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EXPERIMENTAL STUDY ON A NOVEL WETTABILITY ALTERATION AGENT IN TIGHT SANDSTONE GAS RESERVOIR

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This paper introduces a hydrophobic wettability alteration agent named FCS that effectively eliminates «water blocking» by forming a tight molecular film on the sandstone surface. Wettability alteration experiments show that a tight molecular film forms, making it hydrophobic with a contact angle greater than 90°. The inner wall of a capillary tube after FCS treatment changes from liquid-wetting to gas-wetting, and the capillary pressure becomes a positive driving force. Experimental study demonstrates that altering wettability of tight sandstone to produce a hydrophobic surface is a viable method for recovering permeability and eliminating «water blocking».

Keywords: water blocking, wettability alteration, tight gas sandstone reservoir, hydraulic fracturing.
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1. Introduction

Hydraulic fracturing is commonly used in tight reservoirs but during the fracturing process, large quantities of fluids are lost in formation. Liquid invasion is referred to as «water blocking», which is the main damage in tight reservoirs as well as low-permeability and ultra-low-permeability reservoirs.

Many scholars have carried out research on «water blocking». Early studies by McLeod and Coulter [1]showed that alcoholic acid mixtures of isopropyl alcohol or methanol and hydrofluoric/ hydrochloric acid help water removal and improve the cleanup rate in gas wells. Al-Anazi et al. [2] investigated the possibility of methanol treatment to remove water blockage. Kumar [3] and Bang [4,5] reported the increase in the gas relative permeability of sandstone reservoir cores treated using a nonionic surfactant soluble in a methanol/water mixture. Unfortunately, all of these techniques provide only a temporary solution to the problem and are not applicable in some cases because of the reservoir condition or economic deficiencies [6-8].

Tang and Firoozabadi [9,10] measured the relative permeability before and after treatment using a fluorochemical polymer, but a reduction in the gas relative permeability was observed. Noh and Firoozabadi [11,12] used two chemicals, a fluorochemical surfactant and fluoroacrylate copolymer, to test core samples. Their experimental results demonstrate that this treatment is effective in recovering the permeability of tight reservoir cores and altering the wettability to gas-wetting to increase gas production. Since then, many scholars, including, Fahimpour [13] and Bertoncello [14], conducted wettability alteration research on the gas-wetting of tight sandstone and low-permeability reservoirs. All of these studies have been limited to conventional experimental evaluations on imbibition, displacement and irreducible water saturation and the verification of the effect of wettability alteration on the resolution of water blocking from the macroscopic perspective.

This paper introduces a hydrophobic wettability alteration agent named FCS that effectively eliminates «water blocking» by forming a tight molecular film on the sandstone surface. The change in the wettability of the sandstone surface and capillary inner wall was studied after FCS treatment. The effect on the direction of the capillary pressure was determined via microscopic visualization experiments.

2. Experiments

2.1. Materials

Formation water was from HF-3 well of JianNan tight sandstone reservoir and the total salinity is 37.685 mg/L.The injected gas for displacement was Nitrogen with a density of 1.36 g/cm^3 and a viscosity of 0.0176 mPa·s at ambient conditions. The filtrate was from a commercial gum fracturing fluid and the density is 2.25 g/cm^3. The tight sandstone core samples were obtained from XuJiahe 6 Member of JianNan tight sandstone reservoir. The core samples were cylindrical with a diameter of 2.54 cm and a length of 5.06 cm. The glass capillary tubes were hollow cylinders with a diameter of 1mm and length of 5cm.

2.2. Experimental setup

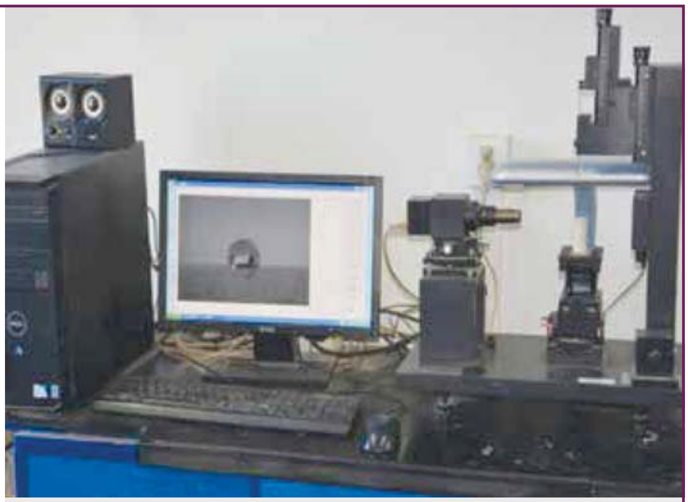
The experimental setup shown in figure 1(a) was used to analyze elements and examine surface appearance of tight sandstone cores surface before and after FCS treatment. Figure 1(b) was used to measure solid-liquid contact angle.

