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Preparation of the modified limestone possessing higher permeability of gas well based on fluorinated silica: Effect of catalyst

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ABSTRACT

During natural gas production from gas condensate reservoirs, due to drops in bottom hole pressure below the dew point, liquids drop out and form condensate blockage which results in significant loss of gas and condensate productivity. A new method for stimulating gas–condensate wells is changing the rock wettability in near well-bore regions by chemical treatments. The aim of this study was to employ two comparative methods of chemical treatments for altering the rock wettability from strong liquid-wetting to intermediate gas-wetting. First the surface of rocks was modified by using sol–gel process under acid- and/or base-catalyzed conditions. Then the effects of two different chemical treatments were examined by various experimental tests such as Fourier transform infrared (FTIR), thermogravimetric analyses (TGA), electron dispersive analysis of X-ray (EDX) and scanning electron microscopy (SEM) followed by static contact angle, coreflood test and porosity measurements. The results showed that, such methods could alter the wettability significantly. It was noticed that there were some differences in the experimental results related to sol–gel structure. Compared to a base-catalyzed process which showed higher contact angle value, an acid-catalyzed process tended to produce more linear branched-polymeric networks with fewer cross-linkages and could penetrate into the limestone core easier. The final evaluation of the coatings in terms of their effectiveness by coreflood test showed that the improvement factors were 0.78 and 0.56 for the acid- and base-catalyzed treatments, respectively.

1. Introduction

The global demand for natural gas energy is predicted to increase steadily over the coming few decades and it is rapidly reaching the level of oil demand as a primary world's source of energy. Therefore, this increase is leading to the forecast of the production outcome and the challenges which we may be encountering during the gas production of natural gas reservoirs. In many gas condensate reservoirs, when flowing bottom-hole pressure drops below the dew point pressure of the fluid, the liquids including both condensate and water are build up either on the walls of pores or throats of the pores of porous media. Such trapping liquids can reduce relative permeability and subsequently result in significant loss of gas and condensate productivity.

Over the years, several techniques have been proposed to reduce the condensate banking and enhance gas well deliverability [1,2]. Among these methods, hydraulic fracturing, gas cycling and solvent injection such as methanol have been suggested by many researchers [3–5]. An interesting successful method has been proposed by altering the wettability of the rock from liquid-wetting to intermediate gas-wetting. The liquid low mobility is an important factor in condensate accumulation causes by strong liquid wetting of rocks around the well bore region. Therefore, today there is a great interest in wettability alteration-based technologies by injection of surfactants, which sound more permanent and more efficient to recover the productivity in the reservoirs. For obtaining such water- and oil-repellent surface, it is necessary to prepare one type of surface with very small surface tension. Since surface tension of functional groups is in the following order: $-CF_3 < -CF_2 < -CH_3 < -CH_2$, this can be illustrated by using fluorinated compounds with having benefits to enhance water- and oil-repellency [6]. Thus, fluorinated surfactants usually remain the most common surfactants with unique properties to alter the wettability of reservoir rocks. These agents have good ability to lower the surface tension of systems below 20 mN/m and they are effective in an injection well at very low concentration [7]. It was claimed that fluorinated compounds can reduce both the water-wet and oil-wet rock tendencies as well as

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the interaction of the water and condensate with the reservoir surface.

Recently, a number of approaches have been reported for various surfactants on the improvement of gas well productivity. Li and Firoozabadi [8] altered the wettability of rocks to intermediate gas wetting by using fluoro-polymers consisting of FC754 (water soluble cationic surfactant) and FC722 (water insoluble fluoro-polymer). The results showed that in glass capillary tube, contact angle altered from 50 to 90° and from 0 to 60° by using FC754 for water–air and decane–air systems, respectively. Mohanty et al. [9] performed a chemical treatment, using 10 surfactants to change the wettability of carbonate and sandstone rocks from water wet to neutral wet conditions. He showed that among fluorosilanes, with higher number of fluorogroups, samples tend to become less water wet, and 1 day of aging period with 1 wt% concentration is sufficient for altering the wettability. Tang and Firoozabadi [10], Kumar [11], Bang [12], Liu et al. [13] and Saikia [14] experimentally investigated the improvement in gas and condensate relative permeability by using flouro surfactants and several coreflood tests to alter the wettability of sandstone and limestone.

In fact, altering the rock wettability toward non-wetting by surfactants would allow the hydrocarbons to displace water, leaving lower liquid saturation and an increased flow of hydrocarbons through capillaries and flow channels formation to the production wellbore [15]. The surfactants used in previous studies were generally composed of a head group and a fluoroalkyl tail. The head groups can consist of alkyl moiety groups, which have ability to chemically bond and associate with the rock surface. The surfactant tail contains perfluoroalkyl groups which minimize the surface free energy. For a successful chemical treatment, the surfactant should be soluble in solvent under reservoir conditions, form strong association with the rock surface to have a durable treatment and provide good oil/water repellency characterizations [12].

