Shale Microstructure Characteristics under the Action of Supercritical Carbon Dioxide (Sc-CO₂)

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Abstract: Supercritical carbon dioxide (SC-CO₂) is suitable to extract low-polar organics and to assist in the dissolution of pores and fractures in shale. In this work, we investigate the effect of temperature on the structure of five shale samples via high pressure reaction assisted with SC-CO₂. Shale samples were analyzed using X-ray diffraction, field emission scanning electron microscopy, and ImageJ software. Due to the extraction of CO₂, after Sc-CO₂ treatment, carbonate and clay content decreased, while quartz and plagioclase increased slightly, which improved gas and oil flow in microscopic pores and shale cracks. Shale samples showed an increase in surface fracture area as experimental temperature increased. Since Sc-CO₂ fluid density and solubility increase with temperature, more organics can be extracted from shale pores and fractures, resulting in newly formed pores and fractures. As a result, the threshold temperature for shale high-temperature Sc-CO₂ cracking was confirmed to be 400°C, and the fracture area increased by more than 45% at this temperature. Based on the findings of this study, Sc-CO₂ technology can be used to potentially recover low-maturity shale oil efficiently.

Keywords: shale; exploitation; Sc-CO₂; microscopic features; mineral composition

1. Introduction

With the continuous expansion of energy consumption in various countries, global conventional resources are gradually decreasing, and shale oil is gaining more attention. The technically recoverable resources (TRR) of the global shale oil are 618.47 × 10⁸ t [1]. Shale oil is mainly classified into mature shale oil, medium maturity shale oil, medium-low maturity shale oil, and low maturity shale oil according to the vitrinite reflectance R₀. The preliminary evaluation of TRR for medium-low maturity shale oil ranges from 700 to 900 × 10⁸ t; the economically recoverable resources range from 200 to 250 × 10⁸ t [2,3]. As the petroleum industry develops in the future, shale oil will become an increasingly important replacement resource. However, the medium-low maturity shale oil reservoirs have extremely poor physical properties and low free hydrocarbon content, so the current technology cannot be used effectively.

There has been some confirmation of the feasibility of converting shale oil in-situ by heating or injecting high-temperature fluids. Various heating methods have been tried at home and abroad, including electric heating, fluid convection heating, and radiation heating. As a result of its fast heating speed and relatively mature technology, fluid convection heating is the preferred method of converting and exploiting shale oil in-situ [4]. Thus, scholars proposed to use high-temperature Sc-CO₂ as a thermal convection medium, which can improve the recovery rate of shale and make CO₂ sequester in the shale layer. It strongly supports carbon peaking and carbon neutrality strategic goals.

Several studies have shown that Sc-CO₂ can generate complex fractures with high conductivity [5,6], prevent formation damage, and reduce the produced wastewater [7,8].
Additionally, it is beneficial to displace oil and improve permeability [9,10]. Sc-CO$_2$ dissolves in water to form an acidic fluid that dissolves most feldspar minerals, widens pore-throat channels, changes reservoir physical properties, and effectively improves recovery [11,12].

As CO$_2$ approaches its critical point, Huang et al. [13] observed that its viscosity increases significantly. Since the Sc-CO$_2$ surface tension is nearly zero, it has super seepage and mass transfer properties. Injection of Sc-CO$_2$ can quickly enter the pore and fracture. Due to the dissolving ability of Sc-CO$_2$, it is possible to generate new fractures and pore structures in shale reservoirs, or its original pore structure can be changed, thereby increasing shale oil production [14,15]. In spite of this, the effect of Sc-CO$_2$ on the pore structure of shale is still unclear. In their study [16], Gupta et al. pointed out that Sc-CO$_2$ is useful in improving reservoir permeability. Angeli et al. [17] carried out experiments of Sc-CO$_2$ on shale cores, mainly aiming at the microstructure properties of rocks [18]. Sc-CO$_2$ soaking time affects the uniaxial compression properties of shale by affecting pore structure and mineral composition.

