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An Experimental Investigation of Wettability Alteration in Carbonate Reservoir Using γ-Al_2O_3 Nanoparticles

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Abstract

Wettability alteration is one of the most important methods for oil recovery from sandstone and carbonate reservoirs. The effects of salinity, pH, temperature, and chemicals such as surfactants and fatty acids on the alteration of the wettability were described in previous studies. In recent years, attention has been directed to nanoparticles as a wettability alteration agent. The effect of some nanoparticles on the wettability alteration and oil recovery of sandstone and a few carbonate reservoir rocks have been investigated in several works. In this study, the effect of γ-Al_2O_3 on the wettability alteration of one of the Iran carbonate reservoirs is presented. The results show that the adsorption of γ-Al_2O_3 nanoparticles on the calcite surface changes the wettability from oil-wet to water-wet. At a γ-Al_2O_3 nanofluid concentration of 0.5 wt.%, the maximum change in contact angle was observed. It was observed that the oil recovery increased by 11.25% when 0.5 wt.% γ-Al_2O_3 nanofluid was injected into the core sample in a tertiary mode. This work illustrates the successful application of gamma alumina nanoparticle in enhancing oil recovery in carbonate rocks through the wettability alteration of rock surfaces.

Keywords: Wettability Alteration, γ-Al_2O_3 Nanoparticles, Contact Angle Test

1. Introduction

Based on the International Energy Agency (IEA), 64 million (bbl/day) of capacity additions are needed by 2030. A significant part of oil in place in the discovered reservoirs cannot be recovered by primary recovery methods. Some economical and efficient methods are required to make an important contribution to world oil supply in the long term (Bondor, 2010). An important part of these methods is related to the wettability of the reservoir rock. Wettability is the tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids (Anderson, 1986). Wettability conditions is strongly affected by several factors such as rock mineralogy, the constituents and conditions of pore surfaces, the adsorption or deposition of oil constituents on the rock surface, oil composition, reservoir characteristics, etc. (Ghedan et al., 2010). More than half of the world oil reservoirs are carbonate, about 80% of which are classified as neutral to oil-wet (Chabert et al., 2010). In these reservoirs, undesirable capillary pressure prevents the spontaneous imbibition of water from the natural fractures into the matrix blocks (Strand et al., 2006). Thus, regarding the fact that most of the carbonate reservoir matrix rocks are oil-wet, the amount of oil recovery by water injection process is not satisfactory. Numerous experimental works have been published introducing factors that affect

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wettability alteration in carbonate rocks. Some of these factors are surfactants, electrolytes, pH, temperature, salinity, etc. (Rao, 1999; Golabi et al., 2012; Adibhatla and Mohanty, 2006; Rezaei Gomari and Hamouda, 2006; Chattopadhyay et al., 2002). In recent years, attention has been drawn to the effect of nanoparticles on the wetting behavior of reservoir rocks. Wettability alteration by nanoparticles is due to their adsorption on rock surface and forming a water-wet layer on it; thus the viscous forces required to overcome capillary forces are reduced dramatically. Nanoparticles are materials of less than 100 nm in size and fall into three broad categories, namely metal oxides, nanoclays, and carbon nanotubes. Most of these studies are carried out in the sandstone reservoirs (Quinfen et al., 2010; Binshan et al., 2005; Binshan and Shugao, 2002; Roustaei et al., 2012; Binshan and Tailiang, 2008; Skauge et al., 2010). Only a few papers address the wettability alteration by nanoparticles in the carbonate reservoirs (Karimi et al., 2012). As shown by Karimi et al. (2012) the properties of nanoparticles are mainly governed by their surface energies and therefore the adsorption of nanoparticles on a solid surface can significantly change the surface energy and wettability. The concentration of nanofluid can affect the contact angle. Vafaei and Podowski (2005) reported that the variations in contact angle as a function of concentration depend on substrate material and particle size, and for the same mass concentration, smaller-sized particles lead to larger change in contact angle. As opposed to lager-sized particles, free energy increases for smaller-sized nanoparticles.. Nanoparticles are solids and need a fluid to carry them into the formation. Ogolo et al. (2012) observed that the type of fluid used for dispersing the nanoparticles has a very important role in enhanced oil recovery. Karimi et al. (2012) reported that the presence of surfactant in the nanofluid can remove the asphaltene phase from surface or can contribute to the building blocks of nanostructures. Various nanoparticles can be tested for enhanced oil recovery and wettability alteration issues. Gamma-alumina nanoparticles have been considered as one of the most promising advanced materials for a variety of applications due to its distinctive chemical, mechanical, and thermal properties (Rozita et al., 2010). Al_2O_3 nanoparticles are a good agent for oil recovery when used with distilled water and brine as dispersing agents (Ogolo et al., 2012). It can reduce oil viscosity and thereby increasing oil recovery (Nares et al., 2007).