Since the well performing surfactant needs to have multiple contacts of the molecules with the surface for a strong and permanent treatment, therefore, polymeric surfactants show a higher probability of success compared to small surfactant molecules [16]. Among polymerization methods, "*sol–gel*" process is found to be an effective and substantial technique to form coating films with various geometrical structures and modify the properties of substrates [17,18]. Sol–gel processes consist of two mechanisms including hydrolysis and condensation. The reactions are so slow that acid and base catalysts such as mineral acids or ammonia, which are most generally used in sol–gel processing, have to be introduced. Earlier, we reported the synthesis of fluorinated nano-silica using sol–gel method under basic conditions by changing the ratio of the reactants and tried to alter the wettability of reservoir rocks [19].

In this study, we have tried to compare the acid and base-catalyzed (HCl and NH_4OH) sol–gel treatments, using nonafluorohexyltriethoxysilane (FAS-9) and triethoxysilane (TEOS) on the wettability alteration of reservoir rocks. The increase in gas deliverability was our major motivation for the wettability alteration of the reservoir rocks under reservoir conditions. The samples used for this work were selected from Sarkhun reservoir, one of the limestone gas condensate reservoirs located in Hormozgan, Iran. Sarkhun has low gas permeability and it is predicted that it may undergo condensate blockage in near future [16].

The structure of this paper is as follows: first, we presented the chemicals and experimental treatment processes. The effect of the surfactant is discussed by various tests such as Fourier transform infrared (FT-IR) spectroscopy, thermogravimetric analyses (TGA), electron dispersive analysis of X-ray (EDX) and scanning electron microscopy (SEM), followed by wettability alteration test using contact angle measurements. We also present the recovery performance by coreflood experiments on Sarkhun limestone before and after wettability alteration at reservoir conditions. Finally, we compare and discuss the experimental results at the last section of this study.

2. Experimental

2.1. Materials

Core samples were obtained from Sarkhun, a limestone reservoir with low gas permeability, between 2 and 2.5 md. We used cores with approximately 1.5 inch in diameter. The average pore diameter, distribution of pore size, porosity, and total surface area of the cores are listed in Table 1. It is noted that a mercury intrusion porosimeter (Pascal 404, Thermo Finnigan) was used to obtain mercury intrusion curves in porous media.

The chemicals used in our work included a fluorinated surfactant, nonafluorohexyltriethoxy silane 95% purchased from ABCR, abbreviated here as FAS-9 in this article and ethanol 99.8 wt% (Merck, Germany) as solvent. We also used n-heptane, n-decane and methane to prepare synthetic gas mixture. Tetra-ethoxysilane (TEOS, 98%) [$Si(OC_2H_5)_4$], HCl 37 wt% and ammonium hydroxide (NH_4OH) were also used for sol–gel process. All these chemicals were procured from Merck Co. and were used as received. Distilled water was self-made in our PVT laboratory, Shiraz University, Iran. Synthetic brine of 2.0 wt% NaCl was prepared in distilled water with 1.01 specific gravity and 1 cp viscosity at 20 °C. N_2 gas (purity 99.99%) which was provided from Abughaddare Gas Co., Shiraz, Iran was used as dry gas in this study.

2.2. Synthesis of coating solutions

The preparation procedure of sol–gel coating solutions consisting of acid and base catalysts is shown in Fig. 1. Briefly, the first solution was prepared by 30 min mixing FAS-9 and TEOS before dilution with ethanol at room temperature. Distilled water and HCl were subsequently added drop-wise and the stirring continued for 12 h in a capped glass bottle. Thus, homogenous liquid was obtained. The mass ratio of the mixture was 1:0.41:18:1:0.25, TEOS/FAS-9/ETOH/water/HCl.

For the second solution preparation, TEOS and FAS-9 were dissolved in 50% by weight of total ethanol. The solution was then mixed with ammonium hydroxide/ethanol (50% weight remaining amount) solution and stirred at room temperature for 12 h using a magnetic stirrer. The solution was then ultra-sonicated for 30 min. The final mass ratio of the mixture was 1:0.41:18:1.25, TEOS/FAS-9/ETOH/NH_4OH. The detailed preparation technique of the TEOS and FAS-9 nanocomposite was also presented previously in Ref. [19].

2.3. Characterization

Before the wettability alteration measurements, some characterization tests were carried out on both derived samples. Fourier transform infrared (FTIR) spectra were obtained with a Perkin-Elmer RX1 spectrometer to monitor the chemical bonding between the groups of the sol–gel systems. Thermogravimetric analysis (TGA) on sol–gel powders was conducted using TGA/DSC

Table 1
Relevant data on the reservoir rock samples.

Average pore diameter (μm)	Distribution of pore size (μm)	Porosity (%)	Specific area (m^2/g)
8	2–20	27	0.02