application prospect, but instead of water as fracturing liquid in the future (Zhu, 2000; Wang et al., 2012). James (James et al., 2010) made contrastive analysis on the effect of ScCO₂ fracturing and hydraulic fracturing oil field reservoir by microseismic monitoring, the result shown at the same injection pressure and rate conditions, microseismic events generated by ScCO₂ and water has little difference, ScCO₂ fracturing can produce the same effect as hydraulic fracturing. Researches from Richa et al. suggested that after ScCO₂ injected into shale formation, in situ stress state would be changed, reservoir and cap-rock produced different cracks, resulting in some influence on permeability of reservoir and cap-rock (Richa et al., 2010; Hawkes et al., 2005; Streut et al., 2004). In China, CO₂ fracturing technology has achieved significant results in some conventional oil & gas field such as Sukri gas field and Daqing oil field (Xie et al., 2009; Ma et al., 2008).

ScCO₂ is a special non-aqueous fracturing fluid currently under consideration for use in shale gas reservoir reconstruction. CO₂ is part of a class of energized fluids or foams that have been gaining interest, particularly as the limitation with conventional fracturing fluid becomes more apparent (Gupta, 2011; Gupta, 1998). Nuttall(Nuttall et al., 2001) found that CO₂ has an adsorption capacity about 5 times greater than that of CH₄, similarly, Kang (Kang et al., 2010) shown the adsorption of CO₂ and CH₄ on Barnet shale samples, finding CO₂ to adsorb 5-10 times more than CH₄. ScCO₂ offers several significant advantages over water, key potential advantages for CO₂ include increased methane and hydrocarbon production due to miscibility with hydrocarbons, enhanced fracturing properties, enhanced desorption of CH₄ from organics present in the shale, and the reduction of injection and flow-back water. During CO₂ injection in deep shale formation, a series of chemical and physical phenomenon take place. Previous scholars proposed that ScCO₂ can perform similarly to organic solvent by swelling coals and changing their structure (Larsen et al., 1997).

In this paper, we examine the effects of ScCO₂ on shale pore structure using low temperature ni-
trogen adsorption-desorption method to investigate irreducible CO2 induced alterations of micro-, me-
so- and macropores, especially micropores and mesopores, because low temperature nitrogen adsorp-
tion-desorption experiment only can characterize the micro- and mesopores effectively. Moreover, we
used nitrogen adsorption data to calculate fractal dimension used to investigate the fractal characteris-
tics of shale pore system. Our work is to further the effort toward understanding changes in pore struc-
ture after ScCO2 treatment that may be significant for developing shale gas by ScCO2 in China in the
future.

2 Experimental section

2.1 Shale samples

The shale samples used in this experiment were collected from Fuling(FL) and Changning(CN)
formation, located in Sichuan Basin and Ordos Basin, respectively. Sichuan Basin presents a high po-
tential for Marine shale gas exploration and development in China. While some studies suggested that
there is a great development potential of Continental shale gas resources in Ordos Basin (Jiang et al.,
2014; Liu et al., 2013). The base properties of shale samples from Fuling and Changning are typically
shown in Table 1. All the collected samples were broken manually into smaller pieces (4-8mm) for low
temperature adsorption test and powders with a grain size of <150μm for XRD analysis or TOC con-
tent test. Due to relatively long experimental periods required for the ScCO2 treatment, shale samples
should be storage carefully to avoid oxidation and humidity effects. Samples were transported in a
small nitrogen sealed bag to minimize the storage changes.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>TOC/%</th>
<th>Ro/%</th>
<th>Mineral Content/%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Quartz</td>
</tr>
<tr>
<td>FL</td>
<td>2.7</td>
<td>2.4</td>
<td>43.2</td>
</tr>
<tr>
<td>CN</td>
<td>4.8</td>
<td>1.9</td>
<td>47.5</td>
</tr>
</tbody>
</table>

2.2 Apparatus and Methods

Shale is a typical complex porous media material with ultra-low porosity and complicated porous
system that is difficult to classify. The pore structure in terms of the pore size distribution and average
pore size plays a very important role in the exploration, development and evaluation of shale gas. There
are various measurements that can be used for characterizing complex pore structure of shale. Field
emission scanning electron microscopy, transmission electron microscopy, CT-scan can characterize the geometries of pore intuitively (Chalmers et al., 2012; Wei et al., 2013). Meanwhile, mercury injection, low pressure gas adsorption method, small angle neutron scattering can be used to investigate qualitative pore shapes, total pore volume and specific surface area (Ross and Bustin, 2007, 2009; Wu et al., 2013). In this study, we choose low pressure nitrogen adsorption analysis method to characterize the pore structure in shale.