This paper presents the effect of γ-Al_2O_3 on the wettability of one of the Iran carbonate reservoirs. The experimental procedures and impact of γ-Al_2O_3 on the alteration of wettability are described in details. Core flooding experiments were conducted to investigate the effect of γ-Al_2O_3 nanoparticles on oil recovery during a tertiary recovery process.

2. Experimental

Gamma-Al_2O_3 nanoparticles were prepared by Tecnan Company. The properties and transmission electron microscopy (TEM) image of this nanomaterial are given in Table 1 and Figure 1 respectively. Crude oil with a viscosity of approximately 16 cP and a density of 0.8629 gr/cc (at 22 °C) was taken from Ahwaz oil field located in the southwest of Iran. Kerosene was used in a pendant drop device for contact angle measurements. The core plug used in this study was carbonate rock obtained from one of the Iran oil producing formations. This plug had a diameter of 3.65 cm and a length of 5.7 cm with porosity and average permeability of 17.3% and 0.807 mD respectively. NaCl salt with purity of 99.9% was provided by Merck Company for preparing synthetic brine with salinity of 180000 ppm as a saturating fluid in core plugs and used in the cell of the pendant drop device during contact angle measurements.

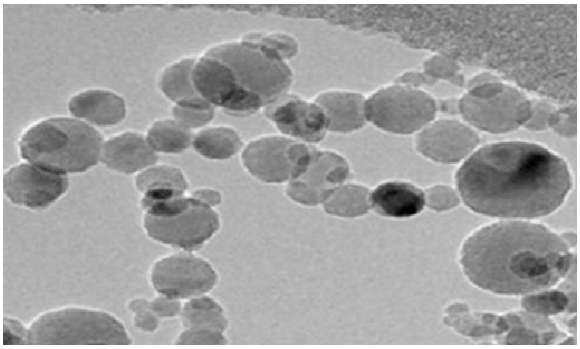

Figure 1
TEM image of γ-Al_2O_3 nanoparticles.

Table 1
γ-Al_2O_3 nanoparticle properties.

Property	Value
Chemical formula	γ-Al_2O_3
Color	White
Morphology	Spherical
Particle size	10-20 nm
Specific surface area	90-160 m^2/g
Purity	99.995 %
Density	3.65 g/cc

For performing contact angle tests, the core plugs were initially cut in small slices of 1.2 cm in diameter with a thickness of 0.4 cm using a trimming machine and polished to achieve a flat and smooth surface. The slices were aged in brine with salinity of 180000 ppm for two weeks and then positioned vertically in crude oil for another two weeks in order to create oil-wet conditions. During this process the temperature was increased to 60 °C for reducing the time required to achieve oil-wet conditions. Next, oil-wet calcite slices were washed with toluene and dried at 50 °C for 24 hours. For measuring the initial wettability of slices, the contact angle tests were run with the pendant drop device.