2.3. Experimental procedure

1. Confirmation of the optimal dosage

Prepare FCS solutions with different concentrations. Soak tight sandstone cores with similar permeability in the FCS solution for 1 h. Wash surface of the cores with distilled water, and then, dry them in air. Drip the same quantity of distilled water on the surface of

(a) Experimental set-up of energy spectrum analysis and surface appearance of cores



(b) Experimental set-up of solid-liquid contact angle measurement

Fig.1. Experimental setup of FCS performance evaluation

cores treated by FCS. Measure the solid-liquid contact angle using five-point measurement method. Plot the concentration against the contact angle, and confirm the optimal dosage of FCS from the curve.

2. Film structure of hydrophobic surface

The elements on the surface of tight sandstone cores were subjected to an energy spectrum analysis using a Quanta200F scanning electron microscope (fig.1(a)). The cores were soaked in 1% FCS solution for 1 h, and then, the surfaces were washed with distilled water and dried in the air.

The elemental composition of the surfaces of cores was analyzed after FCS treatment to explain film structure of wettability alteration of tight sandstone surfaces treated by FCS.

3. Change in wettability on the surface of cores

Three similar permeability cores were used to conduct the experiment. One of the three was soaked into FCS solution at room temperature, and another was soaked in FCS solution heated at 80 °C for 30 min. After 1 h, these two cores were washed with distilled water and dried in the air. An equal quantity of fracturing filtrate was dripped on the surface of the three cores one by one, and the contact angle was measured after 1 min to evaluate the change in the wettability.

4. Change in the hook face of capillary in the micro-fractures

Because of high content of quartz in tight sandstone reservoirs, a glass capillary was used to simulate the microfracture of a tight sandstone core. Two glass capillaries with the same pipe diameter were taken to conduct the experiment. One was soaked into FCS solution heated at 80 °C for 30 min, and the capillary was taken out after 1 h. Fracturing filtrate was sucked into each of the two capillaries, and then, natural gas was pumped at 0.2 ml/min speed to displace the liquid phase. The change of the hook face direction was observed by optical microscopy to study impact of wettability change of capillary inner walls on the direction of the capillary pressure.

5. Compatibility and surface tension

The FCS solution was prepared at the optimal concentration to mix with formation water and fracturing filtrate in equal volumes. At room temperature and 80 °C, the mixture solution was checked for delamination or sedimentation after 2 h.

Cleanup additive and FCS were prepared in an equal proportion solution and measured by an automatic interfacial tensiometer after heating for 2 h at 80 °C to determine the influence on the surface tension effect of the FCS solution following high-temperature processing.

3. Experimental results

3.1. Optimal dosage

After being treated with FCS solutions of different concentrations, the surface wettability of cores experienced changes. The optimal dosage of FCS can be confirmed by the corresponding relationship between solid-liquid contact angle and concentration. The results are presented below.

Figure 2 illustrates that the solid-liquid contact angle increases with an increasing dosage of FCS, indicating the strengthening of gas wettability at the surface of cores. When the concentration of FCS reaches 1%, the solid-liquid contact angle reaches its peak; as it exceeds further, the solid-liquid contact angle reaches a plateau, indicating that further increases in the concentration of FCS have no impact. Hence, 1% is determined to be the optimal dosage.

3.2. Film structure of hydrophobic surface

When FCS contacts the sandstone surface, its alkene oxygroup connects with the hydratable silane on the surface of sandstone through covalent bonding. FCS contains a great number of repetitive alkene oxygroup units, each of which will connect with the hydratable silane on the surface of sandstone, forming a thin and tight polymer film, as shown in figure 3 and figure 4.

