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Effect of Gas-wetting on Dispersing Properties of Clay Minerals in Condensate Gas Reservoir

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Abstract: The condensate gas reservoir output could be enhanced significantly with the gas-wetting reversal FC-1. However, changes in the wettability have been shown to affect dispersion properties of clay minerals in condensate gas reservoir. With the gas-wetting realized on the montmorillonite (MMT), zeta potential and cation exchange capacity (CEC) change with wettability reversion were studied in this paper, and the mechanism of it was also analyzed. The *zeta* potential of 100 $\sim$ 200 mesh MMT reached to -17.27mV and gradually approached to non-dispersion condition; with FC-1 concentration increased, CEC decreased sharply from 2.14 to 0.2. The microstructure of MMT was analyzed by SEM and TEM, and conclusions were drawn that fluorocarbon chain FC-1 had been attached on the surface of MMT particles and formed a gas-wetting reversal film which maintains their stability.

Keywords: Gas-wetting, montmorillonite, dispersion, zeta potential, cation exchange capacity.

1 Introduction

Condensate gas reservoir is a kind of complex oil/gas accumulation between oil and gas reservoir, which exists in gas form under original temperature and pressure [Sun (2003)]. Pressure-decline is a conventional method in oil/gas exploitation, however, this may not be an appropriate approach for gas condensate reservoir. The retrograde condensation near wellbore as pressure drops below the dew point occurred easily, leading to a sharp decline in gas output [Pang and Liu (2010); Delavarmoghaddam (2009)]. To address these problems, the gas-wetting reversal method has been applied to enhance the condensate gas reservoir recovery [Li and Firoozabadi (2000); Firoozabadi (2005)]. However, changes in the wettability

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would affect the dispersion of clay minerals in rocks, thus the wellbore stability is sure to be affected.

The former research on clay minerals dispersion and drill cuttings expansion is methodical. The influence factors of the investigation include chemic composition and crystal structure of clay minerals, dispersiveness of clay (specific surface) and theory of pH influence [Delville (1993)]. However, the expansion and dispersion changes by wettability reversion have not yet been studied.

In this paper, MMT is converted to gas-wetting with the gas-wetting reversal FC-1 which is developed by our lab and had good performances in field application [Li and Jiang (2012); Feng (2012)], and the dispersion properties, including zeta potential and CEC are measured. The relation between MMT dispersion and gas-wetting, and the mechanism of it are also studied.

2 Materials and approaches

2.1 Instruments and reagents

Electric mixer, drying oven, ZetaSizer NanoZS, electric furnace, conical flask, Quanta 200F scanning electron microscopy, JEM-2100 LaB_6transmission electron microscope.

Gas-wetting reversal FC-1, MMT, methylene blue, H_2SO_4, H_2O_2. MMT is used to simulate the clay minerals in rocks and the content are shown in Tab.1.

Table 1: : Clay mineral information bu X-ray diffraction

Clay mineral	S	I/S	I	K	C	C/S
Content,%	91	/	3	6	/	/

2.2 Experimental steps

2.2.1 The gas-wetting reversion of MMT

Several grams of 100-200 mesh and 200-400 mesh MMT are immersed in 100mL FC-1solution with concentration of 1% for 4 hours. After the gas-wetting reversal agent being fully absorbed on the MMT surface, the mixture is placed in an 105° oven for drying for 24 hours, and then grinded and cooled in room temperature .

2.2.2 Zeta potential measurement

The solution with a concentration of 1% is made by the gas-wetting MMT in 2.2.1 which is added to distilled water. This suspending liquid is stirred for 5min in the condition of high speed, and diluted to a concentration of 0.05% after being stirred for 30min and kept still for 24hours. The ZetaSizer NanoZS is adopted to test the zeta potential. All experiments were performed at room temperature (22°±3°) , and the pH value of suspending liquid tested is about 7.