The shale and ScCO₂ reaction was carried out in a high pressure (HP) sealed container that was specially designed to study the physical, chemical changes in shale as response to exposure to ScCO₂. The main component of apparatus is ISCO syringe pump and HP container. In addition to this, some fittings are needed (e.g., valves, vacuum pump and pressure gauges), all placed within a controlled temperature oil bath, as shown in Fig. 1. The CO₂ gas from a gas bottle, injected by an ISCO pump to the operation pressure to 16MPa, simultaneously, set temperature to 40°C (313K), CO₂ fluid will reach a supercritical state in the HP container. The reaction time was at least 5 days to ensure equilibrium.

Fig. 1. Schematic of system used for ScCO₂ treatment experiment. Every test should be vacuumed to avoid the influence of residual air.

The whole procedure involves two types of tests: ScCO₂ treatment and low temperature nitrogen adsorption-desorption measurement with and without ScCO₂ treatment. A selected sample was dried in an air oven at 90°C for at least 24 hours and then used for the N₂ adsorption-desorption experiments and then for ScCO₂ treatment. After treatment, the sample should be used for the N₂ adsorption-desorption experiments again (i.e. one sample before and after ScCO₂ treatment should be carried out N₂ adsorption-desorption experiment).

Low temperature adsorption-desorption measurements were conducted with ASAP 2020M Sur-
face Area Analyzer and Pore Size Analyzer of State Key Laboratory of Coal Mine Disaster Dynamics and Control following Chinese National Standard GB/T19587-2004 and GB/T21650.2-2008. N$_2$ adsorption-desorption isotherms were obtained under relative pressure (p/p$_0$) ranging of 0.01–0.0998 at 77K. Information on the specific surface area, total pore volume and pore size distribution can get from N$_2$ adsorption-desorption isotherms. We use BET (Brunauer-Emmett-Teller) equation from N$_2$ adsorption data under the p/p$_0$ ranging from 0.05 to 0.35 to calculate the specific surface area (Brunauer et al., 1938). Taking the single point adsorption at p/p$_0$=0.99 as the total volume. And pore size distributions were obtained by application of the BJH (Barrett-Joyner-Halenda) model from N$_2$ desorption isotherms (Barrett et al., 1951). According to the International Union of Pure and Applied Chemistry (IUPAC) classification (Rouquerol et al., 1994), based on the pore size, pores of materials are divided into three categories: micropore (pore size<2nm), mesopore (2nm<pore size<50nm) and macropore (pore size>50nm).

Fractal analysis was widely used for describing the pore structure of porous material in the past (Avnir and Jaroniec, 1989), and the quantitative evaluation of fractal geometry is to describe by fractal dimension D that is used as an index of structural complexity and surface roughness of the solid (Pfeifer and Avnir, 1983). In general, the fractal dimension D is vary from 2 to 3, and the lowest value 2 corresponds to perfectly smooth surface, however, the upper value 3 is corresponds an irregular and rough surface (Pfeifer and Avnir, 1983). Based on the N2 adsorption data, fractal dimension D can be calculated by the FHH (Frenkel-Halsey-Hill) model (Pfeifer and Avnir, 1983), which can be described as follows (Avnir and Jaroniec, 1989; Yao et al., 2008):

\[
\ln(V) = (D-3)\ln[\ln(p/p_0)] + \text{constant}
\]  

Where \( V \) is the adsorbed volume of N$_2$ at each equilibrium pressure \( p \); \( p_0 \) is the saturation vapor pressure; \( D \) is the fractal dimension. Therefore, according to the FHH model, there is a linear relationship between \( \ln(V) \) and \( \ln\ln(p_0/p) \), and fractal dimension value D can be derived by the slope of fitting curves.

