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# Wettability modification by fluoride and its application in aqueous phase trapping damage removal in tight sandstone reservoirs

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ABSTRACT

External fluid invading into reservoir could induce formation damage in form of phase trapping in tight sandstone reservoirs (in-situ permeability $<0.1$ mD). Aqueous phase trapping damage occurs commonly in drilling and completion operations. Once aqueous phase trapping damage happens, it could hardly be removed, as a result of which gas production will not be promising. The objective of this study is to experimentally investigate the wettability alteration by quaternary ammonium fluoride salt and its potential to mitigate aqueous phase trapping damage in original water-wet, tight sandstone gas reservoirs. Wettability alteration from water wetting to gas wetting was achieved as water contact angles on core chip surface treated by 0.1 wt% fluoride were larger than 90° at 27 °C. There was hardly change in contact angles when temperature rose up to 80 °C and 100 °C respectively. The results of contact angle and surface tension tests indicated that the optimal fluoride concentration is 0.1 wt%. Atomic Force Microscope (AFM) analysis revealed that large amounts of fluoride adsorbed on mica surface, forming an irregular micro-nanometer structure. The modified structure enhanced hydrophobicity of surface and promoted the flowback of the invading fluid foreign to reservoir. Fluid rheology tests were carried out by viscometer and the results showed good compatibility between fluoride and drill-in fluid. The result of the core flow test indicated that both the flow back rate and gas relative permeability were significantly improved by 40% and 20% respectively.

## 1. Introduction

Increasing world demand on energy prompts an increased emphasis toward unconventional resources. Tight sandstone gas accounts a major portion of the current exploitation market among unconventional gas production (Abdelaziz et al., 2011; Wisam and Jennifer, 2014). However, tight sandstone gas reservoirs are exposed to many production problems and formation damage due to unfavorable geologic status, i.e., low permeability ($<0.1$ mD), narrow throats, remarkable amounts of potential capillary suction energy and extra-low initial water saturation (Bennion et al., 2004; Gupta,2009). As a result, fluid invading into the reservoir can be easily entrapped within porous medium during drilling and completion operations, making reservoirs suffer from phase trapping damage (Bennion et al., 1996; Cai et al., 2012; Mahadevan et al., 2007). Provided the reservoir is water-wet and the fluid invading into the reservoir is water-based, it could be recognized as aqueous phase trapping damage (Bennion et al., 1996; You and Kang, 2009).

Recently, there have been many studies focused on factors affecting aqueous phase trapping damage (Abass et al., 2007; Bennion et al., 1992, 2004; Holditch, 1979), damage laboratory evaluation (Bennion et al., 1991), consequence and prevention or treatment of aqueous phase trapping damage (Bahrami et al., 2012; Bennion and Thomas, 2005; Bennion et al., 1994, 2000; Jamaluddin et al., 2000; Wang et al., 2012). Capillary imbibition and entrapment of the invading aqueous are the main reasons of aqueous phase trapping damage. The entrapment of liquid within pore throats is attributed to the unfavorable capillary force, $P_c=2\sigma\cos\theta/r$ (Cai et al., 2014). Once aqueous phase trapping damage occurred, gas relative permeability can be substantially reduced by approximately 95% of the original value (Bennion et al., 1996) and the damage could hardly be removed, leading to a disappointing gas production (Xie et al., 2009). In general, most of tight sandstone gas reservoirs are water-wet due to special physicochemical properties of silicate minerals existing on the surface. Li and Firoozabadi (2000) proposed that modifying reservoir wettability from water wetting to gas wetting can mitigate aqueous phase trapping damage and improve gas production, which provided a new idea for controlling aqueous trapping damage. Water capillary imbibition behavior in tight sandstone gas reservoirs can be inhibited by wettability alteration (Liu et al., 2009;

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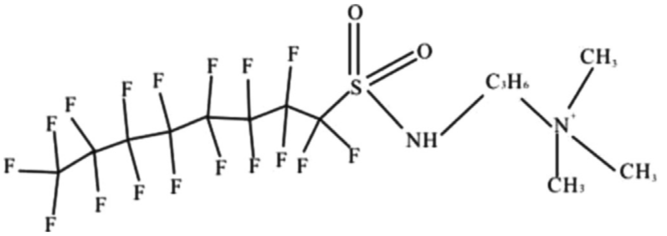

**Fig. 1.** Molecular structure of quaternary ammonium fluoride salt FW-134.

You and Kang, 2013). Wettability modification can be achieved by certain ionic compound (Bera et al., 2012). Fluoride was selected as the modifier due to its better aqueous stability and lower surface free energy (Al-Anazi et al., 2007; Fahes and Firoozabadi, 2005; Liu et al., 2006; Panga et al., 2006; Tang and Firoozabadi, 2002). Li and Liu (2008) reported an earlier field application of wettability modification by fluoride. Micellar solubilization and ion-pair formation have been postulated as mechanisms of wettability alteration in some literatures (Anderson, 1986; Austad and Milter, 1997; Bera et al., 2011; Li and Horne, 2003; Li et al., 2004; Salehi et al., 2008, 2010; Seiedi et al., 2011; Standnes and Austad, 2000; Wu and Firoozabadi, 2009; Wu et al., 2006). Nevertheless the previous mechanism studies focused mostly on hydrocarbon surfactant. More underlying experiments on wettability modification by fluoride are required.

