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Influences of subcritical and supercritical CO_2 treatment on the pore structure characteristics of marine and terrestrial shales

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ABSTRACT

To better understand and implement the CO_2 sequestration project, it is of significance to investigate the interaction of shales with CO_2 and its potential effects on the pore morphology. In this study, two marine shale samples and two terrestrial shale samples were prepared and treated with subcritical CO_2 (30 °C and 5 MPa) and supercritical CO_2 (80 °C and 20 MPa) in a geochemical reactor. Various methods, including low-pressure carbon dioxide adsorption (LP-CO_2A), low-pressure nitrogen adsorption (LP-N_2A), high-pressure mercury intrusion porosimetry (HP-MIP) and fractal theory, were used to gain insights into the changes in the shale pore structure after 14 days of CO_2 saturation. According to the results, the phase states of CO_2 obviously affected the variations of pore structure parameters during the physical and chemical reactions in shales. Interactions of supercritical CO_2 with shales created a more obvious effect on the pore structure compared to those of subcritical CO_2, which was attributed to the greater dissolution and expansion effect as well as the extraction mechanism associated with supercritical CO_2. After exposing the shale samples to subcritical CO_2, the pore size distributions (PSDs) of the treated shale samples were lower than those of the raw samples at all diameter scales, indicating that the number of pores decreased due to the reactions. Furthermore, it was found that after supercritical CO_2 treatment, the micropore and mesopore structure parameters of the marine shale samples obviously decreased with an increase in macropore structure parameters, leading to the reduction in fractal dimensions in smaller pores, while the terrestrial shale samples appeared to represent a contrary trend. These findings will provide experimental evidence for further assessment of the mechanisms for CO_2 geological sequestration with enhanced shale gas recovery.

1. Introduction

With the growing demand for clean energy, shale gas, as a typical unconventional gas resource, has attracted increasing attention worldwide. It is found that the utilization of shale gas can effectively reduce the concern for air quality problems and pressure on global climate changes, since it releases a small amount of greenhouse gas and almost no sulfur dioxide (SO_2) when producing the same amount of electricity power compared to other fossil fuels [1]. However, as one of the key technologies for shale gas development, hydraulic fracturing consumes huge amount of water resource, resulting in a “competition for water” problem which may influence the development of local agriculture and industry. Recently, supercritical CO_2 ($ScCO_2$), as a non-aqueous fracturing and drilling fluid, exhibits several advantages over water, including promoting the desorption of methane, enhancing fracture propagation and reducing flow-blocking mechanisms [2], which can be applied to the shale gas development, especially for areas lacking water. Therefore, the shale gas reservoirs have been considered as a promising geological locations for the CO_2 sequestration, which can enhance shale gas recovery while also achieving CO_2 storage (CS-ESGR) [3].

In contrast to conventional reservoirs, organic-rich shales are typically impermeable sedimentary rock characterized by complex petrophysical and geochemical systems. Based on the pore classification reported by the International Union of Pure and Applied Chemistry (IUPAC), the pores can be defined as micropores (pore diameter smaller than 2 nm), mesopores (pore diameter in the range of 2–50 nm) and macropores (pore diameter larger than 50 nm) [4]. In general, the heterogeneous pores are associated with organic matter and mineral compositions, and vary widely in size, types and morphology. Thus, it is still a challenging task to accurately characterize the multi-scale nanopore system in shale reservoir. In recent years, various techniques, such as field emission scanning electron microscopy (FE-SEM) imaging

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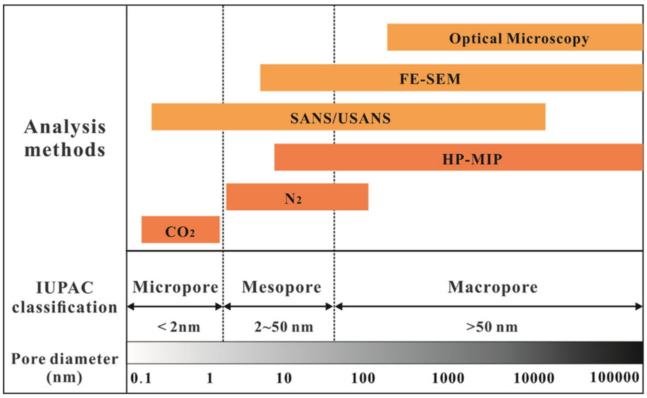

Fig. 1. Comparison of the different methods used to investigate pore size in shales.

[5], high-pressure mercury intrusion porosimetry (HP-MIP) [6], low-pressure gases (CO_2 and N_2) adsorption (LPGA) [7], and small-angle and ultra-small-angle neutron scattering (SANS/USANS) [8], are applied to acquire qualitative and quantitative information of pore morphology in shale reservoirs as illustrated in Fig. 1. Among these techniques, the combination of LP-GA and HP-MIP is considered to be a simple and effective method to investigate the pore structure in shale.

Shale reservoir has the capacity to store an extensive amount of CO_2 due to its complex compositions with huge surface area. With the injection of CO_2 into shale formations, complicated geochemical reactions occur between them, resulting in uncertainties for the CS-ESGR projects. Some researchers have performed numerous CO_2-brine-rock chemical reaction experiments to explore the mechanisms of geological CO_2 storage. These researchers reported that the dissolution of CO_2 in formation water created the carbonic acid, leading to the dissolution and precipitation of the minerals as listed in Eqs. (1)–(6) [9–12]. Generally, the kinetics rate of these geochemical reactions were related to the temperature and pressure. When the temperatures and pressures are above the critical point of CO_2 (T_C of 31.08 °C and P_C of 7.38 MPa), the CO_2 will be compressed to a supercritical state ($ScCO_2$) [13], which has distinct characteristics in terms of density, viscosity and diffusion ability compared to subcritical CO_2 ($SubCO_2$). According to the findings of Yin et al. [14] and Perera et al. [15], $ScCO_2$ saturation caused a more significant modification to the mechanical properties of shales and coals compared to $SubCO_2$ saturation due to higher dissolution capacity and greater chemical potential of $ScCO_2$. Zhou et al. [16] found that the CO_2 adsorption isotherms exhibited an enhanced propensity when the CO_2 phase varied from gaseous to supercritical state. Moreover, it was also suggested that the amount of swelling caused by CO_2 adsorption clearly depended on the phase state of CO_2 [17]. $ScCO_2$ adsorption-induced expansion was approximately two times larger than that caused by $SubCO_2$ adsorption.