Furthermore, the physicochemical reaction between Sc-CO$_2$ and shale may change the original mineral constituent of shale, and it is well known that the mineral constituent affects the stimulation of shale reservoirs. Lyu et al. [19,20] found that the dissolution of minerals formed many new pores on the shale sample, but their effect was weaker than CO$_2$ with water treatment. The influence of Sc-CO$_2$ was more important than that of gaseous CO$_2$. Jiang et al. [21] found that after Sc-CO$_2$ soaking, a great deal of white materials on the shale surface disappeared, elements of silicon, calcium, and oxygen decreased, and the percentage of carbon and magnesium increased. Yin et al. [22] compared the shale samples and found that the primary macropores and micro-cracks after Sc-CO$_2$ treatment were reduced due to adsorption expansion, and new pores and cracks were generated due to extraction and dissolution. After Sc-CO$_2$ was applied to the sample, Lu et al. [23] found that the mineral composition and microstructure changed significantly. The calcite content decreased significantly, the proportion of main mesopore volume decreased, and the proportion of macropore volume increased. The above studies showed that the difference in shale mineral composition significantly impacts the microstructure. The mineral constituent of shale samples changed after the action of Sc-CO$_2$; it is speculated that a variety of minerals were dissolved, including calcite, montmorillonite, and anorthite, and the interaction led to irreversible variations in the pore morphology of shale, and the primary microstructure was destroyed. An in-situ conversion method for a shale oil development injection with high-temperature Sc-CO$_2$ is a new direction. The pore expansion and permeability enhancement of shale reservoirs under high-temperature Sc-CO$_2$ environments are still unclear, especially for the mineral constituent and permeability enhancement before and after Sc-CO$_2$ soaking.

In summary, the research selected shale samples from a C7 shale formation in Ordos Basin to study the surface microscopic pore structure parameters and their changes after interacting with Sc-CO$_2$. The high-temperature and high-pressure autoclave equipment, X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), and ImageJ software characterized the surface cracks and their changes after Sc-CO$_2$ treatment. This study aims to understand how physicochemical reactions between Sc-CO$_2$ and shale affect microscopic fracture variations on the surface of shale samples.

2. Materials and Methods

2.1. Shale Properties and Preparation

Samples were taken from a well site in Qingyang, Shanxi province. On average, each sample contained 12.57% organic carbon (TOC) and 0.6% vitrinite reflectance (Ro). According to the requirements of the argon ion polishing machine for the test sample, the shale was processed into a cube-shaped sample with a size of 15 mm × 15 mm × 5 mm, and the surface was polished with 3000-grit sandpaper until there were no visible scratches. The processed samples were wrapped with filter paper sealed to prevent moisture and...
other foreign matters. XRD experiments were performed on samples obtained from the same shale, which were crushed and screened through a 200-mesh screen. For the purpose of preventing oxidation and moisture damage, all samples were stored in polyethylene sealed bags.

2.2. Experimental Method

2.2.1. Experimental Method of Shale Surface Structure

To observe the shale surface’s structural features, the FE-SEM experiment was carried out on the shale sample after the argon ion spectrometer. Secondly, we placed the shale sample in a high-temperature and high-pressure corrosion autoclave. Sc-CO$_2$ treatment was carried out in the autoclave. The treatment temperatures were 100 $^\circ$C–500 $^\circ$C with a gradient of 100 $^\circ$C, the pressure was 20 MPa, and the treatment time was 24 h. Finally, we used ImageJ software to analyze and study the surface micromorphology of shale samples before and after Sc-CO$_2$ treatment.

2.2.2. Experimental Method of Mineral Composition

An X Pert PRO MPD X-ray diffractometer was used to analyze the shale samples. The XRD mineral constituent test can offset the influence of sample differences by mixing rock powders from multiple experiments.

3. Results and Discussion

3.1. Influence of Shale Surface Structure

The SEM observation of untreated and Sc-CO$_2$ treated samples shows the microstructure of the shale surface in Figure 1. Under Sc-CO$_2$ soaking, the primary pores and fractures of the shale dissolve. Due to the extraction and dissolution of the in-situ substances within the shale, the microstructure of the shale surface is transformed, resulting in new pores and fractures, as well as increased structural connectivity that facilitates oil and gas seepage. The shale surface contains a lot of white matter that contains C, O, Mg, Al, Si, Ca, and Te before Sc-CO$_2$ treatment, which are shaped as circular and sub-circular quartz grains, clay material, and carbonate. A great deal of white matters vanished after treatment. According to our research, this is due to silicate minerals such as kaolinite, illite, and anorthite in shale. The percentages of main elements, such as Si, Ca, and O, decreased, and the percentages of C and Mg increased after Sc-CO$_2$ treatment. Moreover, it can be inferred that Sc-CO$_2$ dissolves minerals such as montmorillonite and anorthite, reducing the white matter attached to the shale surface. The surface morphology of shale samples becomes more complex after Sc-CO$_2$ treatment, a great deal of pores and micro-cracks are formed, the sketch of mineral particles is obvious, the dense agglutinate of mineral particles is destroyed, and the roughness of organics increases due to extraction, and the number of newly dissolved pores and fractures increases.