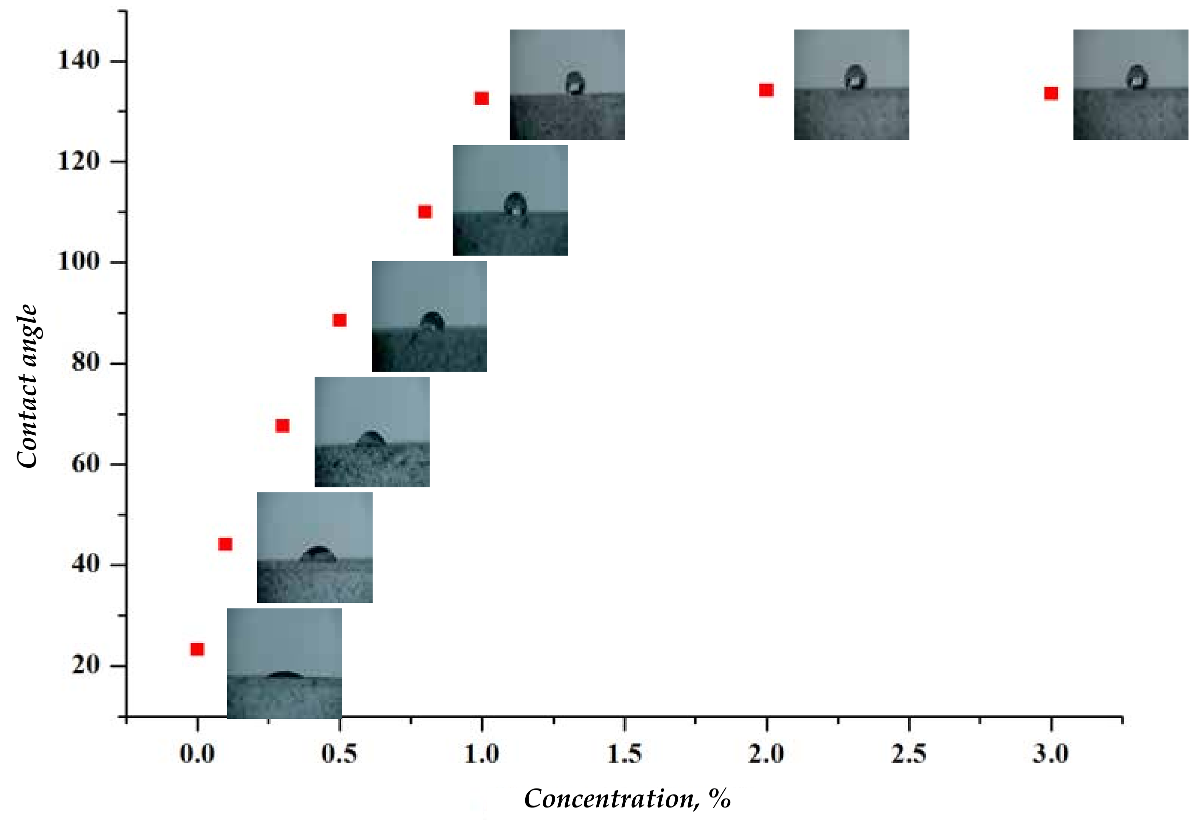


Fig.2. Relationship between solid-liquid contact angle and concentration

Figure 3 illustrates that the original surface of the sandstone is rough and uneven and that clay components are exposed at the surface. Figure 4 illustrates that the surface of sandstone soaked in 1% FCS is even and flat, and little clay is exposed at the surface. When soaked in the 1% FCS solution, the original pores of sandstone have not been blocked.

The energy spectrum of sandstone surface treated by FCS was analyzed using a Quanta200F environment scanning electron microscope to further verify adsorption characteristics of the FCS molecular film. A tight sandstone core was cut into two thin slices that were soaked in 1% FCS solution and distilled water for 1 h for the analysis. The results are shown in table 1.

Table 1 illustrates that silicon and oxygen are the main elements on the surface of tight sandstone core. In this experiment, the silicon content is 50.62%, the oxygen content is 32.82%, and the fluorine is 1.22%, which is an extremely low value. However, after treatment by FCS, the fluorine content significantly increases, whereas the contents of silicon and oxygen decrease, which shows that the attachment of FCS to the surface of sandstone forms a tight polymer film, thus preventing contact between the probe and the elements on the sandstone surface

3.3. Change in the wettability of sandstone core

Solid-liquid wettability can be analyzed by

Table 1

Elemental analysis of sandstone surface before and after treatment by FCS

Element	Soaked in distilled water		Soaked in FCS solution	
	Mass Percent, %	Atomic Content, %	Mass Percent, %	Atomic Content, %
O	32.82	46.26	12.60	28.32
F	1.22	2.32	10.68	14.26
Na	1.38	2.24	2.86	3.12
Al	12.48	9.88	16.32	13.78
Si	50.62	43.61	42.27	39.42
K	4.23	2.36	4.21	2.43
Fe	5.38	2.34	4.78	2.22

