Study on the Effect of CO2-Brine-Rock Interactions on Reservoirs during the CO² Geological Storage

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ABSTRACT

Injecting CO² into the reservoir can achieve geological storage of $CO₂$ while improving recovery, which can effectively mitigate $CO₂$ emissions. The balance between reservoir rocks and formation water is disrupted by the injected $CO₂$, resulting in changes in porosity, permeability, and formation water characteristics as well as mineral corrosion and precipitation. These changes ultimately impact the safety and capacity of $CO₂$ storage. In this paper, the $CO₂$ -Brine-Rock interaction mechanism and its effect on the reservoir are studied by using sandstone cores from the Qiuling Oilfield in China as experiment objects, through indoor core flooding experiment, nuclear magnetic resonance (NMR) experiments, and ion analysis of the reaction solution. The experimental results show that the porosity and permeability of the cores increased slightly after $CO₂$ flooding, and the increase in porosity at the entrance is higher than that at the export; The content of Na⁺, Ka⁺, HCO₃, CO₃² ions increase and the content of Mg²⁺, Ca²⁺, $Ba²⁺$ ions decrease in the final reaction solution. The results of this study provide theoretical support for further research on the $CO₂$ capture mechanism and geological storage of $CO₂$ in water-bearing reservoirs.

Keywords: CO₂ storage, CO₂-Brine-Rock interaction, CCUS, nuclear magnetic resonance

1. INTRODUCTION

The large amount of $CO₂$ emissions is one of the main causes of global warming, and $CO₂$ capture, utilization and storage (CCUS) technology is an important means to effectively reduce $CO₂$ emissions. Currently, geological storage of $CO₂$ is mainly focused on deep saline aquifers, depleted oil and gas reservoirs, deep unmineable coal seams, and basalt CO₂ mineralization storage^{[\[1\]](#page-7-0)}. Injecting $CO₂$ into reservoir reservoirs is an important way to realize CCUS as it improves crude oil recovery while allowing geological storage of $CO₂$. $CO₂$ injected into the

reservoir undergoes a series of chemical reactions with formation water and rocks, changing the physical properties of the reservoir and thus affecting the geological storage of CO₂.

In recent years, many scholars have conducted a large number of scientific studies on $CO₂$ -Brine-Rock interactions. LIN et al. $^{[2]}$ $^{[2]}$ $^{[2]}$ studied the effect of injection pressure and temperature on the corrosion rate of $CO₂$ dissolved in formation water on dense sandstones in reservoirs through dynamic drive-off experiments. When the injection pressure of $CO₂$ increased from 15 MPa to 25 MPa, the increase in porosity increased from 3.0% to 6.2% and the increase in permeability increased from 25.5% to 34.4%; When the temperature increased from 44℃ to 64℃, the increase in porosity decreased from 3.0% to 1.7%, and the increase in permeability decreased and then increased, generally ranging from 20.3% to 35.0%. Tang et al.^{[\[3\]](#page-7-2)} simulated the $CO₂$ injection and storage process in water-bearing gas reservoirs based on static and dynamic experiments, and found that $CO₂$ -Brine-Rock interactions can cause rock minerals to dissolve and detach from the matrix, forming free particles, which are then suspended in the fluid-filled pore space and flow along with it, with the final porosity enhancement ranging from 0.13% to 5.94% and permeability enhancement ranging from -66.7% to 8.14%. Although scholars have conducted a lot of research on CO2-Brine-Rock interactions, they are all based on the change of the overall physical propertied of the core. In this paper, through indoor core flooding experiment, T1 and T2 nuclear magnetic resonance experiments, and ion analysis of the reactive fluid, we have investigated the change of the porosity of the core at the front, middle and back of the core, and explored the mechanism of its occurrence, so as to provide theoretical support for the subsequent further study of $CO₂$ -Brine-Rock interactions in the sandstone reservoirs.

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It provides theoretical support for the further study of CO2-Brine-Rock interaction in sandstone reservoirs.

2. EXPERIMENTS ON CO2-BRINE-ROCK INTERACTIONS

2.1 Mechanism of CO2-Brine-Rock interactions

The $CO₂$ -Brine-Rock system is a complex seepage system coupled with process such as flow, mass transfer, dissolution, sedimentation, and sediment transport^{[\[4\]](#page-7-3)}. After $CO₂$ is injected into the reservoir, the balance between formation water and rock will be broken, as shown in Fig. 1, part of $CO₂$ is dissolved in the formation water, which reacts with water to generate carbonic acid and ionize H+, and then dissolves the cement and some minerals in the rock, thus increasing the porosity and permeability, and at the same time, accompanied by secondary minerals and ionic precipitates, which transport under the carrying effect of fluid, and block the smaller pore throat structure when they encounter it, thus reducing the flow space of $CO₂$ and even reducing the efficiency of CO2 subsequent waves, and ultimately affecting the geological sealing of $CO₂$ and further contact with the formation water and the reservoir, and ultimately affects the effectiveness of geological storage of CO₂.

