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Investigation on the physics structure and chemical properties of the shale treated by supercritical CO_2

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ABSTRACT

Shale gas is the second largest source of unconventional fuel in the world. Supercritical carbon dioxide (SC-CO_2) fracturing not only allows effectively breaking paper to the shale gas recovery but also could the replace of methane with carbon dioxide. In this method CO_2 adsorption in the shale affects the physical and chemical structure of the shale formations. Therefore, the change of reservoir physical properties will affect the efficiency of fracturing. The main objective of this study is to investigate supercritical CO_2 (SC-CO_2) effects on the physical structure (porosity, deformation, and mechanical properties) and chemical structure (mineral components) of the shale. Four types of experiments were conducted: (1) pore characteristics by low-pressure nitrogen adsorption. (2) the mineral composition of the shale test. (3) The CO_2-induced (adsorption-induced and pressure-induced) deformation of the shale teste. (4) The triaxial compressive strength and tensile strength of samples test. The results show that shale pore properties could be change by the SC-CO_2. The specific surface of the shale decreased and the porosity and average pore size increased. The mineral content of the shale minerals (except quartz) decreased after SC-CO_2 treatment. The samples exhibited swelling strains caused by SC-CO_2. At low pressures, shale deformation was mainly caused by adsorption, while deformation at higher pressures was mainly caused by pressure. After the SC-CO_2 treatment, the tensile strength, triaxial compressive strength, and elastic modulus of the shale decreased. The strength decreased as the treatment time increased. The changes in the strength of shale could be explained by two mechanisms: the dissolution effect of SC-CO_2 and the adsorption/pressure-induced strain. It indicate that supercritical carbon dioxide can change the characteristics of shale reservoir, and it could reduce the fracturing pressure of supercritical carbon dioxide fracturing and enhance the efficiency of fracturing.

1. Introduction

Shale is a fine-grained sedimentary rock, which is generally considered as a seal and natural barrier to oil and gas migration. Shale can form a reservoir and act as a source rock for unconventional petroleum and gas [1,2]. However, reservoir shale typically has low porosity, low permeability, and high clay content [3–6]. Gas can be extracted from shale by injecting CO_2 into the shale formations. Using this method, CO_2 can be stored in shale formations and gas recovery is increased [7–10]. However, injection of CO_2 into the reservoir can change the mechanical properties of the rock and these changes may influence the stability of the wells and affect the efficiency of fracturing. Therefore, it is important to investigate physical and chemical changes of the shale that is treated by the supercritical CO_2 (SC-CO_2) state.

Over the past decade, many studies investigated the influence of SC-CO_2 on shale. Busch et al. [11] studied Australian shale and showed that the dissolution of carbonates by SC-CO_2 affects the shale porosity, permeability and diffusion characteristics. Lahann et al. [12] measured the changes in pore structure in shale injected with SC-CO_2. They found that the specific surface area of shale in a SC-CO2 environment under high temperature conditions is more obvious greater than low temperature, but the different samples were chosen to test the pore characteristic. Jiang et al. [13] found that after shale was treated with SC-CO_2, the specific surface area and porosity of the shale changed, likely due to changes in the pore structure and permeability caused by sorption of SC-CO_2 [12,14,15], but the pore structure of shale was measured in Jiang‘s experiment with a PM33-GT-12 mercury porosimeter. It is not suitable for examining the material content of micropores and mesopores.

Griffith et al. [16], Gibbs et al. [17], Scherer et al. [18] and Pan et al. [19] showed that gas adsorption affects shale in two ways. First, sorption of CO_2 increases the swelling strain on the shale. Lu et al.

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measured the swelling strain of shale caused by supercritical CO_2 and found that the maximum volumetric strain was between about 0.15 and 0.16% and that the CO_2-induced swelling of shale could be calculated by a simplified local-density equation [20], but in this study, the strain caused by gas pressure was not obtained. Day et al. measured the swelling caused by the introduction of CO_2 into Australian coals and showed that the maximum volumetric strain was between about 1.7 and 1.9% [21]. Recently, Ferian et al. [15] studied the strain induced by CO_2 in low-rank coal and reported that the maximum volumetric strain was on the order of 1.65%. Other researchers proposed a theoretical model to describe CO_2-induced swelling in coal [19,22–25]. Second, the adsorbed gas changes the strength of the samples. Perera et al. [26] measured the strength of coal under SC-CO_2 conditions and found that the coal strength decreased under the effect of SC-CO_2. These processes induced a strain between the adsorbing CO_2 layer and the coal matrix during the process of adsorption while expending the surface energy of the coal matrix. Similar studies were performed by Lin et al. [27], who exposed cement to CO_2 at different phase conditions and showed that the sample corrosion caused by liquid CO_2 was stronger than that by gas CO_2. However, to the best of our knowledge, there is a few studies reporting the corrosion of shale by CO_2, and the strength of shale under SC-CO_2 conditions is not well understood.