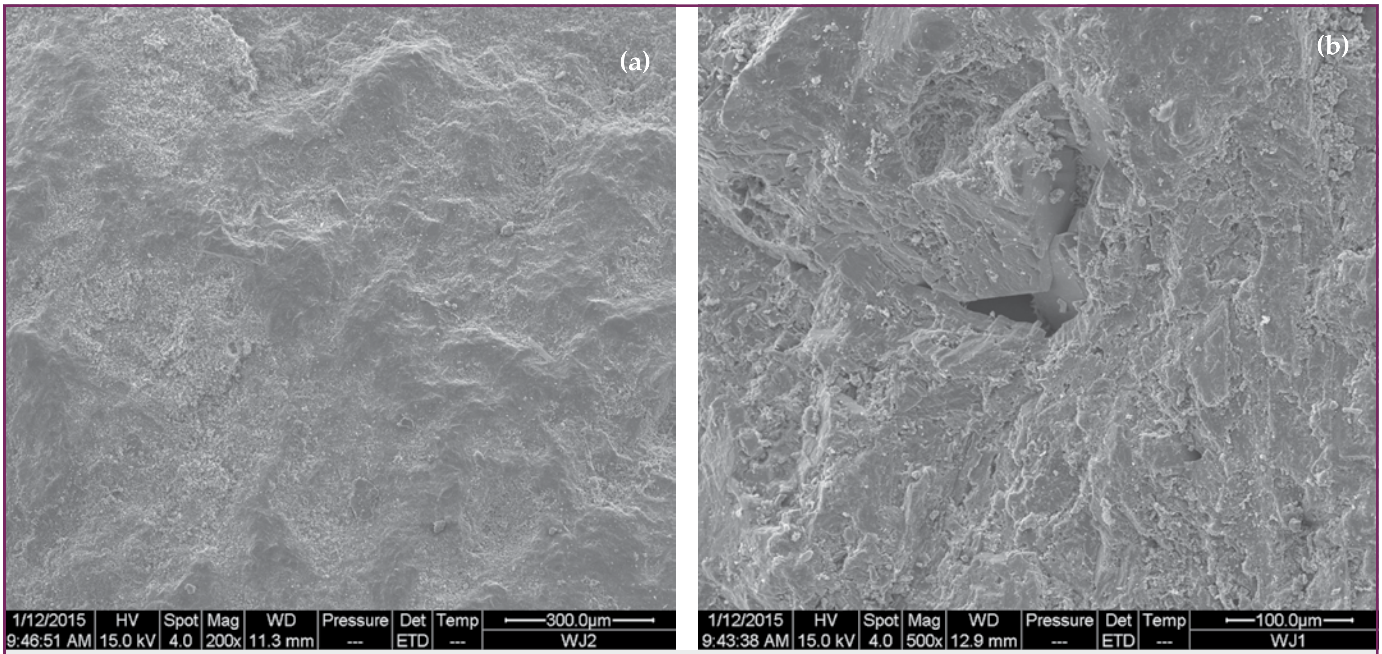


Fig.3. Original surface of sandstone

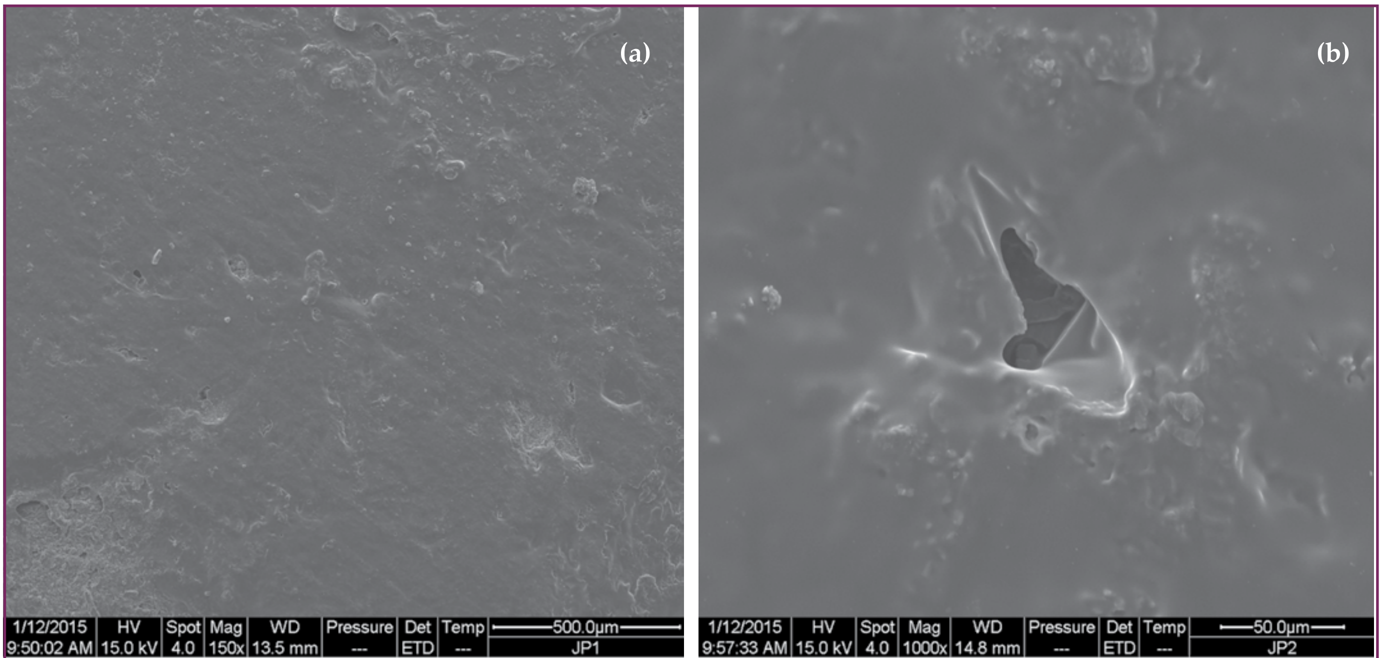


Fig.4. Surface of sandstone soaked in 1% FCS after 1 h

measuring contact angle. A solid-liquid contact angle below 90° indicates a good wettability of liquid on solid and a strong surface hydrophilicity of the solid; a solid-liquid contact angle of larger than 90° indicates a poor wettability of liquid on solid and that the solid is strongly hydrophobic. Approximately 5 μL filtrate of fracturing fluid was dripped onto the surface of sandstone core. After 30 s, the surface wettability of sandstone cores before and after treatment with 1% FCS solution was compared, and the experimental results are shown in figures 5-10.

