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Mechanisms of wetting modification by fluoride to mitigate phase trapping

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ABSTRACT

Wettability alteration has a positive impact on mitigating the damage caused by water trapping. However, the related mechanisms are not quite clear. In this paper, the use of a quaternary ammonium fluoride salt to alter wettability and its potential to mitigate damage caused by aqueous phase trapping in the original water-wet, tight sandstone was investigated. Wettability alteration from water wetting to gas wetting was achieved after the core samples were treated with fluoride. After treatment, the water contact angles were larger than 90°. These contact angles slightly decreased when the temperature rose to 80 °C and 100 °C. The water surface tension decreased from 71.8 mN/m to 20.7 mN/m with the addition of fluoride and later varied over a small range. The contact angles and surface tension tests indicated that the optimal fluoride concentration was 0.1 wt%. The addition of fluoride slightly increased the viscous shear of the drill-in fluid. The flow back rate of the invading liquid with fluoride (85.1%) was almost double that of the liquid without fluoride (45.2%). With the removal of more water, the gas permeability recovery of cores after the circulation of drill-in fluids with fluoride improved by 20%–30% compared with that of drill-in fluids without fluoride.

High performance liquid chromatography (HPLC) tests showed that there was hardly fluoride in the filtrate. The results confirmed that fluoride adsorbed onto the rock when the fluid circulated through the sample. This phenomenon was also proved by scanning electron microscopy (SEM) analysis, which showed that uneven molecular aggregation and amounts of adsorptions were more likely to occur at defect points. The adsorption of fluoride onto the rock surface resulted in a new irregular microstructure with a lower surface free energy, which decreased from 72 mJ/m^2 to 12 mJ/m^2 after fluoride adsorption. The results showed that the modified structure favors water removal.

1. Introduction

Aqueous phase trapping damage commonly occurs during drilling and completion operations. The capillary force P_c is responsible for trapping liquid. P_c is a function of surface tension σ, contact angle of wetting phase θ and capillary radius r, and can be expressed as:

$$Pc = 2\sigma \cos\theta / r. \tag{1}$$

For water-wet reservoirs, the imbibition and entrapment of water by capillary suction is ubiquitous. In the past decades, scholars have extensively researched capillary imbibition in porous media. Li et al. (2006) studied the influence of initial water saturation on recovery by spontaneous imbibition in gas/water/rock systems. Cai et al. (2010) proposed an analytical expression stating that the mass of imbibed liquid is a function of the fractal dimensions of pores and tortuous capillaries, the minimum and maximum hydraulic diameter, porosity, fluid properties, and the fluid–solid interaction. Cai and Yu (2011) further derived a law stating that the average growth in height of a wetting liquid in porous media is a function of the fractal dimension for tortuosity. We can see that wettability is a key parameter affecting fluid flow in porous media. Wettability alteration from oil-wet/mixed-wet to strongly water-wet has long been recognized as an efficient recovery process that enhances water imbibition and expels more oil from the matrix to the fractures in fractured carbonates (Najafabadi et al., 2011; Salehi et al., 2010). However, water wetness in tight sandstone gas reservoirs is unfavorable, as water imbibition and entrapment in capillaries reduces gas deliverability (Xie et al., 2009). Methods have been proposed to mitigate damage

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caused by aqueous phase trapping to recover gas production. These include hydraulic fracturing (Penny et al., 1983), gas injection and volatile solvent injection (Mahadevan et al., 2007). However, these methods take more time and have temporary effects.

According to Jadhunandan and Morrow (1995), liquid saturation in reservoirs can be reduced by altering the rock wettability to intermediate wetting. Li and Firoozabadi (2000) proposed that modifying reservoir wettability from water wetting to gas wetting can mitigate aqueous trapping damage and enhance gas well deliverability. These authors used fluoride agents to obtain gas wetting in Berea sandstone and Kansas chalk. Later laboratory studies conducted by Tang and Firoozabadi (2002), Fahes and Firoozabadi (2007), Kumar et al. (2006), and Adibhatla et al. (2006). Feng et al. (2012) used the emulsion polymerization process to synthesize a type of fluoroacrylate copolymer emulsion. These authors experimentally demonstrated that the fluoropolymer can change the wettability of porous media to gas wetting and suppress the imbibition of water and oil into rock. Sharifzadeh et al. (2013) used a type of monomeric surfactant and conducted the sol–gel process to prepare a fluorinated polymeric network that behaves as a repellant towards water and oil. They believed that the fluorinated polymer could protect gas condensate reservoirs from undergoing condensate blockage in the near future. Mousavi et al. (2013) prepared fluorinated silica nanoparticles to alter rock wettability in the Near-Wellbore Region in gas condensate reservoirs. The nano-structured fluorinated nanoparticles on the pore surface formed a smooth film coating that behaved as a water and oil repellent by lowering the surface energy, thereby allowing for wettability alteration from liquid wetting to gas wetting. However, the potential reservoirs have absolute permeability values larger than 1 mD and pore radii larger than 1 micro. Thus, a consensus has been reached that fluorinated agents are favorable for obtaining liquid flow through wettability alteration.