Fig.1 Schematic of CO2-Brine-Rock interactions

2.2 Experimental material

The cores used in the experiments were taken from typical sandstone in the Qiuling oilfields of Xinjiang, which is rich in oil reserves, with complex and variable reservoir pore-throat structure, large span of porosity and permeability, and strong heterogeneity. Two sandstone cores with similar porosity and permeability parameters in the same stratigraphic position were selected, the specific parameters are shown in Table 1, and the types of minerals contained in the cores and their mass fractions are shown in Table 2.

The parameters such as ionic composition and mineralization of formation water are shown in Table 3, and the brine used in the experiment is configured according to the cation and anion composition and content in the table.

2.3 Experimental methods

The device for indoor core flooding experiment is shown in Fig. 2, utilizing the HW-II incubator equipment to maintain the temperature at 50°C. The specific experimental process is as follows:

(1) Prepare 500mL of brine according to the ion composition and content shown in Table 3, then place two core samples in a vacuum pump and adjust the pressure to -0.1MPa. Extract air from the core samples for 12 hours to make them in a vacuum state and saturate them with brine for 1 hour. After 4 hours, remove the core samples and dry the surface moisture. Scan the core samples with a SPEC-NMR core analyzer to obtain the initial NMR T1 and T2 curves of the two core samples for subsequent comparative analysis.

(2) Place The treated cores in a gripper in a incubator and install the equipment in order. Maintain the temperature at 50℃, first let the crude oil at a flow rate of 0.1mL/min constant speed drive the core to saturate the oil, to be stopped when the oil content of the outlet end of 100%; and then $CO₂$ - saturated brine at a flow rate of 0.05mL/min constant speed drive the core to the outlet end of the water content of 98%, continue to drive 10h after the end of the experiment, take out the core of the core for the oil washing and drying, and then measure the porosity and permeability. and finally the first step was repeated to scan the NMR after saturating the brine to obtain the NMR spectra of the two cores after simulating the $CO₂$ -Brine-Rock interactions in the reservoir. Finally, the first step of the operation is repeated to obtain the NMR T1 and T2 curves of the two cores after the experiment.

(3) Record the pump injection volume after water appeared at the outlet end during the experiment. At the same time, the produced liquid collected in the graduated cylinder is subjected to oil-water separation, and the ion composition and content of the water after the experiment are obtained through an ion analyzer.

Fig.2 Indoor core flooding experimental equipment

3. RESULTS AND DISCUSSIONS

3.1 Analysis of changes in porosity and permeability

During the experiment, when the $CO₂$ -saturated brine comes into contact with rocks, firstly, due to the flushing effect of the fluid, some mineral particles peel off from the rock surface and are carried and transported by the fluid; Secondly, accompanied by a series of chemical reactions involving mineral dissolution and precipitation, as shown in Table 4. Calcite and cement will completely dissolve, while feldspar and clay minerals will generate secondary minerals while dissolving, and quartz will hardly dissolve, accompanied by a large

amount of ions dissolved in saltwater, such as K^+ , Na⁺, Ca^{2+} , Mg²⁺, etc.

As shown in Table 5, after $CO₂$ dissolves in brine, the concentration of $CO₃²$ ions increases, reaching the ionic solute product (Ksp) of some precipitates such as $MgCO₃$ and CaCO₃, and smaller precipitate particles will gradually form. In addition, quartz particles located on

the surface of pores and encapsulated by cement are released due to the dissolution of surrounding rocks. These particles migrate under the action of fluid transport, with larger particles settling at the bottom of pores and smaller particles being carried out of the core or blocked at the pore throats.

The CO2-Brine-Rock interactions cause mineral dissolution and migration, thereby changing the pore throat structure of the core, enhancing connectivity, and resulting in changes in the porosity and permeability of

the core. The NMR T1 and T2 curves of two core samples before and after the experiment are shown in Figures 3 and 4.

Fig.3 NMR T1 curves

The longitudinal relaxation time in the NMR T1 curves of core measurement refer to the time required for fluid molecules to recover from an excited state to an equilibrium state under the action of an external magnetic field. It can distinguish different fluid types and their distribution in the core, and the signal strength can reflect the amount of fluid contained in that area. In this experiment, the NMR T1 curve of the core under saturated saline water conditions are measured, so the signal strength can be used to represent the degree of pore size in the core.