To study the effect of nanoparticles on the wettability alteration, different concentrations of 1.5 wt.% and 0.5 wt.% of nanofluid were prepared by dispersing measured quantities of γ-Al_2O_3 nanoparticles in distilled water by means of magnetic stirrer and an ultrasonic probe for 180 minutes. Then, the 1.5 wt.% solution was diluted to 1 wt.% and 0.7 wt.% solutions and the 0.5 wt.% solution diluted to 0.3 wt.% and 0.1 wt.% solutions. The calcite slices were aged vertically in these nanofluids for 8 hours at room temperature and were then dried for measuring contact angle according to the procedure mentioned before. To ensure the integrity of measurements, tests were repeated for each nanofluid concentration.

A scanning electron microscope (Leo 1455 vp model) was used to analyze the surface of calcite slices before and after aging in crude oil and after aging in nanofluids. It was used to characterize the surface morphology and mineralogy of calcite slices.

The core flooding apparatus simply consists of an ISCO pump which is very sensitive to flow rate (low flow rate of 10^{-5} cc/min up to 25 cc/min) with a maximum pressure of 7000 psi. A Hassler type,

stainless steel core holder withstanding pressures up to 5500 psi was used for the core sample. A rubber-sleeved core holder into which a carbonate rock was placed was subjected to an external confining pressure. A vacuum pump was used to discharge the air from the core. Before the core flood experiments, the core plugs were cleaned by soxhlet apparatus in contact with toluene vapor for one week. The cleaned samples were then placed in oven at a temperature of 150 °C for 48 hours. A vacuum was applied to the core for three hours to make sure that there was no air left in the core. The core was saturated with brine (with salinity of 180000ppm) at room temperature to determine its porosity and permeability. ISCO pump injected crude oil at a flow rate of 0.3 cc/min into the core until irreducible brine saturation was reached and the core was then aged in crude oil for 5 days to restore reservoir conditions. Afterward, 4 pore volumes of distilled water were flooded into the plugs as a secondary recovery process. In the next step, 4 pore volumes of γ-Al_2O_3 nanofluid were injected into the core plug to investigate the impact of this nanoparticle on oil recovery as a tertiary recovery process. Figure 2 shows a schematic of the core flood setup.

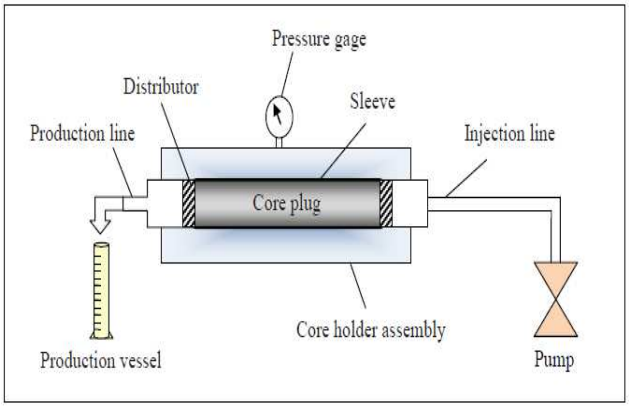

Figure 2
A schematic of core flooding setup.

3. Results and discussion

3.1. Contact angle measurement

Wettability was evaluated by measuring contact angle between oil drop and calcite slice in synthetic brine for several systems. The contact angle measurements were repeated as mentioned before and supreme variation between the measured data for each case was about 10°; thus contact angle data contain a maximum error of ±5°. The oil/water contact angle for oil-wet calcite slice before the employment of nanofluid was about 119° as shown in Figure 3, which proved oil-wet conditions.

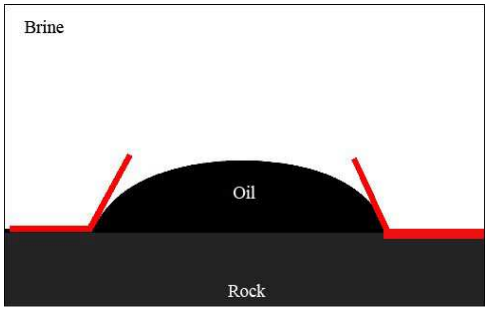

Figure 3
Contact angle test result on oil-wetted calcite slice.