In the case shown in figure 5 and figure 6, fracturing filtrate was dripped onto the surface of sandstone core. The initial wetting angle was 15.85°, which decreased to 2.26° after 30 s. Both of the wetting angles are smaller than 90°, indicating that the sandstone is initially hydrophilic.

The water phase can spread more easily on a hydrophilic surface, forming a «water film». When the water phase enters the pores and microfractures of this type of sandstone, the capillary pressure will resist the outflow, making it harder for the water in the pores and microfractures to leave and causing «water blocking».

Figure 7 and figure 8 show that after the surfaces of sandstone cores are treated with FCS solution, the initial contact angle is 132.6°, which decreases to 131.8° after 30 s. Both contact angles are larger than 90°. This indicates that the wettability of sandstone cores to a water phase has become worse, whereas that of the gaseous phase has increased. This trend is because FCS forms a «hydrophobic surface» on the surface of sandstone cores.

The wettability experiments demonstrate that sandstone cores treated by FCS are transformed from

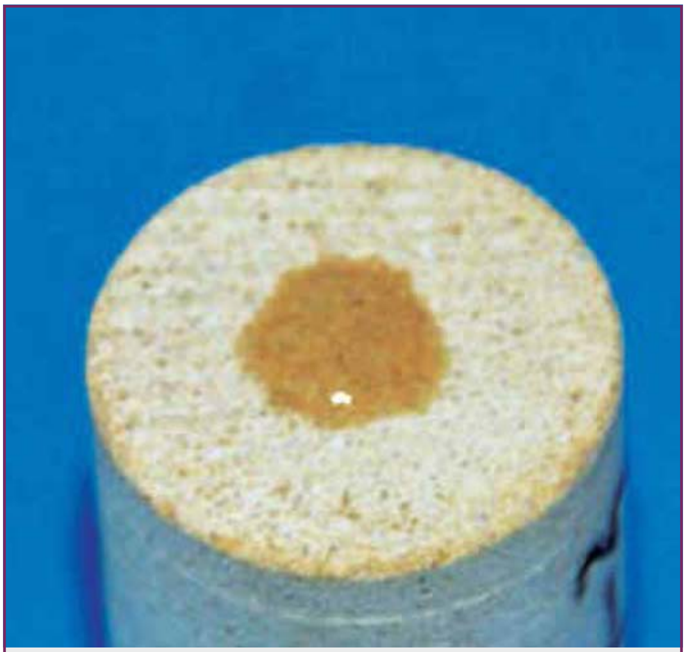


Fig.5. Shape of fracturing filtrate immediately after dripped onto the surface of tight sandstone core

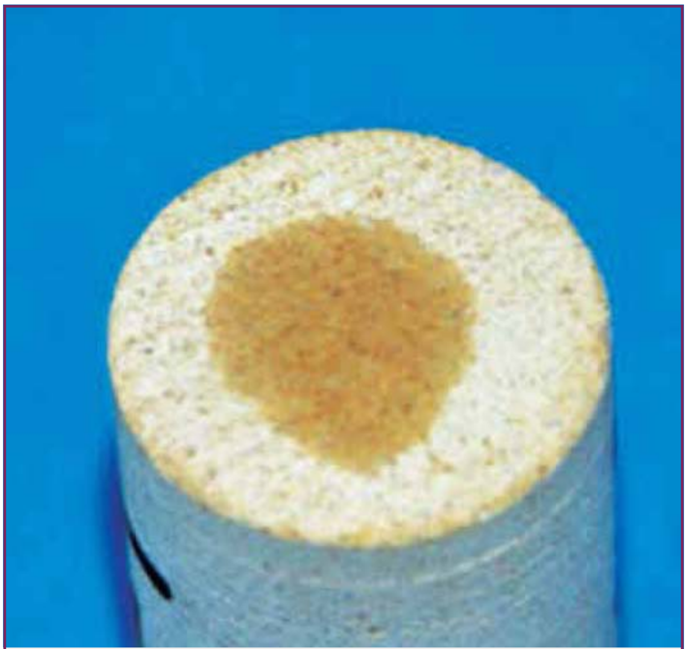


Fig.6. Shape of fracturing filtrate dripped onto the surface of tight sandstone core after 30 s

water-wetting into gas-wetting. The surface of the sandstone is no longer hydrophilic, which enables the flow-back of fracturing fluid and the outflow of natural gas from the pores and microfractures in the tight sandstone reservoir.

