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Experimental Study on Wettability Changes of CO_2 Flooding in Tuff Sandstone Reservoir

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ABSTRACT

The composition of tuffaceous sandstone is complex, and it is easy to react with CO_2, resulting in significant changes in wettability during CO_2 flooding. However, the change mechanism for wettability is still unclear. Therefore, researches are carried out in laboratory to study the wettability change mechanism during CO_2 flooding in a tuffaceous sandstone reservoir. A high temperature and high pressure reactor is used to establish a reaction environment of CO_2-water-minerals, the maximum temperature is 65℃, and the maximum pressure is 20 MPa. The changes of wettability, mineral composition and mineral morphology of tuffaceous sandstone reservoir rock samples were measured by contact angle meter, EDS energy spectrometer and scanning electron microscope (SEM). The SEM results show that the mineral morphology changes significantly after CO_2 contacted with the tuffaceous rock, from the original smooth and flat surface to a large corrosion pit on the surface. The contact angle increases by an average of 18.77° after CO_2-water-mineral reactions, and the wettability changes from strong water-wet to neutral-wet. The mineral composition also changes significantly after CO_2-water-mineral reactions, which is mainly manifested by the increase of Al content with a maximum increase of 142%, and the decrease of Si and K content with a maximum decrease of 32% and 54%, respectively. The change mechanism of wettability is mainly due to the transform of mineral potassium feldspar to kaolinite, and the temperature and pressure will further promote the growth of kaolinite. The innovation is to study the reaction of CO_2, water and minerals for the tuffaceous reservoir, and the mechanism of wettability change are revealed by the CO_2-water-mineral reactions. And the influence of wettability change on miscible CO_2 flooding recovery are also studied in this paper.

Keywords: Tuffaceous sand, CO_2-water-rock reaction, wettability, mineral composition, Mineral morphology

1. INTRODUCTION

An ultra-low permeability reservoir in the periphery of Daqing Oilfield has strong reservoir heterogeneity, low porosity and low permeability, and it is difficult to be developed by conventional methods[1,2,3,8,10]. Geological research shows that the reservoir is mainly tuff sandstone, a kind of sedimentary rock rich in terrigenous sedimentary clastics and volcanic clastics, which is easy to react with CO_2 and water[15,22,23,25]. Field tests show that CO_2 flooding can effectively improve the development effect of this ultra-low permeability reservoir.However, due to the characteristics of tuff sandstone, when CO_2 is injected into ultra-low permeability reservoirs, CO_2 will have complex interactions with formation water and rock minerals[11,24,26,27,28], causing changes in reservoir wettability[13,14,16]and affecting the subsequent gas injection development effect[4,6,18].

Lots of research have been done at home and abroad on the characteristics of CO_2-induced reservoir wettability changes. Some researchers believe that the wettability of reservoir rocks becomes more hydrophilic after exposure to CO_2[5,9,17,20]. For example, the research

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by Miao Xiaorui et al.[5] showed that after exposure to CO_2, sandstone core slices have the wettability changes from oil wetting to neutral wetting or water wetting. Some other studies have shown that the wettability of reservoir rocks transforms to neutral wetting after the reaction[7,19,21]. For example, Chiquet et al.[12] showed that under high pressure CO_2-water-shale system, rock wettability turns to center wetting. However, the above studies on wettability changes caused by CO_2 are mostly aimed at rock types such as conventional sandstone and shale. There are few studies on wettability changes of tuff sandstone before and after CO_2 flooding, and almost no reports have been reported. Therefore, it is necessary to carry out relevant research.

In this paper, a tuff sandstone ultra-low permeability reservoir in the periphery of Daqing Oilfield was taken as the research object. In order to clarify the relationship between CO_2 and rock wetting, static experiments were used to study the physical properties of tuff sandstone before and after CO_2 exposure with the help of high-temperature and high-pressure reactors, the rock-mineral reaction mechanism of its wettability change revealed in this paper, as well as its influence rule on CO_2 flooding performance, can provide technical support for the subsequent improvement of CO_2 flooding development.