The SEM images of calcite slice before and after aging in crude oil show the accumulation of crude oil components and the formation of a thin film on the surface of calcite slices (Figure 4). These components are polar constituents, especially carboxylic groups, which are adsorbed onto the rock surface and change the wettability of the surface to oil-wet conditions (Thomas et al., 1993).

a) b)

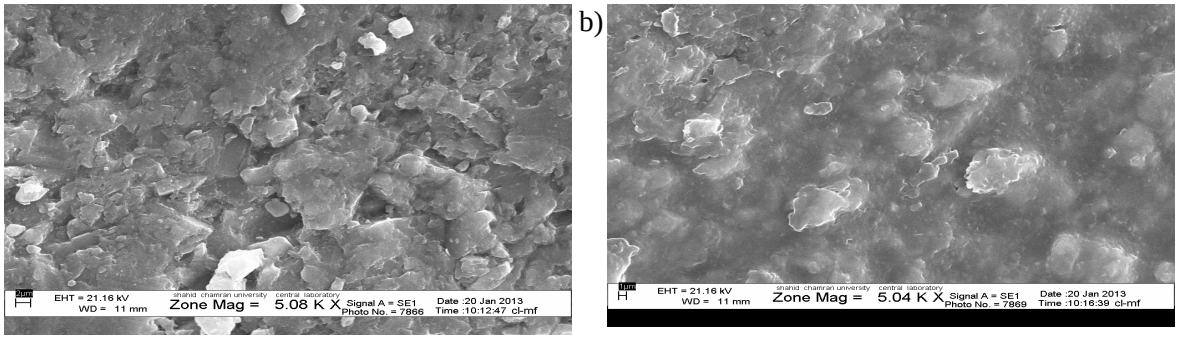

Figure 4
SEM images for (a) water-wetted calcite slice and (b) oil-wetted calcite slice.

The results of contact angle measurements after the application of nanofluid are shown in Figure 5. These results show the wettability alteration of calcite slices from oil-wet to water-wet conditions by a reduction in contact angle; they also demonstrate the dependence of final contact angle on nanofluid concentration. The adsorption of nanoparticles onto the rock surface changes surface energy and alters the wettability of calcite slices.

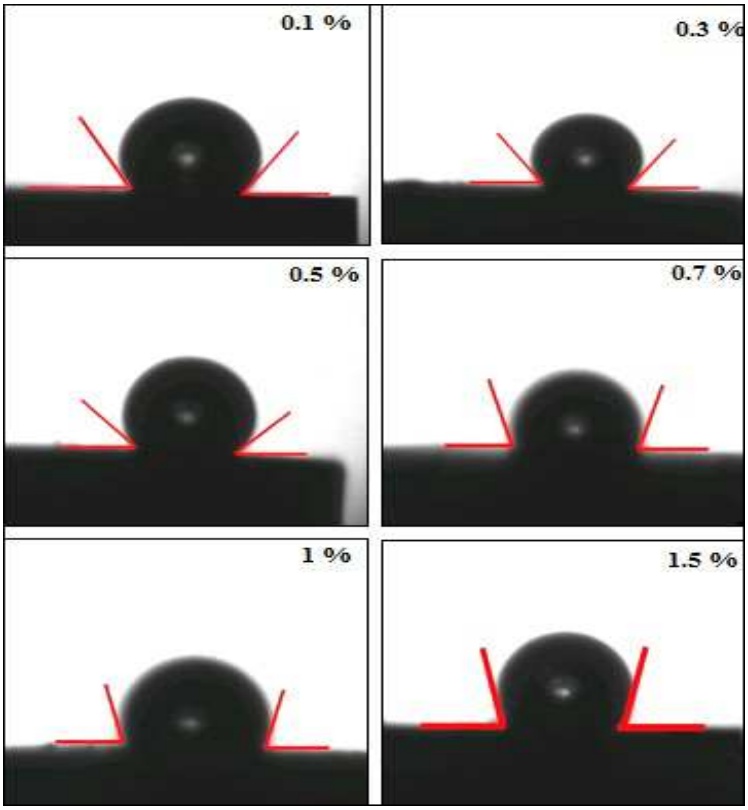

Figure 5
Contact angle test results for calcite slice after aging in γ-Al_2O_3 nanosolutions with different weight fractions.