In this study, wettability alteration is achieved by quaternary ammonium fluoride salt (purity 99.9%) with both hydrophobic groups and hydrophilic groups (Fig. 1). Firstly, contact angles and surface tensions with fluoride concentration between 0% and 0.3% were measured and the optimal concentration for lower capillary viscosity force was finally determined. Contact angles of water-based drill-in fluid at different temperatures with optimal fluoride concentration were also measured. Secondly, Atomic Force Microscope (AFM) was applied to image surface morphology to understand mechanisms of the wettability alteration by fluoride. Finally, core flow test by circulating drill-in fluid at the core plug's end was performed to examine the feasibility of controlling aqueous phase trapping damage in tight sandstone gas reservoir. In order to ensure the flow test done in the right way, we gave the priority to rheology test to examine the performance of drill-in fluid and its compatibility with fluoride. The methodology is described as follows.

## 2. Experiment section

### 2.1. Materials

In this study, tight sandstone core samples with permeability less than 0.1 mD from target gas reservoir were used for contact angle test and core flow test, shown in Table 1. Mica was used for imaging surface morphology by AFM. Quaternary ammonium fluoride salt was applied as wettability modifier. Distilled water, potassium chloride (KCl) and sodium chloride (NaCl) were used for synthetic solution. Drill-in fluid from target gas field was used for core flow test. Dried $N_2$ (purity 99.99%) was used as power source.

### 2.2. Apparatus and methodology

#### 2.2.1. Measurement of contact angle

The static contact angle ($\theta$) for the water–gas–rock system was measured by a goniometry setup (U. S. Patent 5.268.733). Core samples were cut into chips of $\Phi 25\ \text{mm} \times L 50\ \text{mm}$ and aged in solution with fluoride concentration between 0% and 0.3% at 27 °C. Aqueous droplet with constant volume of 20 μl was placed in direct contact with the core surface and then the magnified photograph of the droplet was projected on dial. Furthermore, photographs of drill-in fluid filtrate on core chips before and after treatment at 27 °C, 80 °C, and 100 °C were taken as well.

#### 2.2.2. Measurement of surface tension

Generally, the reduction of surface tension ($\sigma$) can lead to a relative reduction in capillary imbibitions force, $P_c = 2\sigma \cos\theta / r$. This is favorable for mitigating aqueous phase trapping damage. Surface tension of water–gas system with fluoride concentration from 0 to 0.3 wt% was measured by tension-meter (JZHY1-180) at 27 °C. The standard deviation does not exceed $\pm 0.1$ mN/m.

#### 2.2.3. Surface morphology of mica treated by fluoride

Atomic Force Microscope (AFM) was adopted to obtain the apparent absorption morphology of mica at 27 °C. Mica was selected for two reasons. On one hand mica has similar structure with Illite which is the main component of clay mineral in tight sandstone. On the other hand mica surface is relatively smooth for obtaining the adsorption imaging. Mica was cut into square plate by 10 mm × 10 mm × 2 mm and was saturated by aqueous solution (0.1 wt% fluoride) for 10 min. After that the mica plate was cleaned by distilled water and dried by $N_2$ flush. The tests were performed in10 μm × 10 μm scanning area with 1.489 Hz scanning speed under tapping mode.

#### 2.2.4. Drill-in fluid rheology

The priority was given to drill-in fluid rheology tests as the rheological property is of primary concern in the formation for any type of fluid (Olatunde et al., 2012). Thus, rheology was measured by viscometer prior to core flow test to testify the compatibility between fluoride and water-based drill-in fluid. Rheological parameters, such as viscosity AV, plastic viscosity PV and yield point YP, were calculated. The viscometer is calibrated in revolutions per minute (RPM).

#### 2.2.5. Core flow test

The system used for core flow test, including mud circulating loop and instrumental system, is illustrated by Fig. 2. The core holder cell is equipped on the fluid container. The rotation of the four rotors induces the circulation of fluid. Core and fluid for flow tests are shown in Table 1 above.

Firstly gas permeability $K_{0i}$ was measured by flowing dry nitrogen gas through core samples at constant confining pressure of 10 MPa and varying differential pressure. Then the drill-in fluid was circulated across the face of the core for 60 min at differential pressure $\Delta P = 3.5$ MPa, rate of shear $V = 40\ \text{s}^{-1}$ and $T = 80$ °C. During the circulation, the communicative filtration as a function of

**Table 1**
Core physical properties and working fluid for core flow test.

| Core# | Length, mm | Diameter, mm | Porosity, % | Permeability, mD | Pore volume, ml | $S_{wi}$,% | Weight, g | Fluid type |
|---|---|---|---|---|---|---|---|---|
| S2-7 | 49.6 | 25.1 | 3.74 | 0.017 | 0.921 | 20 | 69.13 | Drill-in fluid |
| S2-15 | 38.7 | 25.1 | 3.79 | 0.012 | 0.725 | 20 | 70.14 | |
| D-82 | 63.4 | 25.3 | 15.51 | 0.051 | 4.929 | 21 | 71.22 | Drill-in fluid+0.1%fluorid |
| A-57 | 63.3 | 25.2 | 15.99 | 0.058 | 5.054 | 23 | 70.08 | |