3 Results and discussions

3.1 Low temperature N$_2$ adsorption-desorption isotherms

The adsorption-desorption isotherms for all shale samples are shown in Fig.2, which belong to the
type IV isotherm that with hysteresis loop according to IUPAC (Sing et al., 1985). This type of isotherm demonstrated that shale samples have diverse pore structure with micropore, mesopore and macropore (Sing et al., 1985). The isotherm of desorption branch at high relative pressure (p/p₀>0.40) is inconsistence with the adsorption due to the capillary condensation effect, resulting in a hysteresis loop (Gregg and Sing, 1982). However, the hysteresis loop is open at a low relative pressure (0<p/p₀<0.40) for some shale sample (Fig. 2b) but close for others (Fig. 2a, FL-1#; c, CN-1 and CN-1#; d, CN-2 and CN-2#). In previous study, the shape of hysteresis loop can be used to understand the morphology of pore shape in solid (Sing et al., 1985; Chalmers et al., 2012). According to the classification of IUPAC (Sing et al., 1985), the hysteresis loops of shales may be classified as type H2 (Fig. 2a, FL-1#; c, CN-1 and CN-1#; d, CN-2 and CN-2#) and H4 (Fig. 2a, FL1#; b, FL-2 and FL-2#). Type H2 hysteresis loop is associated with open pores that contain mainly ink-bottle shaped pores and a bit of cylinder pores or parallel plate pores (Sing et al., 1985; Yang et al., 2014). In contrast, type H4 is usually observed in slit shaped pores generated by layer structure (Sing et al., 1985; Chalmers et al., 2012; Yang et al., 2014).

![Fig. 2 Low temperature N₂ adsorption-desorption isotherms of all samples. (a, FL-1 and FL-1#; b, FL-2 and FL-2#; c, CN-1 and CN-1#; d, CN-2 and CN-2#)](image)

We can see from Fig. 2, the N₂ adsorbed amount of ScCO₂-treated sample is lower than the un-
treated. That is to say, the N2 adsorbed capacity of shale is weakened by ScCO2-treatment. There are a mainly reason about this issue: ScCO2 as a kind of organic solvents, which dissolved the part organic matter in shale and reduced the micro- and mesopores content of shale, because micro- and mesopores mainly developed in organic matter of shale. Similarly, the shape of N2 adsorption isotherm at low relative pressure (0<p/p0<0.10) can indicate micropore content in shale, the closer to the Y-axis, the more micropores. That is also supports the conclusion above.

3.2 Pore structure parameters and pore size distribution

The results of shales from low temperature N2 adsorption-desorption analysis before and after ScCO2 treatments are shown in Table 2, demonstrating that specific surface area and total pore volume of treated samples are less than before while the average pore size is increased. It is observed from Table 3 that the specific surface area and total pore volume of Fuling shale ScCO2-treated showed an average decrease of 22% and 15%, respectively, while the specific surface area and total pore volume of Changning shale ScCO2-treated showed an average decrease of 42% and 18%, respectively. Simultaneously, the average pore size of Fuling and Changning showed an average increase of 10% and 49%, respectively. As we can see from Table 4, micropore surface area and pore volume of Fuling shale showed average decrease of 35% and 21%, respectively, whereas the Changning shale ScCO2-treated showed average decrease of 75% and 78%, respectively. Compared to micropore, mesopore has minor changes associated with ScCO2 exposure. Due to the higher TOC and clay mineral contents of Changning shale, it shows strong sensitivity to ScCO2, because ScCO2 can produce dissolution effect and adsorbed caused swelling on shale.