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow CO_3^{2-} + 2H^+ \quad (1)$$

$$SiO_2\ (\text{quartz}) + 4H^+ \leftrightarrow Si^{4+} + 2H_2O \quad (2)$$

$$2KAlSi_3O_8\ (\text{K-feldspar}) + 2H^+ + H_2O \leftrightarrow 2K^+ + Al_2Si_2O_5(OH)_4 + 4SiO_2 \quad (3)$$

$$CaAl_2Si_2O_8\ (\text{plagioclase}) + 2H^+ + H_2O \leftrightarrow Ca^{2+} + Al_2Si_2O_5(OH)_4 \quad (4)$$

$$CaCO_3\ (\text{calcite}) + H^+ \leftrightarrow Ca^{2+} + CO_2 + H_2O \quad (5)$$

$$CaMg(CO_3)_2\ (\text{dolomite}) + 4H^+ \leftrightarrow Ca^{2+} + Mg^{2+} + 2CO_2 + 2H_2O \quad (6)$$

Recently, in-situ field implementations have been conducted to evaluate the feasibility of the CS-ESGR project. In 2016, the Virginia Center for Coal and Energy Research (VCCER) conducted a successful ‘huff-and-puff’ test. Approximately 510 tons of carbon dioxide were successfully injected into the Chattanooga shale formation, which is located in north-central Tennessee in the United States. The results showed that there was an obvious increase in gas flow rate as well as the gas quality after a long-term CO_2 soaking phase, confirming the injectivity and sequestration potential of the CO_2 in shale gas reservoir [18]. Meanwhile, in 2017, the Shanxi Yanchang Petroleum Company (China) performed non-aqueous fracturing and transformation tests on four shale gas wells in the terrestrial Yanchang formation, using CO_2 as the fracturing fluids. They found that the average daily production of the wells reached its highest level after the injection of CO_2, and the retention rate of carbon dioxide in the shale formation was approximately 60%–70%, indicating that a significant amount of CO_2 could be sequestrated [19]. These successful practices will be summarized and then applied in both terrestrial and marine shale reservoirs in China in the future. However, some fundamental mechanisms behind the CS-ESGR projects remain unclear. Since the sorption and transport behaviors of the fluids are controlled by the heterogeneous porous medium, knowledge of the variations in multi-scale pore structure after CO_2 treatment is critical for implementation of the CS-ESGR projects.

In recent years, numerous studies have investigated the influences of CO_2 exposure on the pore morphology of coals under various geological conditions. [20–24]. They suggested that these variations in pore structure depended on both coal ranks and phase states of the injected CO_2. However, to the best of our knowledge, the studies of the effect of $SubCO_2$ and $ScCO_2$ treatment on pore structure modifications of shale formations, especially comprehensive studies on the multi-scale pore structure, are relatively rare. Wu et al. [25] investigated the impacts of CO_2 exposure on the permeability of Utica shale samples and found that the CO_2 adsorption would induce volumetric expansion, leading to the reduction in porosity and permeability. Lahann et al. [26] combined the LP-CO_2A and LP-N_2A methods to determine the influence of CO_2 on micro- and mesopore structure parameters of the Indiana shale samples. The results showed that there was a slight increase in surface area as a result of temperature and CO_2. Yin et al. [27] documented that the $ScCO_2$ treatment had a significant influence on the micropores of the Longmaxi shales. After treatment, the number of micropores and the specific surface area showed a significant decrease. According to Pan et al. [28], the Longmaxi and Chang-7 shale samples exhibited different variation patterns in the micro- and mesopore structure parameters after long-term $ScCO_2$ saturation. Jiang et al. [29] also studied the influences of $ScCO_2$ exposure on the microstructure of Longmaxi shales by the HP-MIP technique. They reported that the porosity and surface area of the shale samples increased with the increasing of immersion pressure and time.

It can be seen from the above literature reviews that the characterization of variations in shale pore structure during CO_2 exposure is complex and has not been adequately studied. Furthermore, due to the pressure decline during fracturing engineering, the $ScCO_2$ may transform into $SubCO_2$ at the beginning of the injectivity [14]. Considering the distinct characteristics between $SubCO_2$ and $ScCO_2$, it is also essential to comprehensively evaluate how well CO_2 can influence the microstructure of shales under different phase states. This paper, therefore, focused on a comparison of the potential variations in nanopore structure system of shales with the exposure of CO_2 at sub- and supercritical state, aiming to provide new perspective to better implement the CS-ESGR project. Furthermore, two different types of sedimentary shales, including marine and terrestrial shales, were selected as samples to provide basic knowledge for the evaluation of the CO_2 storage in shale formations with different sedimentary backgrounds. Several methods, such as low-pressure carbon dioxide adsorption (LP-CO_2A), low-pressure nitrogen adsorption (LP-N_2A) and high-pressure mercury intrusion porosimetry (HP-MIP), were used to characterize the changes in micro-, meso- and macropore structure system of shales before and after CO_2 treatment.