Therefore, four types of experiments were carried out to investigate the physical and chemical characteristics of the shale treated by SC-CO_2 in this work. The low-pressure N_2 adsorption method was used to test the pore properties. X-ray diffraction (XRD) was used to analyze the mineral content of the shale samples. The CO_2-induced strain, triaxial compressive strength, elastic modulus, and tensile strength of the original (untreated) samples were measured. Then, the shale samples were immersed in SC-CO_2 in a high-pressure reaction cell, and the measurements repeated on the treated samples and compared with those of the untreated samples.

2. Materials and methods

2.1. Materials

The shale used in this work was collected from an outcrop of the Longmaxi Formation of the lower Silurian near Yibin City, Sichuan Province, in the Sichuan Basin. The total organic carbon content (TOC) of the material was 7.88% and the vitrinite reflectance (R_0) value was 2.85%. These values are within the optimal range for the occurrence of shale gas (TOC ≥ 2%, 1% ≤ R_0 ≤ 3%) [28]. No visible cracks and impurities were observed in the samples, so the samples were assumed to have similar characteristics.

Carbon dioxide, nitrogen, and helium gases were purchased from Cheng Du Ke Yuan Gas Co., LTD with a purity of 99.995%, 99.9995%, and 99.9995%, respectively.

Samples with particle size of 250 μm were prepared for pore structure tests. The shale is first broken and then the samples of 250um is selected with a sieve. For the XRD testing, the samples were ground to powder; cylindrical samples were prepared for the mechanical and deformation tests and one of such sample was shown in Fig. 1.

The samples were drilled perpendicular to the stratification of the shale. The ends of each specimen were polished to a smooth finish, parallel (less than 0.01 mm) and perpendicular to the axis (angle deviation not more than 0.05°). Cylindrical core samples, 50 mm in diameter and 100 mm in length were prepared for the strain test, triaxial compressive strength test, and elastic modulus test. Samples 50 mm in diameter and 25 mm in length were prepared for the tensile strength test [28].

2.2. Pore structure measurement

The pore structure of the samples was tested by an ASAP2020 micropore analyzer (Micromeritics, USA). The surface areas, pore volume, and pore size distribution were calculated from the N_2 adsorption isotherms at 77 K.

2.3. XRD characterization

An X-ray diffractometer (Panalytical B.V., Almelo, Holland) was used to obtain the material content of the shale over a 2θ range of 2–45° and a scan rate of 0.02°/2 s at the MLR Chongqing Mineral Resources Supervision and Test Center.

2.4. Measurement of shale deformation caused by CO_2 exposure

we used the “high pressure, high temperature adsorption deformation testing apparatus” to measure the gas-induced strain on the shale. More details of the apparatus can be found in the previous work by Ao et al. [30] and Lu et al. [20].

2.5. Measurement of the mechanical properties of shale with CO_2 exposure

The MTS-815 rock mechanics test system (MTS, MN, USA) was used to measure the triaxial compressive strength and elastic modulus of the shale samples. The AG-I 250kN Tensile tester (Shimadzu, Japan) was used to measure the tensile strength of the samples.

2.6. Experimental procedure

CO_2 can exist in a supercritical state at temperatures over 304.13 K and pressures over 7.38 MPa. The temperatures of shale formations with high organic content over the critical temperature of CO_2, while the pore pressure in such formations is 15–20 MPa [31]; under these conditions CO_2 will exist in a supercritical state. And the time of hydrofracture in the shale gas recovery is usually 2–3 days [10]. Therefore, the shale samples were treated at 15 MPa, 308 K and lasted 24, 48, 72, 96, and 120 h. Four types of experiments were carried out in this study.

- To examine the effect of SC-CO_2 on the mechanical properties of shale, triaxial compressive strength tests (Due to the change of the mechanical properties of shale mechanical properties under the action of carbon dioxide are the main objectives, the reservoir confining pressure conditions of the mechanical properties of the shale is not need, the same confining pressure of 6 MPa was chosen) and tensile strength tests were carried out on the untreated and treated samples. The samples were placed in a high-pressure reaction cell, and the sealing property of the system was checked with helium. The high-pressure reaction cell was then placed in a constant-temperature device at the target temperature for 1 h, and a plunger pump (ISCO, Lincoln, NE, USA) was used to inject CO_2 into the container to a preset pressure. The gas injection was stopped once the pressure stabilized. The samples remained for a predetermined time under SC-CO_2 conditions and were then carefully removed from the high-pressure reaction cell. The triaxial compressive strength, elastic modulus, and tensile strength measurements of the untreated and treated samples were compared. Because of the absolute variation existent in the samples, 5 samples were analyzed under each testing condition.
- XRD measurements were performed on the powdered samples which were mixed adequately. As these samples were very similar, no repeat experiments were needed.
- CO_2-induced swelling in shale can be attributed to two effects: adsorption and gas pressure. To determine the contribution of these two factors to the measured displacement results, two different gases were used in the strain tests. First, the swelling strain was measured in the CO_2-saturated shale. Second, the deformation strain was measured in the shale by no-adsorption gas (He). Ao et al. [29] and Lu et al. [20] presented the experimental process in detail. The