The SEM images in Figure 6 indicate the adsorption of γ-Al_2O_3 nanoparticles on the calcite slice

surface. These images show the construction of nanostructures on the rock surface, which changes the wettability to water-wet conditions. The maximum reduction in contact angle by γ-Al_2O_3 nanoparticle was detected at a concentration of 0.5 wt.%. As shown in Figure 7, the wettability alteration is developed by increasing the concentration of γ-Al_2O_3 nanofluids from 0.1 wt.% to 0.5 wt.%; but above a concentration of 0.5 wt.%, contact angle is increased and wettability is changed to neutral wet conditions.

a) b)

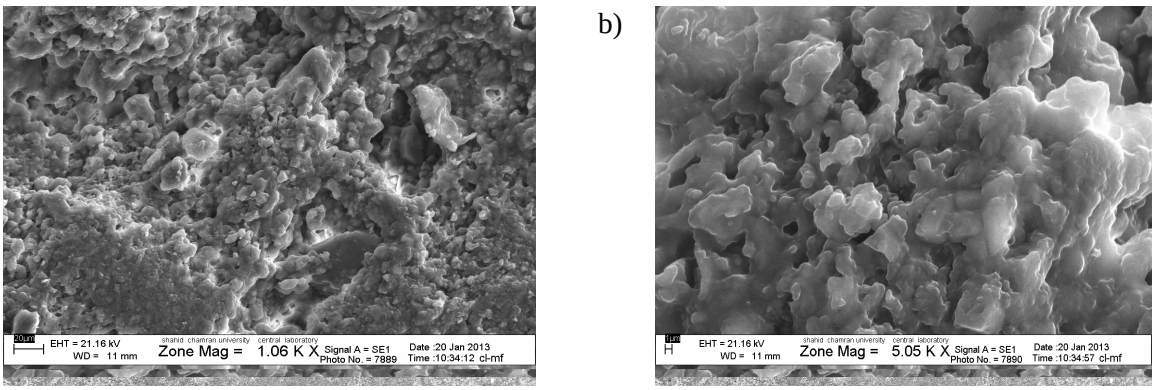

Figure 6
SEM images γ-Al_2O_3 nanoparticles adsorption on calcite surface with a magnification of (a) 1000 and (b) 5000.