2.2.3 CEC measurement

The CEC of MMT is estimated by the MBC. The solution with a concentration of 4% is made by the gas-wetting MMT in 2.2.1 added to distilled water and kept still for 24hours. The 2mL solution being taken is added into a conical flask with 10mL distilled water. The 15mL H_2O_2 solution of 3% and 0.5mL sulfuric acid of 2.5mol/L are added into it. Slowly boil it for 10min but not dried, and then dilute it with water to 50mL.

The methylene blue solution of 0.01mol/L is dripped into the conical flask in dose of each 0.5mL and shake for 30s.Under the state of solid suspended, a drop of liquid is dripped on the filter paper with stirring rod, when the dye shows turquoise ring around the dyed solid, the end point of titration has been reached. When the turquoise ring extends outward from spots, shake conical flask for 2min and take a drop on the filter paper, if the turquoise ring is still apparent, it has reached the ending. Otherwise, continuing previous operations until the ring is showed on the filter. The MBC is calculated according to Formula 1.

$$MBC = \frac{V_m}{V} \tag{1}$$

MBC——methylene blue capacity;

V_m*——methylene blue consumption;*

V—— sample volume;

2.2.4 Structural analysis

The MMT treated by FC-1 is observed by Quanta 200F scanning electron microscopy and transmission electron microscope, and the energy spectrum is also analyzed.

3 Results and discussion

The clay minerals of X-ray diffraction analysis from Tab.1 shows that the main component of clay samples selected is MMT, which relatively accounts for 91% of the total, and contains a small amount of kaolinite and illite.

3.1 *Zeta potential of gas-wetting MMT*

When the zeta potential of clay is less than -60mV, it belongs to the extreme dispersion, when the zeta potential is -40mV, it belongs to the strong dispersion, when the zeta potential is about -20mV, it belongs to the possible dispersion; when the zeta potential is around -10mV, it does not belong to the dispersion.

As shown in Fig.1, with the concentration of FC-1increases, the zeta potential of MMT increases gradually. It transformed gradually from the strong dispersion to possible dispersion. When the concentration of the gas-wetting reversal agent eventually reaches 100%, the zeta potential rise to17.27mV and it approaches the non-dispersion state.

Under the same conditions of gas-wetting reversion treatment, the increased amplitude of the zeta potential of 200-400 mesh MMT is more than that of 100-200 mesh. The reason is that the surface area of 200-400 mesh is larger and the gas-wetting reversal agent is absorbed by its surface to form a membrane, so the decrease of its surface negative charges leads to the increase of the zeta potential

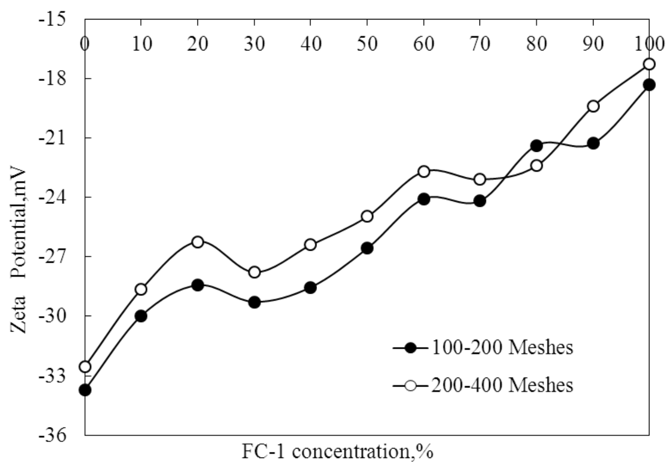


Figure 1: Relation between FC-1 concentration and zeta potential

3.2 *CEC of gas-wetting MMT*

It can be seen from Fig.2, the CEC MMT sharply declines with the concentration of the gas-wetting reversal agent increases. MBC drops from 2.14 to 0.2. It is obvious that the CEC of the MMT after gas-wetting reversion declines and stability enhances. The reason is that the gas-wetting reversal agent FC-1 is absorbed by the surface of MMT to form a stable membrane, which protects its internal negative charges and prevent neutralization reaction of cation and negative charges. It is similar to the zeta potential rule.