The NMR T1 curves show that the porosity at the entrance end of the ZT-1 and ZT-2 cores changed considerably at the end of the experiment. After the flow of CO2-saturated brine, the pore volume within 50 mm from the inlet end of core ZT-1 was significantly enlarged, and the pore volume within 60 mm from the inlet of core ZT-2 was similarly enlarged, and the magnitude of enlargement was greater. The reason is that the rock minerals at the inlet end are dissolved by carbonic acid and also scoured by the fluid, so that some solidified minerals such as quartz particles that cannot be dissolved are also scoured away from the pore surface, resulting in an increase in porosity and permeability of the core in this section, and a better pore connectivity.

In the middle section of the core (50-100 mm), the magnitude of pore change was relatively small, and the pore volume at the end of the experiment was slightly higher than the initial core pore volume. On the one hand, carbonic acid dissolution of the core led to the enlargement of the core pore space; on the other hand, the particles transported from the front end of the core blocked some of the pore throats, and subsequent particles continued to accumulate in the blockage, which led to the reduction of the pore volume. In both cores, the pore volume was slightly enlarged due to the strong influence of dissolution.

At the back end of the core (100-110 mm), the pore volume at the end of the experiment in both cores was slightly lower than the initial pore volume, mainly due to the fact that a large number of particles produced at the front end and middle section migrated to the back end and were deposited or blocked at the pore throats, which resulted in a decrease in the pore volume of the cores, and consequently a decrease in porosity and permeability, and a deterioration of the pore connectivity.

The T2 transverse relaxation time can distinguish the complexity, connectivity, and fluid mobility of rock pore structures^{[\[6\]](#page-7-5)}. By observing the size distribution of pores through NMR T2 curves, it is easier to observe the overall porosity changes before and after the experiment. The NMR T2 curves of two core were measured after the experiment, and the pore classification criteria were set as shown in Table 6.

Table 6 Classification criteria for pore types

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T2/ms	Pore type
< 0.5	Micropore
$0.5 \sim 10$	Small pore
$10 - 400$	Mesopore
>400	Macropore

Pores are classified into four types based on relaxation time, namely micropore, small pore, mesopore, and macropore. After passing through the CO₂-saturated brine flow, the rock core undergoes mineral dissolution and precipitation, thereby changing the pore size.

Both cores showed a slight increase in micropores, a decrease in small pores, a decrease in mesopores between 10-50ms, an increase in mesopores between 50-400ms, and an increase in macropores after the $CO₂$ -Brine-Rock interactions. The reason is that the fluid in the flow process is difficult to enter the micropores, mainly

into the mesopores and macropores, $CO₂$ -saturated brine dissolves the minerals, making the mesopores and macropores significantly increased, accompanied by the generation of sediment particles in the fluid carried under the action of transportation, blocking part of the pores, due to the size of the precipitation particles and the pore throat size of the matching relationship, the blocking occurs mainly in the small pores, once the blockage occurs, the subsequent particles will pile up rapidly, and the pore volume will be further reduced, resulting in the small pores becoming micropores and a small number of mesopores becoming small pores. The main part of the change occurred is the mesopore of 10- 50ms, a very small part of this pore is narrowed by plugging, most of this pore is enlarged by dissolution, and the pore larger than 50ms is enlarged as a whole by dissolution. Among them, ZT-1 core is more heterogeneous and more prone to sedimentation and blockage of precipitated particles, resulting in more small pores, and the range of change of various pores is smaller than that of ZT-2 core, and the range of change of porosity is lower.

The results of porosity and permeability measurements after the cores were washed and dried are shown in Table 7 and Figure 5.

Table 7 Data on porosity and permeability

Fig.5 Changes in porosity and permeability of cores

After a long period of $CO₂$ -Brine-Rock interactions, the porosity and permeability of the two cores increased to different degrees, with the porosity of the ZT-1 core increasing by 2.37% and permeability by 19.85%, and the porosity of the ZT-2 core increasing by 3.43% and permeability by 28.91%.

The porosity and permeability of ZT-2 core is higher than that of ZT-1, because ZT-1 core has more tiny pores, the brine saturated with $CO₂$ is difficult to enter such pores in the flow process, and fewer $CO₂$ -Brine-Rock interactions take place, so the porosity improvement is lower, and the Heterogeneity of this core is higher, and the precipitated particles are more likely to block the tiny pore throats, which has a weaker effect on the improvement of the connectivity. Therefore, the permeability increase is also lower.

Overall, dissolution occurs in the core more than particle sedimentation and blockage, and $CO₂$ -BrinerRock interactions can effectively increase the core pore volume and improve overall connectivity, thus providing space for large amounts of $CO₂$ storage.

