Effect of CO\textsubscript{2} injection on adsorption of methane on shale from the Sichuan Basin in China

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Abstract. In order to understand the change of adsorption capacity of methane (CH\textsubscript{4}) after carbon dioxide (CO\textsubscript{2}) injection into shale at high pressure condition. The pore structure character and adsorption capacity of CH\textsubscript{4} were analysed via low-pressure N\textsubscript{2} adsorption and isothermal adsorption measurements for original and supercritical CO\textsubscript{2} (ScCO\textsubscript{2}) treated shale samples from Jiaoshiba area in the Sichuan Basin. The results show that the ScCO\textsubscript{2} treated samples have lower specific surface areas, less micropore and mesopore, and more macropore compare to original one. For ScCO\textsubscript{2} treated shale samples, specific surface area and micropore decrease with increasing temperature. Furthermore, the absolute adsorption capacity of CH\textsubscript{4} in original shale is higher than that in ScCO\textsubscript{2} treated ones, indicating that micropore specific surface area is probably the main factor controlling adsorption capacity of CH\textsubscript{4} on shale. For all samples, the absolute adsorption capacity of CH\textsubscript{4} increase with increasing pressure from 0 MPa to 43 MPa and then tended to be stable.

1 Introduction
Shale gas, as an unconventional energy source, is profoundly affecting the world energy pattern. Injecting carbon dioxide (CO\textsubscript{2}) into the shale reservoir to improve methane (CH\textsubscript{4}) recovery has become a hot research area, which is significant for shale gas exploitation and CO\textsubscript{2} geological storage [1]. The adsorption capacity of CH\textsubscript{4} in shale is affected by total organic carbon content, pore structure, mineral composition and so on, in which the pore structure is one of the predominant factors, including specific surface area, pore volume and pore size distribution [2]. The critical point and pressure of CO\textsubscript{2} are 31.4 °C and 7.38 MPa, respectively, and most CO\textsubscript{2} will reach supercritical state at deep buried formation. Supercritical CO\textsubscript{2} (ScCO\textsubscript{2}) has features of both liquid and gas, and characterized by high density, low viscosity, strong diffusivity and solubility. As temperature and pressure increase, the ScCO\textsubscript{2} fluid extracts more organic matters in shale, and the extraction rate is also related to total organic carbon (TOC), specific surface area and water saturation [3-4].

The Longmaxi Formation in Jiaoshiba area in the Sichuan Basin is one of the main source rocks for shale gas production in China. The main shale reservoirs in Longmaxi Formation may reach depths up to 2000 m where the hydrostatic pressure could well reach 50 MPa [5]. The temperature and pressure of burial depths of reservoir could reach the supercritical conditions of CO\textsubscript{2}. In recent years, lots of
researches mainly focus on the influence on shale pore structure and CH₄ adsorption capacity after CO₂ injection into shale with pressure below 25 MPa [6], which doesn’t reach actual geological pressure conditions. Therefore, this study examines pore structure and CH₄ adsorption characteristics after CO₂ injection into shale under pressure up to 50MPa.

2 Samples and methods

2.1 Samples

A shale core sample SCES6 from the Longmaxi Formation in Jiaoshiba area of east Sichuan Basin, China was utilized in this study. The shale sample was divided into two parts. The first part was subjected to low pressure nitrogen adsorption measurement for pore structure and CH₄ adsorption experiment for CH₄ adsorbed amount. The second part were treated by ScCO₂ at 50 MPa for 60 h with temperature of 40 °C, 60 °C, 80 °C, 100 °C, respectively. The ScCO₂ treated samples were then subjected to low pressure nitrogen adsorption measurement and CH₄ adsorption experiment, too.

The mineralogical compositions of the samples is dominated by quartz which is 53.6%, and content of clay and plagioclase is 22.0% and 7.7%, respectively, and contents of other minerals like K-feldspar, calcite and dolomite are all less than 5.0%. Clay minerals are predominantly illite. The sample is overmature with R₀ value of 2.4%. The TOC content of sample is 2.0%, and the kerogen type is type I [7].

2.2 Low-pressure nitrogen adsorption measurement

The low-pressure nitrogen adsorption measurements were performed on a Micromeritics ASAP 2020 HD88 apparatus. Nitrogen adsorption data collected on shale samples were interpreted using Brunauer-Emmett-Teller (BET) analysis for surface area, and density functional theory (DFT) for pore volume and varied range of pore size distributions.

2.3 Methane adsorption experiments

The measurements were performed on a gravimetric high pressure sorption analyzer (Rubotherm, ISOSORP-HP III Static) with a magnetic suspension balance. Methane adsorption isotherms of shale sample was measured at temperatures of 80 °C and pore pressures ranging from 0.01 MPa to 50 MPa with 15 designated pressure points. The equilibration time of each pressure point was set to 4 h and CH₄ is high purity of 99.99%.

3 Results and discussion

3.1 Effect of CO₂ on shale pore structures

The N₂ adsorption-desorption isotherms of shale samples analyzed before and after treated by ScCO₂ at different temperatures are shown in figure 1. All samples including the original, ScCO₂ treated shale samples share similar adsorption isotherms and are type II isotherm, indicating that shale pore shape is not significantly altered by ScCO₂ treatment. In addition, the adsorption capacity of all four ScCO₂ treated samples at different temperatures are less than that of the original sample. The adsorption capacities between samples are original > ScCO₂ treated-60 °C > ScCO₂ treated-40 °C > ScCO₂ treated-80 °C > ScCO₂ treated-100 °C, and show that adsorption capacity decreases with increasing temperature for ScCO₂ treated samples overall.
Figure 1. N2 adsorption-desorption isotherms of original and ScCO2 treated shale samples at different temperatures.