Table 2 Pore structure parameters of shale samples from low temperature N2 adsorption-desorption isotherms.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Specific surface area (m²/g)</th>
<th>Total pore volume (cm³/g)</th>
<th>Average pore size (nm)</th>
<th>Sample No.</th>
<th>Specific surface area (m²/g)</th>
<th>Total pore volume (cm³/g)</th>
<th>Average pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FL-1</td>
<td>22.54</td>
<td>0.01729</td>
<td>3.07</td>
<td>FL-1#</td>
<td>20.47</td>
<td>0.01635</td>
<td>3.20</td>
</tr>
<tr>
<td>FL-2</td>
<td>20.90</td>
<td>0.01797</td>
<td>3.44</td>
<td>FL-2#</td>
<td>13.60</td>
<td>0.01344</td>
<td>3.95</td>
</tr>
<tr>
<td>CN-1</td>
<td>26.87</td>
<td>0.02385</td>
<td>3.55</td>
<td>CN-1#</td>
<td>20.54</td>
<td>0.02166</td>
<td>4.22</td>
</tr>
<tr>
<td>CN-2</td>
<td>25.33</td>
<td>0.02149</td>
<td>3.39</td>
<td>CN-2#</td>
<td>10.00</td>
<td>0.01542</td>
<td>6.17</td>
</tr>
</tbody>
</table>

a Specific surface area is calculated by BET equation.

b Total pore volume is determined to be the liquid N2 at a relative pressure of 0.99.
Average pore size = \(4 \times \text{total pore volume/specific surface area.}\)

\# represents that samples have been treated by ScCO₂.

**Table 3** Low temperature N₂ adsorption-desorption measurements comparing of specific surface area, total pore volume and average pore size from samples of Fuling and Changning shale before and after ScCO₂ treatment.

<table>
<thead>
<tr>
<th></th>
<th>FL fresh</th>
<th>FL exposed</th>
<th>Δ/%</th>
<th>CN fresh</th>
<th>CN exposed</th>
<th>Δ/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific surface area (m²/g)</td>
<td>21.72</td>
<td>17.04</td>
<td>-22</td>
<td>26.20</td>
<td>15.27</td>
<td>-42</td>
</tr>
<tr>
<td>Total pore volume (cm³/g)</td>
<td>0.01763</td>
<td>0.01490</td>
<td>-15</td>
<td>0.02267</td>
<td>0.01854</td>
<td>-18</td>
</tr>
<tr>
<td>Average pore size (nm)</td>
<td>3.26</td>
<td>3.58</td>
<td>+10</td>
<td>3.47</td>
<td>5.20</td>
<td>+49</td>
</tr>
</tbody>
</table>

Δ is the percent change.

* Values are average of two repeat measurements.

**Table 4** Surface area and pore volume of micropores, mesopores before and after ScCO₂ treatment.

<table>
<thead>
<tr>
<th></th>
<th>FL fresh</th>
<th>FL exposed</th>
<th>Δ/%</th>
<th>CN fresh</th>
<th>CN exposed</th>
<th>Δ/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micropore surface area (m²/g)</td>
<td>8.31</td>
<td>5.36</td>
<td>-35</td>
<td>9.52</td>
<td>2.32</td>
<td>-75</td>
</tr>
<tr>
<td>Mesopore surface area (m²/g)</td>
<td>10.53</td>
<td>10.74</td>
<td>+2</td>
<td>13.85</td>
<td>10.78</td>
<td>-22</td>
</tr>
<tr>
<td>Micropore pore volume (cm³/g)</td>
<td>0.00359</td>
<td>0.00283</td>
<td>-21</td>
<td>0.00415</td>
<td>0.00091</td>
<td>-78</td>
</tr>
<tr>
<td>Mesopore pore volume (cm³/g)</td>
<td>0.01158</td>
<td>0.01225</td>
<td>+6</td>
<td>0.01757</td>
<td>0.01668</td>
<td>-5</td>
</tr>
</tbody>
</table>

Δ is the percent change.

* Micropore surface and pore volume were calculated by t-Plot method.

b Mesopore surface and pore volume were derived from BJH model.