3.4 Surface tension

Different types of fracturing assistants and FCS were dissolved at the same concentration. A JYW-200B full-automatic interfacial tension apparatus was used to measure the surface tension, and the results are shown in table 2.

From table 2, at a concentration of 0.1%, SLPS has a surface tension of 0.068 mN/m, which is the lowest value. AES has a value of 1.586 mN/m, the highest value, and OP-10 has a value of 0.542 mN/m. FCS is not superior to the other surfactants in decreasing the surface tension, with a value of 0.452 mN/m. This is mainly because the molecular structures of surfactants are considerably smaller than that of FCS, resulting in a weaker repulsive force and smaller steric hindrance. Thus, they can more easily disperse and adsorb to the surface, as the tensions of the hydrophilic part and oleophilic part are the same; thus, they can regularly array on the surface of the liquid and thus decrease the surface tension. Although there are hydrophilic carbon chains in the FCS molecular structure, the carbon chains of

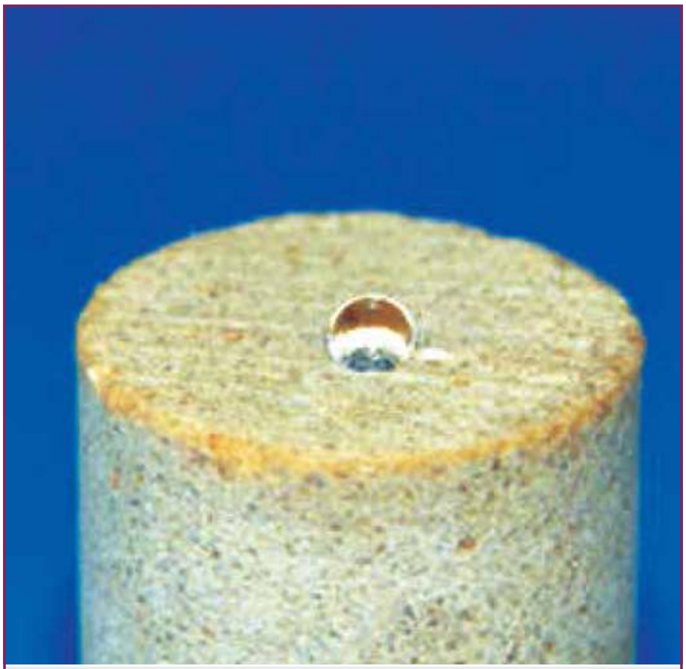


Fig.7. Shape of fracturing filtrate immediately after dripped onto the surface of tight sandstone core treated by 1% FCS

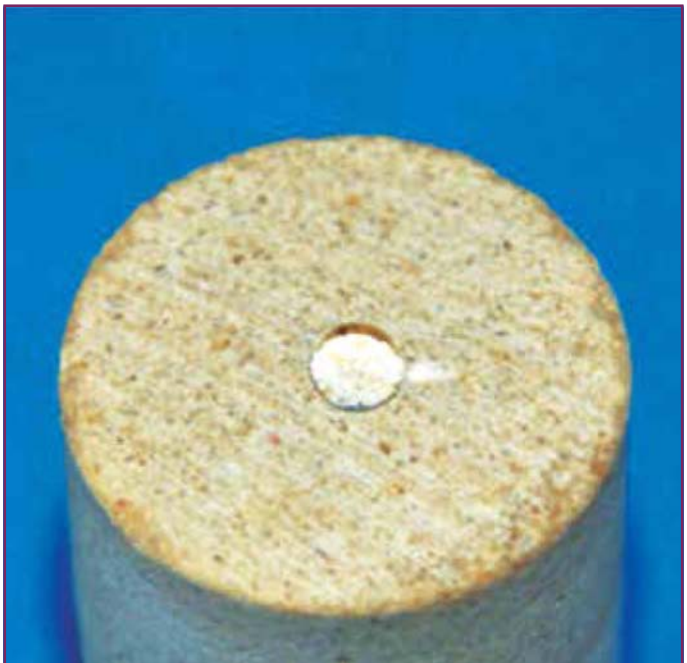


Fig.8. Shape of fracturing filtrate dripped onto the surface of tight sandstone core treated by 1% FCS after 30 s

Table 2

Surface tensions of different fracturing assistants and FCS

Solution	Concentration, %	Interfacial Tension, mN/m
Formation water		32.256
SLPS	0.1	0.068
SDS	0.1	0.328
OP-10	0.1	0.542
AES	0.1	0.856
FCS	0.1	0.452

the hydrophobic part are longer than the chains of the hydrophilic part. During the diffusion process, the slow speed of dragging the hydrophilic carbon chains reduces the surface distribution area of the hydrophilic part of the FCS molecule. Because the hydrophilic part cannot array regularly on the surface, the surface tension is larger.