The specific surface area, pore volume, and average pore diameter of the original and ScCO2 treated shale samples are listed in Table 1. Compared to original shale sample, the ScCO2 treated samples have lower specific surface areas, higher pore volume and average pore diameter. The specific surface area decreases with increasing temperature, while pore volume and average pore diameter increases with increasing temperature for ScCO2 treated shale samples (figure 2a-c). This reveals that effect of ScCO2 has important effect on shale pore structures and are related to temperature. In addition, figure 2d exhibits change of different pore ranges of original and ScCO2 treated samples. It can be seen that proportion of micropore and mesopore are smaller in ScCO2 treated samples compared to that in original one, whereas micropore are larger in the former than that in the latter. The proportion of micropore decreases with increasing temperature, and that of micropore increases with increasing temperature for ScCO2 treated shale samples. It attributes to function of ScCO2 extraction in shale, which leads to increase of average pore diameter and decrease of specific surface area. Moreover, the ability of ScCO2 extraction of organic matter in shale will be strengthened by increasing temperature, resulting in transforming of more micropore and mesopore to mesopore and macropore, respectively. The ScCO2 treated sample at 40 °C exhibits abnormal nitrogen adsorption capacity and pore volume, which is probably because 40 °C is close to critical temperature of CO2. The extraction ability of ScCO2 is stronger at 40 °C, leading to growth of pore diameter and pore volume, and decrease of specific surface area.

Table 1. Pore structure characteristic of original and ScCO2 treated shale samples at different temperatures.

| Sample                | Micropore (%) | Mesopore (%) | Macropore (%) | V_DFT (10^-3 cm^3/g) | S_BET (m^2/g) | APD (nm) | S_BET-micro (m^2/g) |
|-----------------------|---------------|--------------|---------------|----------------------|---------------|----------|---------------------|
| Original              | 30            | 49           | 21            | 9.64                 | 13.57         | 6.35     | 3.02                |
| ScCO2 treated-40 °C   | 23            | 43           | 34            | 14.21                | 11.40         | 6.51     | 1.58                |
| ScCO2 treated-60 °C   | 21            | 44           | 35            | 10.24                | 12.17         | 7.42     | 2.14                |
| ScCO2 treated-80 °C   | 18            | 46           | 36            | 11.08                | 10.59         | 7.82     | 1.69                |
| ScCO2 treated-100 °C  | 20            | 42           | 38            | 12.93                | 10.45         | 7.39     | 1.08                |

V_DFT: DFT total pore volume (pore diameter range from 1.7 to 300 nm); S_BET: BET special surface area; APD: average pore diameter; S_BET-micro: BET special surface area of micropore.
Figure 2. Pore structure characteristics of original and ScCO$_2$ treated shale samples at different temperatures.

3.2 Effect of CO$_2$ on CH$_4$ adsorption capacity on shale

Absolute adsorption isotherms are usually described by the Langmuir model, and equation (1) is one expression of the Langmuir model [9].

$$n_a = \frac{n_0 P}{P_L + P}$$  \hspace{1cm} (1)

Here, $n_a$ is the absolute adsorption capacity, mg/g; $n_0$ is the maximum absolute adsorption capacity at a given temperature mg/g; $P$ is the equilibrium pressure, MPa; $P_L$ is the Langmuir pressure, MPa, which represents the pressure at which the amount of adsorbed methane equals half of the maximum adsorption capacity of methane.

The absolute adsorption isotherms of methane of original and ScCO$_2$ treated shale samples are displayed in figure 3. ScCO$_2$ treated samples have similar shapes of adsorption isotherms with original one, and they are all type I isotherm. At first, the absolute adsorption increases with increasing pressure in the range of 0 MPa to 10 MPa. Then the rate of increase reduces with increasing pressures, reaches a maximum value from 10 MPa to 43 MPa, and absolute adsorption tends to be stable when the pressure is greater than 43 MPa.
Figure 3. Absolute adsorption isotherms of methane for original and ScCO$_2$ treated shale samples.

Figure 4 shows that absolute adsorption capacity of ScCO$_2$ treated shale samples at different temperature are lower than that of original one. Because adsorption capacity of gas is positively correlated with micropore specific surface area, the decrease of surface area in shale due to treatment by ScCO$_2$ would reduce adsorption capacity of methane. Therefore, it is necessary to consider effect of ScCO$_2$ on structure characteristic of shale, shale gas exploration and CO$_2$ storage when produce shale gas by injecting CO$_2$ into shale formation under actual geological conditions.

4 Conclusions
(1) Compare to original shale, ScCO$_2$ treated samples have lower specific surface areas, higher pore volume and average pore diameter. The micropore and mesopore are more in ScCO$_2$ treated samples, whereas micropore become less. In addition, the specific surface area decreases, and the pore volume and average pore size increase with increasing ScCO$_2$ treated temperature. Besides, the proportions of micropore and mesopore decrease, and that of macropore increases with increasing temperature. The reasons for the change of microstructure of shale is that dissolving capability of ScCO$_2$ increases with increasing treated temperature, and ScCO$_2$ extracts more organic matter, which changes the pore structure in shale.

(2) The CH$_4$ adsorption amounts of ScCO$_2$ treated shales are lower than that of the original one, because microporous specific surface area decreases due to ScCO$_2$ influence. In practical applications, ScCO$_2$ plays a positive effect on shale gas exploration, but a negative effect on CO$_2$ storage. This effect should be taken into accounts when estimating the shale gas reserves and CO$_2$ storage potential in Jiaoshiba area of Sichuan Basin.

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