2. EXPERIMENTAL PREPARATION AND METHOD STEPS

2.1 Experimental equipment and materials

Experimental equipment: high temperature and high pressure reaction kettle, contact angle measuring instrument, vacuum pump, HXH-1008 high pressure constant pressure constant speed pump, constant temperature box, pressure sensor, piston intermediate container, measuring cylinder, buffer bottle, Erlenmeyer flask, pipette, glass rod, dropper, beaker, stainless steel pipeline, etc.

Experimental materials: tuff sandstone core slices, high-purity CO_2 gas (analytical purity, >99.95%), simulated formation water (Salinity is shown in Table 1).

Total Salinity (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	SO_4^{2-} (mg/L)	CO_3^{2-} (mg/L)	HCO_3^- (mg/L)	Cl^- (mg/L)	Na^+/K^+ (mg/L)
5083.7	3.2	0.7	5.3	240	1107.5	342.1	821.1

The experimental setup is shown in Fig.1.

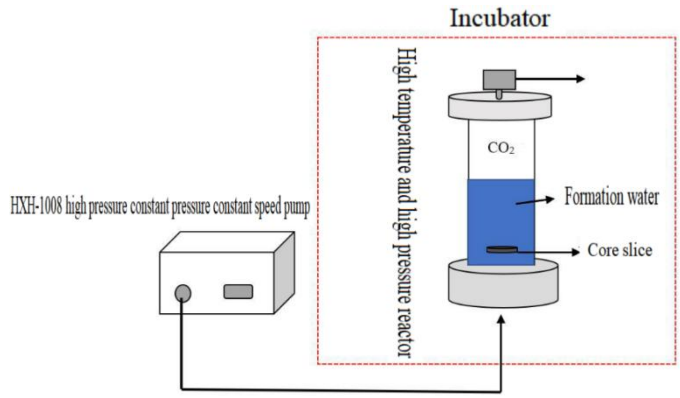

Fig. 1. Diagram of the static contact experimental setup

2.2 Experimental method and steps

To study the change rule and mechanism of rock wettability before and after CO_2 exposure. The initial wettability, mineral composition and mineral morphology of tuff sandstone reservoir rock samples were firstly determined by contact angle measuring instrument, EDS energy spectrometer and Quanta 200F emission environment scanning electron microscope. Then, the static contact experiment device was used to make the tuff sandstone slices fully contact with CO_2 and formation water under temperature and pressure conditions.After the reaction, the wettability, mineral composition and mineral morphology were measured again using the contact angle instrument, EDS energy spectrometer and Quanta 200F emission environment scanning electron microscope.The specific experimental steps are:

(1) The contact angle measuring instrument, EDS energy spectrometer and Quanta 200F emission environment scanning electron microscope were used to measure the wettability, mineral morphology and mineral composition of the tuffaceous sandstone samples before contact, and then the experimental temperature was set at 65℃ and the experimental pressure at 20MPa, the salinity of the formation water is 5000 mg/L. The rock sample, formation water and CO_2 were put in a high-temperature and high-pressure reactor, and were taken out after 24 hours.

(2) Again, the contact angle measuring instrument was used to measure the wettability, mineral composition and mineral morphology of rock samples after CO_2 exposure, and the change of wettability of rock samples before and after CO_2 exposure was analyzed to clarify the mechanism of tuff sandstone wettability change.

(3) Changing the experimental temperature to 45°C, 55°C, and 65°C, the experimental pressure to 15 MPa, 20 MPa, and the formation water salinity to 3000

mg/L, 5000 mg/L, and 8000 mg/L respectively. Then the influence of temperature,pressure and salinity on rock wettability were analyzed.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1 Changes of wettability of tuff sandstone before and after CO_2 flooding

The change of core contact angle (water-wet) under different experimental conditions is shown in Table 2. The data show that after the tuff sandstone core is contacted with CO_2 and formation water, the water-wet contact angle of the core increases and the water-wet degree decreases. And this phenomenon is not affected by reaction conditions such as reaction temperature, pressure, and formation water salinity. Even if the reaction conditions change, the contact angle after the reaction also shows an increasing trend, which leads to a change in the increase of water-wetting contact angle. Therefore, the change of wettability of tuff sandstone core is not directly related to the change of reaction conditions. The analysis may be related to the reaction of CO_2 rocks and minerals. The change of reaction conditions affects the reaction rate of tuff sandstone with CO_2 and formation water, which leads to the increase of water-wet contact angle. This may be further involved with the mechanism of wettability change of tuff sandstone.