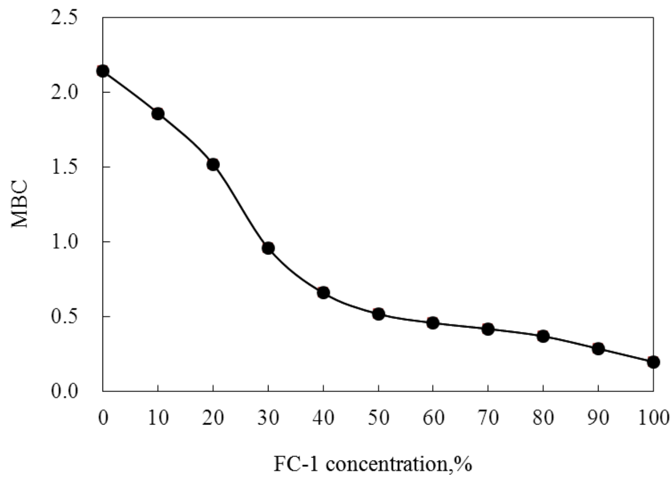


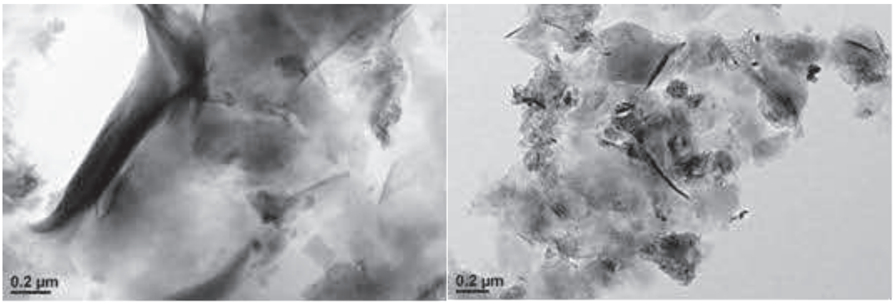
Figure 2: Relation between FC-1 concentration and *MBC*

3.3 SEM and TEM analysis

Scanning electron microscopy (SEM) is an effective method to investigate the aggregation of mineral crystal, and the transmission electron microscopy (TEM) is used to observe microstructure. The energy spectrum observed by SEM and images observed by TEM are shown in Tab.1 and Fig.3.

Table 2: Elements content of MMT

Element	Untreated		Treated	
	Wt%	At%	Wt%	At%
C	0.00	0.00	15.91	25.05
O	36.66	50.02	29.05	34.34
F	0.00	0.00	10.30	10.25
Na	2.44	2.31	1.66	1.37
Mg	3.86	3.47	1.83	1.42
Al	11.81	9.55	7.46	5.23
Si	43.05	33.46	31.76	21.38
Ca	2.18	1.19	2.04	0.96



Natural MMT Gas-wetting MMT

Figure 3: TEM of MMT

It can be seen from Tab.1 that the main elements of natural MMT are silicon and oxygen, and the quality percentage of silicon is 43.05%, oxygen for 36.66% but no fluorine. With the MMT is treated by FC-1, the quality percentage of oxygen drops to 29.05%, the quality percentage of fluorine up to 10.30%. The above results show that the fluorine alkyl of the FC-1 attached on the MMT and form a gas-wetting film to keep stability.

From Fig.3 we can see that the gas-wetting reversal FC-1 has coated the MMT and make it hard to disperse in water. The fluorine alkyl chain coated MMT and orderly occupied the solid/air interface, which makes the surface present hydrophobicity and oleophobicity, and the MMT stability enhanced eventually.

4 Conclusions

Through the above experimental and analysis results, draw the following conclusions:

(1) The dispersion property of MMT which is treated by the gas-wetting reversal agent FC-1 gradually decrease, transform from strong dispersal to non-dispersal.

(2) As the concentration of the gas-wetting reversal agent FC-1 increasing, the CEC of MMT dramatically decreases and the stability enhances.

(3) SEM and TEM results shown that the gas-wetting agent FC-1could attach on the MMT surface firmly and make it hard to disperse in water solution.

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