Micellar solubilization (Austad and Milter, 1997), ion-pair formation (Salehi et al., 2008; Standnes and Austad, 2000), and changes in rock surface charges (Hassan et al., 2015) have been postulated as the mechanisms of wettability alteration. Salinity, surfactant concentration, electrolyte concentration, temperature, etc. also have effects on wettability alteration (Hamouda and Rezaei Gomari, 2006; Gomari, 2009; Gupta and Mohanty, 2011). However, these mechanisms are theoretical and are mainly aimed at hydrocarbon surfactants acting on oil/water/rock systems in carbonate rocks. More experiments to analyze the underlying mechanisms of wettability modification by fluoride are required.

In this paper, quaternary ammonium fluoride salt was used as modifier. The contact angles on the rock surface before and after ammonium fluoride treatment were measured. The surface tension of water with a fluoride concentration between 0 and 0.3% was measured as well. The feasibility of using fluoride to mitigate damage induced by the trapped aqueous phase in tight sandstone reservoirs was examined by evaluating the gas permeability, which was assessed by circulating drill-in fluid at the end of the core plug. To ensure that the circulating test was properly done, we prioritized the rheology tests for the drill-in fluid to examine the impact of fluoride on drill-in fluid performance. During the circulation test, the filtrate was collected for high performance liquid chromatography (HPLC) to determine the amount of fluoride adsorption onto the rock. Scanning electron microscopy (SEM) was also applied to image the surface morphology to understand the mechanisms by which fluoride alters wettability. At last, the surface free energy of the rock before and after fluoride adsorption was calculated.

2. Experimental

2.1. Materials and apparatus

Tight sandstone core samples with an in-situ permeability less than 0.1 mD were obtained from a target gas reservoir for use in this study, as shown in Table 1. Quaternary ammonium fluoride salt (purity 99.9%) was applied as a wettability modifier. Distilled water and potassium chloride (KCl) were used for the synthetic solution. The experimental gas consisted of dried N_2. The drill-in fluid from the target gas field was used for dynamic circulation tests.

The static contact angle (θ) for the water-gas-rock system was measured with a goniometry setup (U. S. Patent 5.268.733). A JZHY1-180 tension meter was used to measure the surface tension. A ZNN-D6 six-speed rotational viscometer was used to measure the rheology of the drill-in fluid. The viscometer was calibrated in revolutions per minute (RPM). The fluid dynamic circulation through the core sample was achieved using a mud circulating loop and an instrumental system, as illustrated in Fig. 1. The core holder cell was connected to the fluid container. The rotation of the four rotors induced fluid circulation, which simulated the shear process in the bottom of the hole. The cores and fluids used in the circulation analysis are shown in Table 1.

After the core flow test, the filtrate obtained from the circulated fluid was tested using HPLC (LC-20AT, Shimadzu) to determine the fluoride adsorption onto the rock surface. To analyze the surface modification by fluoride, SEM was used for imaging surface morphology.

2.2. Methodology

2.2.1. Contact angles tests

Core samples were cut into Φ25 mm chips, which were then aged in a solution containing fluoride for 24 h at room temperature at 80 °C or 100 °C. The concentration of fluoride varied between 0 and 0.3 wt%. The cores were removed and an aqueous droplet with a constant volume of 20 μl was directly placed on the surface. Then, a magnified photograph of the droplet was projected onto a dial.

2.2.2. Surface tension tests

Generally, the reduction of surface tension σ can lead to a relative reduction in the capillary imbibition force, P_c. This is favorable for mitigating damage caused by aqueous phase trapping. The surface tension of the water–gas system with fluoride concentrations ranging from 0 to 0.3 wt% was measured using a tension meter (JZHY1-180) at room temperature. The standard deviation did not exceed $\pm$0.1 mN/m.

2.2.3. Damage evaluation during dynamic circulation of the drill-in fluid

First, the drill-in fluid rheology tests were prioritized because rheological properties are of primary concern in the formation of any type of fluid (Olatunde et al., 2012). The fluid was fully stirred using a high-speed blender, and then the fluid rheology was measured using a ZNN-D6 six-speed rotational viscometer. After the measurements, the fluid was placed in a hot roller furnace and aged for 16 h at 120 °C. Then, the fluid was fully stirred in a blender. After the temperature dropped to approximately 50 °C, the rheology was measured again. Rheological parameters such as viscosity AV, plastic viscosity PV, and yield point YP were calculated.

The circulation setup is shown above, in Fig. 1. At first, the gas permeability K_{0i} was tested by varying the differential pressure and constant confining pressure by 10 MPa. The nitrogen gas