Although the water-wet contact angle of tuff sandstone after reacting with CO_2 and formation water all showed an increasing trend, the changes are still different in the contact angle under different experimental condition. The higher the temperature, the greater the increase in the water-wet contact angle of the tuff sandstone after the reaction. The higher the pressure, the smaller the growth rate of the water-wet contact angle of tuff sandstone. The greater the salinity of formation water, the greater the increase of water-wet contact angle of tuff sandstone. This shows that the change of reaction conditions affects the chemical reaction process of the mineral components in the tuff sandstone with CO_2 and formation water, resulting in changes in the relative proportions of reactants and products. The reaction rate, reaction process and product content are different under different reaction conditions, so the internal mineral composition of the tuff sandstone changes after the reaction , which in turn changes the increase of the water-wet contact angle of the rock.

Table 2 Variation of core contact angle (water wet) under different experimental conditions

number	temperature /℃	pressure /MPa	salinity /(mg/L)	water wet contact angle/°		
				before contact	after contact	contact angle change
1	45			37.06	42.59	5.53
2	55	20	5000	37.23	55.83	18.60
3	65			36.85	78.52	41.67
4		10		37.27	75.93	38.66
5	65	15	5000	38.16	52.09	13.93
6		20		37.36	40.30	2.94
7			3000	36.73	40.17	3.44
8	65	15	5000	37.25	53.09	15.84
9			8000	37.36	57.58	20.22

3.2 Changes in mineral morphology of tuff sandstone before and after CO_2 flooding

Fig.2 shows the change of core mineral morphology before and after CO_2 flooding at different experimental temperatures. Fig.2(a) is the scanning electron microscope image of the tuff sandstone core before the reaction, and the surface of the core slice is relatively smooth. Fig.2(b)-2(d) are scanning electron micrographs of tuff sandstone cores after reaction at 45°C, 55°C, and 65°C respectively. Compared with the slice before reaction, the internal dissolution of the core after reaction is serious, and a large number of precipitated particles are produced. The kaolinite content decreased, and the content of kaolinite precipitation increased significantly. As shown in Fig.2, as the reaction temperature increases, the degree of dissolution of potassium feldspar becomes more serious, and the precipitation of kaolinite particles becomes larger. Therefore, the higher the temperature, the lower the content of potassium feldspar in the tuff sandstone after reaction, the higher the content of kaolinite, the greater the roughness of the core surface, and the greater the increase of the core contact angle.

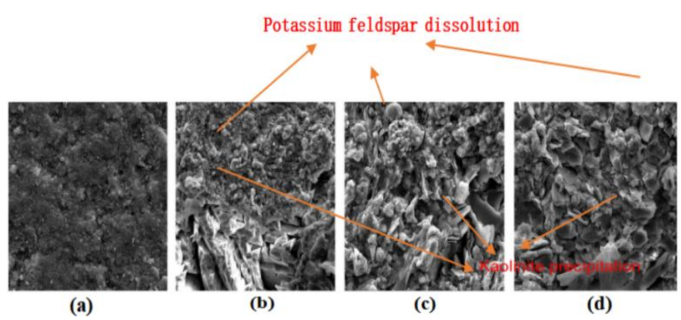

Fig. 2. Changes of core mineral morphology under different experimental temperatures ((a).Slice before reaction; (b).Slice

after reaction under 45℃; (c).Slice after reaction under 55℃; (d).Slice after reaction under 65℃)

Fig.3 shows the change of core mineral morphology before and after CO_2 flooding under different experimental pressures. Fig.3(a) is the scanning electron microscope image of the tuff sandstone core before the reaction. The surface of the core slice before the reaction is relatively smooth and flat; Fig.3(b)-3(d) are scanning electron micrographs of tuff sandstone cores after reaction under the conditions of reaction pressures of 10MPa, 15MPa and 20MPa respectively. Compared with the slice before the reaction, the internal dissolution of the core after the reaction is serious, a large number of precipitated particles are produced, the content of potassium feldspar decreases, and the content of kaolinite precipitates increases obviously. As shown in Fig.3, the reaction pressure increases, the degree of dissolution of potassium feldspar becomes smaller, and the precipitation of kaolinite particles becomes smaller. Therefore, the higher the pressure, the higher the content of potassium feldspar and the lower the content of kaolinite in the tuff sandstone after reaction, and the smaller the increase of core contact angle.