ImageJ software was used for the next analysis to convert the SEM images into two-dimensional binary images (Figure 2) for calculating the variation of the surface crack area after the Sc-CO$_2$ soaking. Then, a histogram was drawn to evaluate the trend of the surface crack presented as the white space in the binary image. As shown in Figure 3b, the fracture area on the surface of the shale after treatment increased to varying degrees, indicating the evolution of micro-cracks after treatment. Shale pore structure is characterized by macropores, mesopores, and micropores. Mesopores and micropores are generally recognized storage spaces in shale. It is worth mentioning that SEM images can only reveal changes in macropores (diameter greater than 1000 angstroms) on the surface. Due to the high diffusivity of Sc-CO$_2$, there will be more changes in rock mesopore and micropore structure [24,25]. These changes will generate effective secondary pores and observably affect the reservoir capacity.
Figure 1. Shale surface structure before and after the Sc-CO$_2$ reaction. (a) SEM images before and after the Sc-CO$_2$ reaction of 100 °C. (b) SEM images before and after the Sc-CO$_2$ reaction of 200 °C. (c) SEM images before and after the Sc-CO$_2$ reaction of 300 °C. (d) SEM images before and after the Sc-CO$_2$ reaction of 400 °C. (e) SEM images before and after the Sc-CO$_2$ reaction of 500 °C.

Figure 2. SEM images of shale after ImageJ treatment ((a1) 100 °C Before; (a2) 100 °C After; (b1) 200 °C Before; (b2) 200 °C After; (c1) 300 °C Before; (c2) 300 °C After; (d1) 400 °C Before; (d2) 400 °C After; (e1) 500 °C Before; (e2) 500 °C After).

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What needs illustration is that under the same temperature condition (100 °C), FE-SEM was used to observe surface crack areas before and after the Sc-CO$_2$ reaction. The data after ImageJ treatment are shown in Figure 3d. With the increase of magnification, the surface crack area of shale decreases. This is mainly because the shale surface is observed by SEM. The smaller the distance, the clearer the image. Then, the observation distance is increased to expand the field of view. When the distance is at a certain value, the surface cracks cannot be seen clearly, and the maximum observation distance is taken to compare the surface crack area at different observation distances. As the range of view increases, the image resolution decreases, so the number of cracks identified by ImageJ decreases, and the calculated total crack area decreases. To solve the above problems, within the maximum distance range, several groups of observation points were taken on the surface of the shale sample, and then the observation distance was decreased, and the average value was taken after observing the change of surface cracks.

An X-ray energy spectrometer (EDS) was used to determine the chemical composition of the shale samples prior to Sc-CO$_2$ soaking (Figure 3a). Proportions of the three main elements, including oxygen, silicon, and carbon, were determined. These elements benefit CO$_2$ mineral capture, including silicate and carbonate minerals. A higher weight percent of quartz minerals was detected in the shale after Sc-CO$_2$ treatment, indicating an increase in oxygen and silicate content. Changes in these elemental compositions impact the specific surface area, pore topological structure and pore volume. After treatment, the carbon ratio decreased due to the dissolution of Sc-CO$_2$ in water to form carbonic acid, and induced the carbonate minerals (i.e., dolomite) precipitation. Shale’s high clay content releases more water, which reacts with Sc-CO$_2$ to produce carbonic acid. The primary cause is that the
dissolution of clays and carbonates produces new quartz grains. The vanishing of the white matter is evidence of this behavior, as discussed earlier (Figure 1). The proportions of the remaining elements Ca, Mg, Al, K, and Fe remained unchanged after Sc-CO₂ soaking. A change in these elements’ content lies on the physicochemical reaction of dominant elements (Si, O, and C). Since EDS analysis is a semi-quantitative method, the change in mineral composition after Sc-CO₂ treatment is further evaluated by XRD analysis.

3.2. Influence of Mineral Composition

The pH is significantly reduced when CO₂ dissolves into shale pores as carbonic acid forms. There are a series of chemical reactions when carbonic acid diffuses into carbonate [26]:

\[
\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 \rightarrow \text{H}^+ + \text{HCO}_3^- \tag{1}
\]

\[
\text{Ca} (\text{Mg})\text{CO}_3 + \text{H}^+ + \text{HCO}_3^- \rightarrow \text{Ca}^{2+} (\text{Mg}^{2+}) + \text{CO}_2 + \text{H}_2\text{O} \tag{2}
\]

This chemical reaction reduces carbonate, clay, and plagioclase [27]. However, the content of quartz and plagioclase increased slightly after the Sc-CO₂ soaking. Carbonate content and clay mineral content decreased accordingly (Figure 4). Due to the extraction of CO₂, dissolving some clay minerals and carbonate minerals reacts with Sc-CO₂, which will result in a slight reduction in the content of these two minerals. Meanwhile, the increase in quartz content is due to a decrease in the total mass of the shale. Therefore, the content of plagioclase increased slightly. Furthermore, the effect reduces existing micropores and fractures and creates new ones.