3.1 Analysis of ions in reaction solutions

CO2-Brine-Rock interaction is accompanied by a series of chemical reactions, including the dissolution of CO2, the corrosion of minerals and the generation of precipitates, the first two reactions will increase the ion content in the brine, and the third reaction will reduce the ion content in the brine. Crude oil is mainly hydrocarbons, which has almost no effect on the ion content in brine, so the ion content in brine can reflect the change of minerals in the core to a certain extent, and the change of ion content in the reaction fluid is shown in Fig. 6 and Fig. 7.

Fig.7 Ion changes in ZT-2 core experiment solution

In the early stage of the reaction, the orthoclase and plagioclase on the pore surface were dissolve rapidly, and the K+ and Na+ contents increased rapidly, reaching a peak when the injection amount reached 0.3PV. The orthoclase and plagioclase exposed on the pore surface were basically dissolved. With the increase of the injection amount, the $CO₂$ -saturated brine further reacted with the newly exposed two types of feldspar and expanded the coverage range. The K+ and Na+ contents were still higher than the initial levels, but showed a gradually decreasing trend. The K+ and Na+ contents were slightly higher than the initial content and tended to stabilize when the injection amount was greater than 1.3PV.

 $CO₂$ dissolved in brine quickly generated HCO₃ and $CO₃²$, which rapidly reacted with $Ca²⁺$ in brine to generate CaCO₃ precipitate, and the Ca²⁺ content in the ionic solution decreased rapidly, and then the $CO₂$ saturated brine came into contact with the core, and the calcite and plagioclase on the surface of the pore space were rapidly dissolved, and the $Ca²⁺$ content in the solution increased rapidly, and it reached a peak value at about 0.5 PV, and the calcite and plagioclase on the pore surface decreased, and less and less dissolution

occurred, so the $Ca²⁺$ content in the solution decreased, and the Ca^{2+} content in the solution stabilized after the injection amount of 1.3 PV, slightly lower than that at the beginning of the experiment, which was equivalent to that in the solution after the original brine was saturated with $CO₂$ only.

The trend of Mg^{2+} content change was similar to that of $Ca²⁺$, but it was mainly produced from illite. Due to the low content of this mineral in the rock core, the degree of Mg^{2+} change in the reaction solution was relatively low. The Ba $^{2+}$ in the original solution rapidly decreased as the CO 3^2 content increased, and then the content slightly decreased and remained stable.

For HCO₃ and CO₃² ions, they increased rapidly after $CO₂$ dissolution, due to the large amount of dissolution of minerals in the early stage as well as the generation of precipitates such as BaCO₃, MgCO₃, and CaCO₃, CO₃²⁻ was rapidly consumed, and $HCO₃$ was continuously converted to $CO₃^{2-[7]}$ $CO₃^{2-[7]}$ $CO₃^{2-[7]}$, so the content of the two anions in the solution after the reaction was reduced, and the content was probably lowest at 0.5 PV. After the mineral dissolution slowed down, the content of the two ions increased rapidly, and the growth rate slowed down after the injection amount of 1.3 PV, at which time the

degree of CO2-Brine-Rock reaction was weak, and the ions that consumed CO32- were basically some of the cations in the original solution, and the mineral dissolution and precipitation almost no longer occurred.

4. CONCLUSIONS

The effects of CO₂-Brine-Rock interactions on reservoir physical properties and the effect of $CO₂$ geologic storage were investigated in terms of porosity, permeability, and mineral dissolution by conducting indoor core flooding experiment, nuclear magnetic resonance (NMR) experiments, and ion analysis of the reaction solution on two cores, and the following conclusions were obtained:

(1) The two cores have different degrees of change in the pore volume of the front, middle and back parts, in which the pore volume of the front end is enlarged the most, the middle section is slightly enlarged, and the back end is almost unchanged, or even will be reduced. Overall the porosity and permeability of the two cores are improved to different degrees, in which the porosity of ZT-1 core is increased by 2.37% and permeability by 19.85%; the porosity of ZT-2 core is increased by 3.43% and permeability by 28.91%.

(2) CO2-saturated brine can dissolve calcite and feldspar in the core in large quantities, as well as a small amount of clay minerals. K^+ , Na⁺, Mg²⁺, Ca²⁺ in the reaction solution all show a trend of rapid increase, then slow decline and finally stabilization; $Ba²⁺$ shows a trend of rapid decline, then slow decline and gradual stabilization; and HCO₃ and CO₃² all show a trend of rapid increase, then decline and then slow increase. Compared to the initial solution, the solution after injection of 6 PV shows a slight increase in K⁺, Na⁺, CO₃²⁻ and a large increase in $HCO₃$; a slight decrease in Mg2+ and Ca²⁺, and a large decrease in Ba2+.

(3) Overall, $CO₂$ -water-rock interactions increase the pore volume and connectivity of the core, providing more space for the application of $CO₂$ oil drive and its capture and storage.

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