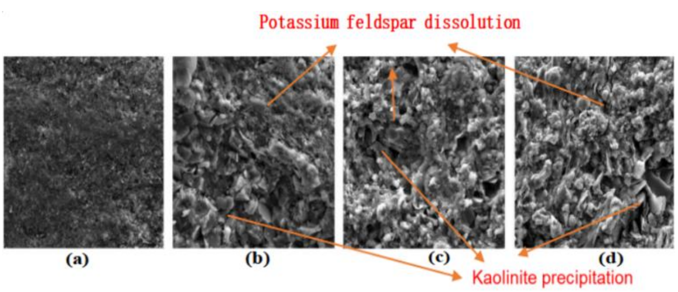

Fig. 3. Changes of core mineral morphology under different experimental pressure conditions. ((a).Slice before reaction; (b).Slice after reaction under 10MPa; (c).Slice after reaction under 15MPa; (d).Slice after reaction under 20MPa)

Fig.4 shows the changes in core mineral morphology before and after CO_2 flooding under different formation water salinity conditions. Fig.4(a) is the electron microscope scanning image of the tuff sandstone core before the reaction. Fig.4(b)-4(d) are scanning electron micrographs of tuff sandstone cores after reaction under the conditions of reaction pressures of 3000mg/L, 5000mg/L and 8000mg/L, respectively. Compared with before the reaction, the internal dissolution of the core after the reaction is serious, a large number of precipitated particles are produced, the content of potassium feldspar decreases, and the content of kaolinite precipitates increases obviously. As shown Fig.4, the salinity of the reaction formation water increases, the degree of dissolution of potassium feldspar becomes more serious, and the precipitation of kaolinite particles becomes larger. Therefore, the higher the salinity of the formation water, the lower the content of potassium feldspar and the higher the content of kaolinite in the tuff sandstone after reaction, the lower the roughness of the core surface, and the greater the increase of the core contact angle.

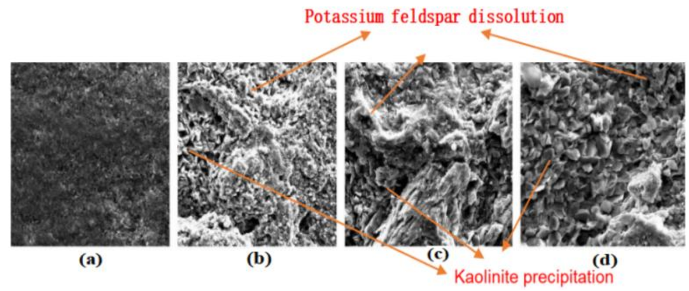

Fig. 4. Changes of core mineral morphology under different formation water salinity conditions. ((a).Slice before reaction; (b).Slice after reaction under 3000mg/L; (c).Slice after reaction under 5000mg/L; (d).Slice after reaction under 8000mg/L)

3.3 Changes of mineral components of tuff sandstone before and after CO_2 exposure

The changes of tuff sandstone mineral components before and after the reaction under different experimental conditions are shown in Table 3. The data show that the weight percentages of Al, Si, K and other elements before the reaction are 5.96%, 42.37%, 3.98% and 47.69%, respectively. After contacting with CO_2, the mineral composition of tuff sandstone changes, and the general trend is that the content of Al element increases, and the content of Si and K element decreases. It shows that in the CO_2-rock-water reaction system, potassium feldspar ($KAlSi_3O_8$) in rock minerals is transformed into kaolinite ($Al_2Si_2O_5(OH)_4$) precipitation[7], and the specific chemical reaction equation is:

$$KAlSi_3O_8+H^+\rightarrow Al_2Si_2O_5(OH)_4+2K^++H_2O+SiO_2$$

According to the chemical equation, after the tuff sandstone is in full contact with CO_2 and water, the potassium feldspar in the mineral will transform into kaolinite, which is manifested by the increase of Al element content and the decrease of Si element content and K element content. Potassium feldspar belongs to hydrophilic minerals, and kaolinite belongs to lipophilic minerals, which leads to the decrease of hydrophilic mineral content and the increase of lipophilic mineral content in rocks. And the roughness of the rock surface further increases with the generation of precipitation, which eventually leads to the increase of the water-wet contact angle of the tuff sandstone rock and the decrease of the water-wet degree of the core.