![Figure 4. Whole rock analysis diagram.](image)

The shale of this formation has a higher clay mineral content (kaolinite and illite), of which 56.3% is illite, 21.5% is illite/smectite, about 16.4% is kaolinite, and finally about 5.8% is chlorite. During the CO₂-shale interaction, clay swelling is the main factor affecting mineral alteration. However, illite and kaolinite do not cause swelling as they do not have enough exchange capacity [28,29]. Low swelling and dispersion of non-swelling clays in water and CO₂ treatment can reduce the swelling degree of hydrated montmorillonite, and it tends to disperse quickly [30]. At the same time, due to the shale heterogeneity, small changes in minerals cannot be accurately detect using XRD [31]. This uncertain experiment leads to a certain degree of error in the mineral weight percent values.

3.3. Characteristics of Shale Fracture under the Action of Sc-CO₂

In addition to being sensitive to pressure and temperature, Sc-CO₂ converts the shale microstructure based on soaking time. The influence of the experimental results on the microstructure of the shale samples is shown in Figure 3b,c and Table 1. The difference in
surface fracture area increases with the increase of Sc-CO₂ dissolution temperature. The temperature affects the solubility of Sc-CO₂, and the mechanism is mainly manifested in two effects of temperature on the solubility of supercritical fluids:

1) The impact of temperature on the density of supercritical fluids: under isobaric conditions, temperature increases decrease the density of supercritical fluids, resulting in a decrease in the solubility of supercritical fluids;

2) Influence of temperature on vapor pressure: temperature increases increase vapor pressure, which increases solubility in supercritical fluids.

Table 1. Change of shale fracture area before and after Sc-CO₂ reaction.

| T/°C | Before/µm² | After/µm² | Difference/µm² | Rate/% |
|------|------------|-----------|----------------|-------|
| 100  | 9.48       | 11.03     | 1.55           | 16.35 |
| 200  | 14.82      | 16.18     | 1.36           | 9.18  |
| 300  | 7.49       | 9.22      | 1.73           | 23.10 |
| 400  | 7.60       | 11.02     | 3.42           | 45.00 |
| 500  | 6.67       | 9.82      | 3.15           | 47.23 |

Before a certain temperature, temperature increases cause the supercritical fluid’s solubility to decrease, primarily because of these two factors; after the extreme temperature point, the increase of the saturated vapor pressure also leads to the increase of the solubility—a significant increase.

Studies have shown that under relatively low pressure (<16 MPa), Sc-CO₂ fluids are little affected by temperature [32]. In high-pressure conditions (>16 MPa), the solubility of Sc-CO₂ fluid increases with the increase of temperature, which has a great influence on the microstructure of shale. When the experimental pressure in this paper is 20 MPa, the temperature greatly influences the fracture area of the shale surface. Therefore, it can be calculated that the surface fracture area increases by 16.35%, 9.18%, 23.1%, 45%, and 47.23%, respectively, at the temperature of 100 °C–500 °C. The Sc-CO₂ treatment temperature significantly affects the fracture propagation of the shale microstructure. It is important to point out that the surface fracture area increases at temperature 200 °C at 9.18%, which is the lowest among the five experimental temperatures. Whether 200 °C is the “extreme temperature point” needs further experiment to certify. When temperature is higher than 400 °C, the incremental surface fracture area is huge and varies a little. It is shown that 400 °C is the threshold temperature for shale high-temperature SC-CO₂ fractures. The seepage capacity of shale will increase extremally when shale formation temperature rises to the threshold temperature.

4. Conclusions

This research studied the variation in the microstructure of shale samples before and after Sc-CO₂ soaking. Sc-CO₂ treatment temperature and shale micromorphology were discussed in relation to the effect and mechanism.

There are various minerals on the surface of shale, including round and sub-round quartz grains, clay, and carbonate, and the surface is very complicated with obvious heterogeneity.

Carbonate and clay are reduced to varying degrees after high-temperature Sc-CO₂ treatment. Spots and pits formed by dissolution were observed on the surface of dolomite and other mineral particles, which improved the flow path of gas and oil in the microscopic pore and fracture of shale.

After the action of Sc-CO₂, the complexity of the surface morphology of shale samples increases, a great deal of pores and micro-cracks form, the sketch of mineral particles is obvious, the dense agglutinate of mineral particles is destroyed, the roughness of organics increases due to extraction, and the number of newly dissolved pores increases.

Shale samples treated at higher temperatures had a greater surface crack area. When the temperature exceeds 400 °C, the incremental surface fracture area is huge and varies
slightly. Additionally, 400 °C is the threshold temperature for shale high-temperature Sc-CO₂ cracking.

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