3.5. Changes in the glass capillary tube hook face

The inner wall of a glass capillary tube forms a hydrophobic surface after the capillary tube is soaked in FCS solution for 2 h. The gas-liquid hook face changes during the process of natural gas displacement, as shown in figure 9 and figure 10.

Figure 9 and figure 10 demonstrate that the inner wall of the original capillary tube is water-wetting, with a solid-liquid contact angle of 53.6°; thus, the water phase tension is larger than the gaseous phase tension. The capillary pressure is opposite to the flow direction of gas and is the resistance to gas flow. The inner wall of capillary tube forms a hydrophobic surface by FCS treatment, and the solid-liquid contact angle is 108.2°. The inner wall of capillary tube changes from liquid-wetting to gas-wetting and the capillary pressure is in the same direction as the gas flow, serving as the impetus to the gas flow.

4. Discussion

This paper introduces a «hydrophobic surface» wettability alteration agent named FCS. FCS alters the surface of sandstone from water-wetting to gas-wetting and thus efficiently relieves the «water blocking» in the long term. FCS contains hydrophilic and hydrophobic carbon chains that can efficiently reduce surface tension and contribute to the flow-back of fracturing fluids.

Previous studies [9-12] on the process of resolving «water blocking» by altering the surface wettability of sandstone considered only the permeability, water saturation, and water imbibition capacity from a macro standpoint and did not study the microcosmic influence of wettability agents. The influence of wettability agents on the liquid surface tension and flow-back of wettability agents has not been the subject of significant relevant research. The effect on the chemical properties of wettability alteration agents has been ignored in relieving «water blocking».

5. Conclusion

The following conclusions can be drawn from these experiments:

1. According to SEM observations, the surface of sandstones changed from rough to smooth after being soaked in FCS. An elementary energy spectrum analysis proved that FCS forms a tight molecular film on the surface of the sandstone;

2. The best dosage of FCS is 1%, as confirmed by measuring the solid-liquid contact angle.

3. An optical microscope was used to observe the change in the solid-liquid contact angle of glass capillary tubes before and after soaking in FCS. The results show that a hydrophobic surface film decreases the water-wetting of glass tube surface and alters it to gas-wetting. The capillary pressure has the same direction as the gas flow and becomes the impetus for the gas flow.

4. FCS has long hydrophobic carbon chains that limit the decrease in surface tension. The surface tension is 0.452 mN/m at a concentration of 0.1%.

5. As the water-wetting gradually changed to gas-wetting, the filtrate would no longer be chained by the resistance of capillary pressure, making it easier for gas to flow out from the tight sandstone cores. FCS dissolved in the liquid phase would help to decrease the solid-liquid surface tension and flow back smoothly, and the damage caused by «water blocking» would thereby be efficiently relieved.

