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Insights into mechanism of wettability alteration caused by CO2-brine-rock interactions from interfacial features of brine-rock viainter molecular forces#

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ABSTRACT

Wettability is a significant attribute in CO_2 geosequestration and CO_2 Enhanced Oil Recovery (CO_2-EOR) operations, and affects the transport law, capture capacity, sealing capacity and leakage possibility of supercritical CO_2 in tight sandstone reservoirs. However, the supercritical CO_2-brine-rock reaction leads to wettability alteration of tight sandstone, and the mechanism remains unclear. In this paper, Zeta potential measurement, Fourier Transform infrared spectroscopy (FTIR) and atomic force microscopy (AFM) were used to characterize the surface properties of tight sandstone. Results show that with the increase of reaction time, the mineral composition of tight sandstone changes, the absolute value of zeta potential decreases, the electrostatic force decreases, but the content of hydrophilic uncharged groups increases, the van der Waals force and hydrogen bond force increase, and finally the hydrophilicity increases.

Keywords: Carbon Capture, CO_2 geosequestration, CO_2-EOR, wettability altertion, CO_2-brine-rock reaction

1. INTRODUCTION

CO_2 geosequestration and CO_2-EOR is an important part of Carbon Capture, Utilizationand Storage (CCUS) technology, which is an internationally recognized disposal method for reducing CO_2 emissions[1-2]. In CO_2/ brine/rock three-phase system, wettability directly affects the saturation of non-aqueous phase fluid, fluid morphology, relative permeability and capillary force[3]. It determines the transport law, capture capacity, sealing capacity and leakage possibility of supercritical CO_2 in reservoir[3]. However, the supercritical CO_2-brine-rock reaction leads to the wettability altertion of tight sandstone[1-2]. Previous studies attributed wettability altertion mainly to rock mineral composition change and surface roughness increase[1-2], and the mechanism remains unclear.

The essence of wettability is the behavior of the CO_2/ brine/rock interface resulting from their respective material properties[4-5]. For instance, the surface properties of tight sandstone and the ionic composition of formation water determine the wettability angle. Inductive coupled plasma emission spectrometer (ICPES) technology can be used to obtain the ionic composition of formation water, but it is difficult to fully characterize the surface properties of tight sandstone. Although surface roughness and surface charge density can be obtained by AFM technique and Zeta potential measurement respectively, the information of surface functional groups lacks reasonable experimental characterization[1-5].

Rock surface is covered with numerous functional groups, generally including C-O group, COOH group, OH group, C=C group, C=O group, etc[6-7]. The interaction of functional groups is manifested as various microscopic forces[6]. Therefore, the intermolecular forces can be used to understand the interface characteristics of CO_2-brine-rock, and then reveal the wettability alteration mechanism of tight sandstone reservoirs[8].

Fourier Transform infrared spectroscopy (FTIR) is the best method to characterize the functional groups on the rock surface. The movement of functional groups obeys the law of quantum mechanics, and the energy absorption will lead to energy level transition[8-9]. At the same time, the vibrational energy of the covalent bond of the functional group atoms will change correspondingly. FTIR can be used to measure the vibration of covalent bonds to identify functional groups. In addition, peak fitting by ORIGIN software can get the content of functional groups[8-9].It has been widely used in petrochemical industry, metal-organic chemistry, biology, medicine and environment[10].

Inspired to improve the understanding of the wettability alteration mechanism caused by CO_2-brine-rock interactions, we injected supercritical CO_2 into tight sandstone cores saturated with 0.1mol/L NaCl solution at constant temperature and pressure. Then, AFM, Zeta potential measurement and FTIR were used to characterize the surface properties of tight sandstone with different reaction times. Ultimately, the micro mechanism of wettability transition of tight sandstone is described by contact angle test.

2. EXPERIMENTAL SECTION

2.1 Materials and setup

Table 1. Petrophysical properties of samples.