When the experimental conditions are changed, the variation range of the mineral composition of the tuff sandstone changes accordingly. As the temperature increases, the extent of the increase of the Al element becomes larger, and the extent of the decrease of the Si element and K element increases. It shows that with the increase of temperature, the rate of chemical reaction increases, the amount of dissolved potassium feldspar and the amount of kaolinite precipitated gradually increase. After causing a reaction, the reduction of hydrophilic mineral content in the core increases, the increase of lipophilic mineral content increases, and the increase of rock water-wet contact angle increases. As the pressure increases, the range of increase of Al element becomes smaller, and the range of decrease of Si element and K element becomes smaller. It shows that as the pressure increases, the solubility of CO_2 in the formation water increases, which inhibits the conversion reaction of potassium feldspar to kaolinite, and the amount of kaolinite precipitation gradually decreases. After causing a reaction, the reduction of hydrophilic mineral content in the core decreases, the increase of lipophilic mineral content decreases, and the increase of rock water-wet contact angle is also smaller. As the salinity of formation water increases, the range of increase of Al element increases, and the range of decrease of Si element and K element increases. It shows that with the increase of formation water salinity, the greater the ion concentration in the formation water, the greater the reaction rate, and the dissolved amount of potassium feldspar and the amount of kaolinite precipitated gradually increase. After causing a reaction, the reduction of hydrophilic mineral content in the core increases, the increase of lipophilic mineral content increases, and the increase of rock water-wet contact angle increases.

Table 3 Mineral composition of tuff sandstone before and after reaction under different experimental conditions

number	temperature /℃	pressure /MPa	Salinity /(mg/L)	Al element /%	Si element /%	K element /%	Other elements /%
0	Before the reaction			5.96	42.37	3.98	47.69
1	45	20	5000	6.72	39.13	3.38	50.77
2	55			8.57	34.45	2.96	54.02
3	65			9.99	28.66	2.27	59.08
4	65	10	5000	10.71	36.39	1.82	51.58
5		15		7.02	39.27	2.96	50.75
6		20		6.59	41.11	3.19	49.11
7	65	15	3000	6.64	39.23	3.91	50.22
8			5000	7.95	33.86	2.98	55.21
9			8000	14.41	30.68	2.83	52.08

4. CONCLUSIONS

The wettability changes of a tuff sandstone reservoir under CO_2 condition were studied, and its influence factors including temperature, pressure and water salinity were also analyzed in this paper. Mainly conclusions can be drawn as follows.

(1) After the tuff sandstone fully contacts and reacts with CO_2 and formation water, the internal corrosion of the reacted tuff sandstone is serious, the content of potassium feldspar decreases, the content of kaolinite precipitation increases significantly, and the water-wet contact angle of the core increases. The general trend is that the degree of water-wet decreases.

(2) After the tuff sandstone rocks fully contacted and reacted with CO_2, the mineral composition changed significantly, mainly showing the trend of increasing the content of Al element and decreasing the content of Si and K element, indicating that in the reaction system, the potassium feldspar in the rock minerals occurs a dissolution reaction, which then transforms into kaolinite precipitate.

(3) The greater the reaction temperature, the greater the chemical reaction rate, the greater the amount of kaolinite precipitation, and the greater the increase in the rock water-wet contact angle;The higher the pressure, the greater the solubility of CO_2 in formation water, which inhibits the dissolution reaction of potassium feldspar, the smaller the amount of kaolinite precipitation, and the smaller the increase in the rock water-wet contact angle. As the salinity of formation water increases, the greater the ion concentration in the formation water, the greater the reaction rate, the greater the amount of kaolinite

precipitation, and the greater the increase in the rock water-wet contact angle.

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DECLARATION OF INTEREST STATEMENT

I solemnly declare that none of the authors involved above have known competing financial interests or personal relationships. It is unlikely to affect the work reported in this article. All authors read and approved the final manuscript.

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