The distribution of pore volume with respect to pore size can be used to represent pore size distribution, including cumulative differential and incremental pore volume distribution curves. Based on the N₂ adsorption-desorption data, we apply BJH model to investigate the pore size range, dominant pore and pore size distribution peak of shale. The pore size distribution of shale samples derived from BJH model are illustrated in Fig. 3. It is observed that pore size had a wide distribution and the pore size distribution peak of shales were between 1 and 20Å, indicating micropores exist in shale. ScCO₂ let the pore size distribution peak of micropores (10-20Å) pore volume decrease greatly that is illustrated in Fig. 3-b, c, d. On the other hand, mesopores pore volume in Fig. 3-a is increase, but it is decrease in Fig.3-b while there is tiny change in Fig.3-c, d. Results of pore size distributions in shale is echo with the results of pore structure parameters in front.
3.3 Fractal analysis

According to the FHH model, the calculated fractal dimensions from N\textsubscript{2} adsorption data are shown in Table 5. Due to most adsorption-desorption isotherms diverge after relative pressure is 0.40, so using the relative pressure is greater than 0.40 of the adsorption data to calculate fractal dimension \( D \). All correlation coefficients are higher than 0.960, demonstrating that there are clear fractal characteristics for shales untreated and ScCO\textsubscript{2}-treated. The fractal dimensions for untreated samples are range from 2.85 to 2.90 with an average value of 2.87, suggesting that there is irregular surface and complexity pore structure in untreated samples. Comparing samples in untreated and treated (Table 5), the fractal dimensions of treated are range from 2.75 to 2.90 with a mean value of 2.83, which is lower than untreated samples, showing that pore structure of untreated samples are more complicated. With the fractal dimension decreasing, the morphology of pore structure in materials transforms gradually from complex to regularity pores (Pfeifer and Avnir, 1983). We can say ScCO\textsubscript{2} make pore surface wall of shale become more smooth, which is good for gas migration in shale.
Table 5 Fractal dimensions derived from FHH model.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>k</th>
<th>D</th>
<th>R²</th>
<th>Sample No.</th>
<th>k</th>
<th>D</th>
<th>R²</th>
<th>Δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>FL-1</td>
<td>-0.13</td>
<td>2.87</td>
<td>0.965</td>
<td>FL-1#</td>
<td>-0.10</td>
<td>2.90</td>
<td>0.960</td>
<td>+</td>
</tr>
<tr>
<td>FL-2</td>
<td>-0.10</td>
<td>2.90</td>
<td>0.976</td>
<td>FL-2#</td>
<td>-0.14</td>
<td>2.86</td>
<td>0.992</td>
<td>-</td>
</tr>
<tr>
<td>CN-1</td>
<td>-0.15</td>
<td>2.85</td>
<td>0.973</td>
<td>CN-1#</td>
<td>-0.19</td>
<td>2.81</td>
<td>0.984</td>
<td>-</td>
</tr>
<tr>
<td>CN-2</td>
<td>-0.14</td>
<td>2.86</td>
<td>0.986</td>
<td>CN-2#</td>
<td>-0.25</td>
<td>2.75</td>
<td>0.986</td>
<td>-</td>
</tr>
</tbody>
</table>

Δ means the changes of fractal dimensions after ScCO₂ treatment, “+” means increase; “—” means decrease.

4 Conclusions

In the paper, the changes in pore structure of shales from Fuling and Changning area associated with ScCO₂ exposure were observed by methods of low temperature N₂ adsorption-desorption data. Each shale sample was treated by solution of ScCO₂ under the temperature of 40°C at a high pressure of 16MPa to investigate the effect of ScCO₂ treatment on the pore structure of shales. The samples with and without ScCO₂ treatment were tested to offer experimental information as a better comparison.

As shown from the N₂ adsorption-desorption data, the specific surface area, total pore volume, average pore size and micro-and mesopores of shale samples are all changed by ScCO₂ treatment. The ScCO₂-shale reaction mainly affects the micro- and mesopores, which led to decrease of micro- and mesopores in the ScCO₂ treated sample. As a result, the surface area, pore volume, pore size distribution and average pore size are changed largely. It is will influence the adsorbed gas content in shale.

The fractal analysis of N₂ adsorption data resulted in determination of fractal dimension D, which can be used to characterize the irregular pore surface and complexity pore structure of shales. As revealed from the results, the ScCO₂-shale reaction led to decrease fractal dimensions in the ScCO₂ treated shale samples. Similarly, the pore surface wall of ScCO₂ treated shale become smoother than before.

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