Sam -ple	Diamet-er(mm)	Length (mm)	Permeabi-lity (mD)	Porosi -ty (%)	Reaction time (h)
C0	24.93	49.99	0.1063	10.99	0
C1	25.06	50.01	0.1024	11.26	6
C2	25.11	50.03	0.0986	10.68	12
C3	24.98	49.95	0.1231	12.09	24
C4	25.09	50.13	0.1128	11.24	48

The samples are from the Yanchang Formation of the Upper Triassic in Ordos Basin, and their properties are shown in Table 1. Firstly, 0.1mol/L NaCl solution was saturated, and then CO_2-brine-rock reaction experiments were carried out at different reaction times. Meanwhile, confining pressure, outlet back-pressure, temperature and injection pressure were set to 15 MPa, 8.5 MPa, 45◦C and 9 MPa, respectively. The experimental device was shown in Figure 1. At each designed reaction time, contact angle, AFM, Zeta potential and FTIR were made.

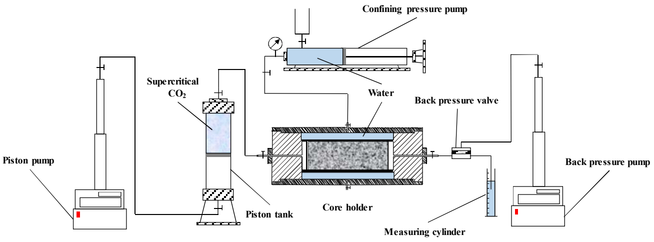

Fig. 1. Schematic diagram of the experimental setup.

2.2 Experimental methods

Contact angle measurement: The test instrument is SINDIN SDC-200 optical contact angle measuring instrument with accuracy of 0.1°. The samples in different states were sliced, dried, and polished successively with sand paper of 500 mesh, 1000 mesh, 2000 mesh, 5000 mesh to reduce the influence of roughness on measurement. The liquid phase method was used to collect contact angle images every 30 minutes until stable droplets were formed. Each measurement was repeated five times.

Zeta potential measurements: 1g rock powder of 200 mesh was added into 0.1mol/L NaCl solution, stirred evenly and stood for 30min to form a stable suspension system. Then the supernatant was taken and the Zeta potential was measured by Delsa^{TM} nano Zeta potentiometer. Each measurement was repeated five times.

FTIR measurements: Mix 0.5 mg rock powder (200 mesh) with 120 mg potassium bromide and compress it into transparent sheet in vacuum. Then, the transparent sections were placed in the MAGNA-IR 560 E.S.P. infrared spectrometer (spectral wavelength range of 400-4000 cm^{-1} and resolution of 4 cm^{-1}) to measure the transmission spectra of the dense rock samples.

AFM tests: Agilent 5500 AFM was used to determine the roughness and surface morphology of the samples after polishing (with a maximum mesh of 5,000). Each sample was scanned 3 times at different locations. The scanning area of the probe is 6 μm × 6 μm, scanning rate is 1.5 Hz, and elastic constant is 0.5 N/m.

2.3 Results

As shown in Figure 2 (a), with the increase of CO_2 injection time, the contact angle decreases continuously and the rock becomes more water-wet. Apparently, CO_2-brine-rock reaction is the main factor for this phenomenon[1-3], which will cause changes in rock surface properties (Zeta potential, surface functional groups and roughness). According to our experimental results (Figure 2 (b)), the absolute value of Zeta potential decreases with the duration of CO_2 injection, preventing water from spreading on the rock surface[3]. Therefore, Zeta potential is not a key factor in wettability alteration.

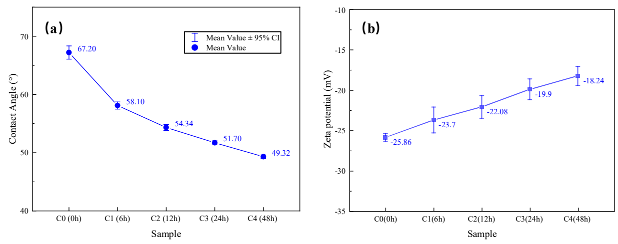

Fig. 2. Results of (a) Contact angle, (b) Zeta potential.