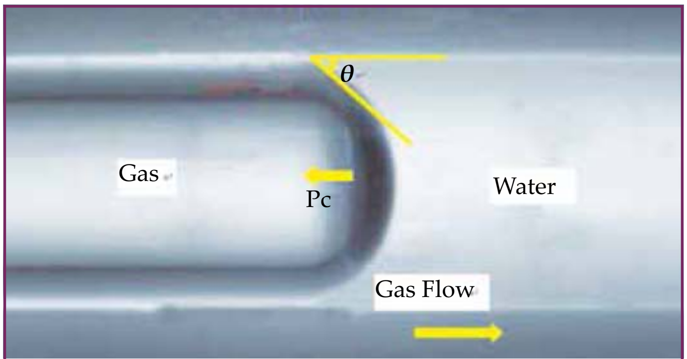


Fig.13. Original hook face of the capillary tube

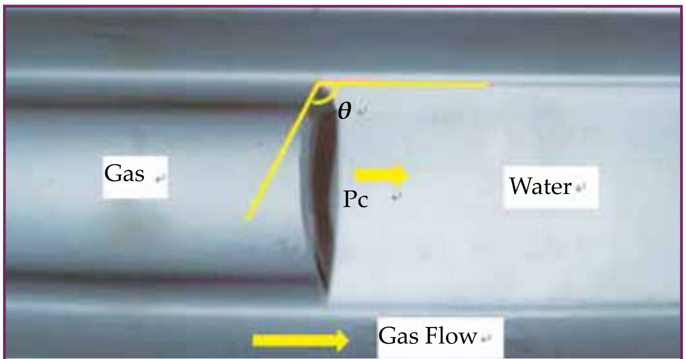


Fig.14. Hook face of the capillary tube after 1% FCS treatment

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References

1. *H.O.McLeod, A.W.Coulter.* The use of alcohol in gas well stimulation //The paper presented at the SPE Eastern Regional Meeting, Columbus, Ohio, 10-11 November 1966.
2. *H.A.Al-Anazi, J.G.Walker, G.A.Pope et al.* A successful methanol treatment in a gas-condensate reservoir: field application //The paper presented at the SPE Production and Operations Symposium, Oklahoma, Oklahoma City, 22-25 March 2003.
3. *V.Bang, V.Kumar, P.Ayyalasomayajula et al.* Relative permeability of gas-condensate fluids: a general correlation //The paper presented at the SPE Annual Technical Conference and Exhibition, TX, San Antonio, September 24-27, 2006b.
4. *V.Bang, G.A.Pope.* A new solution to restore productivity of gas wells with condensate and water blocks //The paper presented at the SPE Annual Technical Conference and Exhibition, Colorado, Denver, 21-24 September 2008.
5. *V.Bang, G.A.Pope, M.M.Sharma.* Phase behavior study of hydrocarbon/water/methanol mixtures at reservoir conditions //The paper presented at the SPE Annual Technical Conference and Exhibition, TX, San Antonio, September 24-27, 2006a.
6. *M.Ahmadi, M.M.Sharma, G.Pope et al.* Chemical treatment to mitigate condensate and water blocking in gas wells in carbonate reservoirs //SPE Production & Operations. -2011. –Vol.26. –Issue 1. –P.67-74.
7. *M.Ahmadi, M.M.Sharma, G.Pope et al.* Chemical treatment to mitigate condensate and water blocking in carbonate gas wells //The paper presented at the SPE Western Regional Meeting, California, Anaheim, 27-29 May 2010.
8. *R.Dutta, C.H.Lee.* Experimental investigation of racturing-fluid migration caused by spontaneous imbibition in fractured low-permeability sands //SPE Reservoir Evaluation & Engineering. -2014. –Vol.17. –Issue 1. –P.74-81.
9. *G.Tang, A.Firoozabadi.* Relative permeability modification in gas/liquid systems through wettability alteration to intermediate gas wetting //SPE Reservoir Evaluation & Engineering. -2002. -Issue 5. –P.427–436.
10. *G.Tang, A.Firoozabadi.* Wettability alteration to intermediate gas-wetting in porous media at elevated temperatures //Transportation of Porous Media. -2003. –Vol.52. –P.185–211.
11. *M.Noh, A.Firooaabadi.* Wettability alteration in gas-condensate reservoirs to mitigate well deliverability loss by water blocking //SPE Reservoir Evaluation & Engineering. -2008. –Vol.11. –Issue 4. –P.676–685.
12. *M.Noh, A.Firoozabadi.* Effect of wettability on high-velocity coefficient in two-phase gas/liquid flow //SPE Journal. -2008. –Vol.13. –Issue 3. –P.298–304.
13. *J.Fahimpour.* Optimization of Fluorinated Wettability Modifiers for Gas-Condensate Carbonate Reservoirs //The paper presented at the EAGE Annual Technical Conference and Exhibition, Denmark, Copenhagen, 4-7 June 2012.
14. *A.Betoncello.* Imbibition and water blockage in unconventional reservoirs: well-management implications during flowback and early production //SPE Reservoir Evaluation & Engineering. -2014. –Vol.

Экспериментальное исследование нового агента, изменяющего смачиваемость в газовых песчаных коллекторах

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Реферат

В статье представлен гидрофобный агент для изменения смачиваемости, который формируя на поверхности песчаника мономолекулярный слой позволяет увеличить фазовую проницаемость по газу. Результаты экспериментов по изменению смачиваемости песчаников и капиллярных стеклянных трубок показали, что на поверхности песчаника образуется плотный мономолекулярный слой, который делает его гидрофобным с краевым углом смачивания выше 90°. После обработки агентом внутренняя поверхность капиллярной трубки переходит из состояния смачивания жидкостью в состояние «смачивания» газом. Результаты экспериментальных исследований показали, что гидрофобизация поверхности песчаника является целесообразным методом восстановления фазовой проницаемости по газу.

Qumlu qaz kollektorlarının islanma qabiliyyətini dəyişdirən yeni agentin sınaq tədqiqatları

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Xülasə

Məqalədə qumdaşının üzərində monomolekulyar qatı yaratmaqla qaza görə faza keçiriciliyin artırılmasına imkan yaradan islanma qabiliyyətini dəyişdirən hidrofob agent təqdim edilir. Qumdaşların və kapilyar şüşə boruların islanma qabiliyyətinin dəyişdirilməsi üzrə aparılan sınaqların nəticələri göstərmişdir ki, qumdaşının səthində sıx monomolekulyar qatın əmələgəlməsi onu islanma bucağı 90°-dən yuxarı olmaqla hidrofoblaşdırır. Agent ilə işlənildikdən sonra kapilyar borunun daxili səthi maye ilə islanma vəziyyətindən qazla «islanma» vəziyyətinə keçir. Sınaq tədqiqatların nəticələri göstərmişdir ki, qumdaşı səthinin hidrofoblaşdırılması qaza görə faza keçiriciliyinin bərpası üçün məqsədəuyğun üsuldur.