After the sample is irradiated by infrared light source, it absorbs light of specific wavelength and produces corresponding absorption peak, forming absorption spectrum (Figure 3). It can be found that the height and area of the absorption peak in the absorption spectrum of the samples have changed, but no new absorption peak has been generated, and the overall trend is similar. Meanwhile, this indicates that CO_2-brine-rock reaction changes the content of surface functional groups, and no new functional groups are formed. Numerous studies have shown that both C-O and C=O groups are hydrophilic and affect the wettability of rock[8-9], so we mainly study the changes of them.

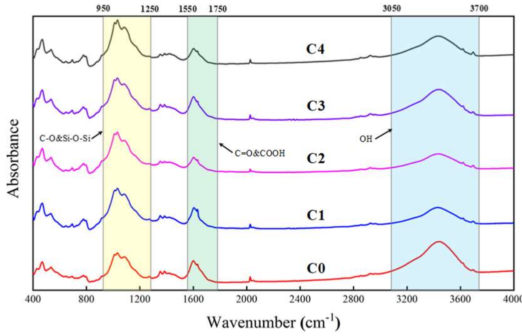

Fig. 3. Results of FTIR spectra.

The adjacent absorption peaks in the infrared spectrum always influence each other as combined frequency peaks[8]. For instance, the combined frequency peaks of Si-O-Si and C-O groups are in the 950-1250 cm^{-1} range, and the combined frequency peaks of COOH and C=O groups are in the 1550-1750 cm^{-1} range[9]. A single functional group can be quantitatively analyzed through the peak fitting function of Origin software. As shown in Figure. 4 (a) and (b), and the C=O groups' peaks at 1657cm^{-1} and 1675cm^{-1}. Obviously, the contents of C-O groups and C=O groups increase with the increase of CO_2-brine-rock reaction time, which may be one of the main factors of wettability alteration.

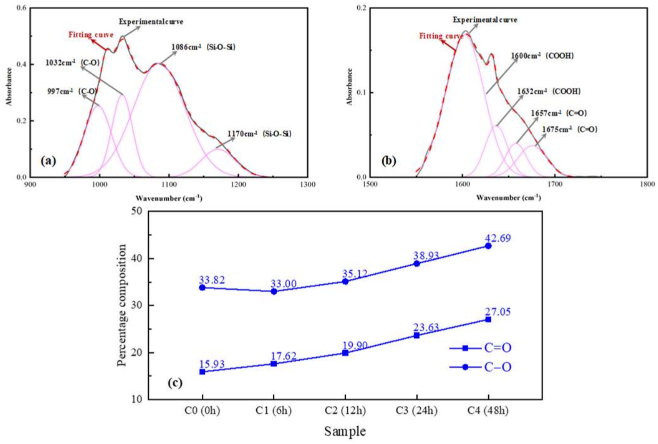

Fig. 4. Schematic diagram of FTIR (Fitting curve of frequency combination peak: (a) 950-1250 cm^{-1}; (b) 1550-1750 cm^{-1}; (c) Change curve of hydrophilic groups content).

The surface roughness of rock is closely related to wettability and rough surface promotes water spreading. The results of AFM are shown in Figure.5, with the progress of CO_2-saline-brine reaction, the roughness of rock surface increases from 4.16nm to 31.53nm. Apparently, the change of surface roughness should also be one of the main factors of wettability alteration.

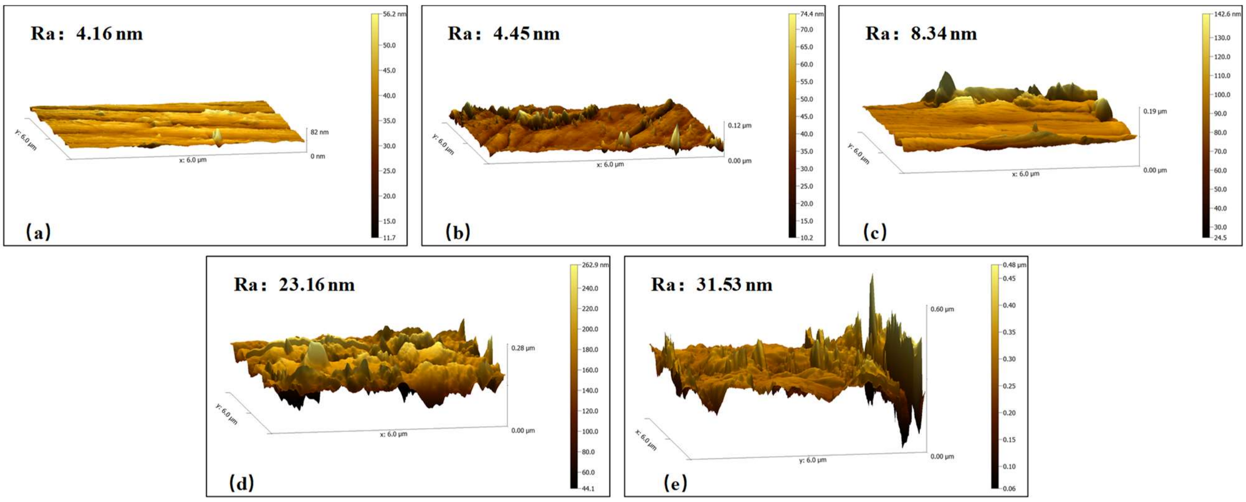

Fig. 5. Results of AFM ((a) C0, (b) C1, (c) C2, (d) C3, (e) C4).

3. DISCUSSION

According to the experimental results, the wettability of tight sandstone changes to hydrophilic continuously with the progress of CO_2-brine-rock reaction, which is manifested by the decrease of contact angle. As shown in Figure 6, we plotted the relationship between rock surface properties and wettability angle into diagram to explore the principle of wettability alteration. Although the decrease of the absolute value of Zate potential reduces the attraction of rock surface charge to counterions in brine, the increase of hydrophilic groups C-O and C=O makes water molecules more easily adsorbed on rock surface. Meanwhile, the increase of surface roughness caused by rock dissolution increases the contact area between rock and brine, and finally the rock becomes more hydrophilic (Figure 7).

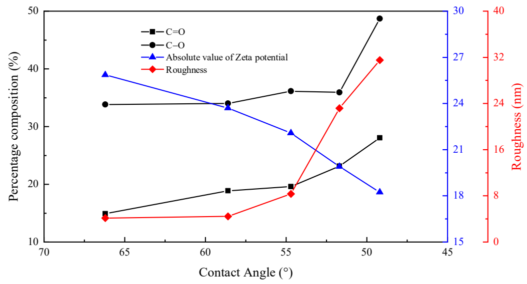

Fig. 6. Analysis diagram of influencing factors of wettability

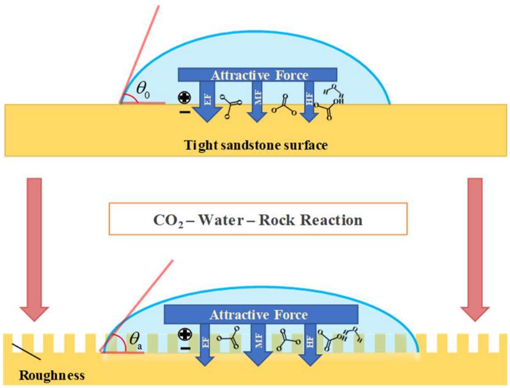

Fig. 7. Schematic of the mechanism of wettability alteration, where MF, HF and EF represent intermolecular force, hydrogen-bonding force and electrostatic force, respectively.

4. CONCLUSIONS

According to the contact angle measurements, Zeta potential tests, FTIR analysis and AFM measurements, it is confirmed that wettability alteration caused by CO_2 injection was mainly caused by the increased hydrophilic groups (C=O and C–O groups) and surface roughness. In addition, wettability is the macroscopic expression of liquid and rock surface under the action of various microscopic forces. Our experimental method can accurately and comprehensively characterize the surface properties of rocks, contribute to a better understanding and control of wettability, and ultimately promote the development of CO_2 geosequestration and CO_2-EOR.

ACKNOWLEDGEMENT

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