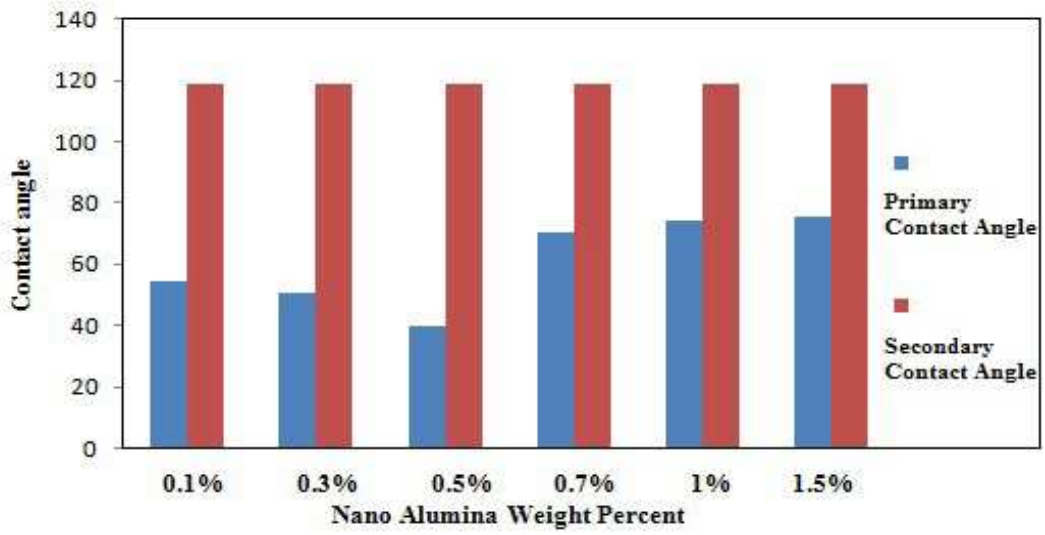

Figure 7
Comparison of contact angle test results for calcite slices before and after aging in of γ-Al_2O_3 nanosolutions for different levels of weight percent.

3.2. Oil recovery

The effect of wettability on oil recovery was investigated by core flooding experiments. As mentioned above, the core flooding test was conducted at room temperature for oil-wet carbonate rocks. 0.5 wt.% γ-Al_2O_3 nanofluid was used in this experiment, because of the high efficiency of γ-Al_2O_3 nanofluid in the wettability alteration of carbonate rocks at this concentration. Water flooding recovery of a core plug was about 65% and, by the injection of nanofluid, oil recovery increased by 11.25% as a tertiary process. The result indicates (Figure 8) that γ-Al_2O_3 nanoparticles can increase oil recovery. When nanofluid is injected into the core plug, oil recovery increases due to wettability alteration to water-

wet conditions by the adsorption of nanoparticles on the rock surface, by the reaction of nanoparticles with immobile oil to induce them to flow, and by the effect of nanofluid on viscosity (Roustaei et al., 2012). However, the adsorption of nanoparticles on the rock surface is a relatively slow process and thus a low nanofluid injection rate (0.1 cc/min) is selected.

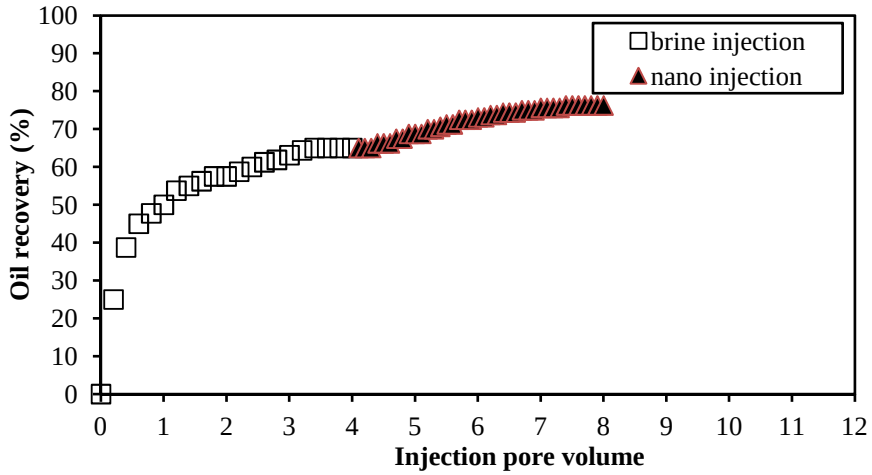

Figure 8
Oil recovery results for water flooding and nanofluid injection.

4. Conclusions

In the current work, the wettability alteration of a carbonate rock and enhancing oil recovery were investigated using γ-Al_2O_3 nanofluid. According to the results, the following conclusions can be drawn:

- γ-Al_2O_3 nanoparticles can be considered as an effective agent in the changing the wettability of carbonate rock surface from oil-wet to water-wet;
- The analysis of calcite slice SEM images before and after aging in nanofluid confirms the adsorption of γ-Al_2O_3 nanoparticles on slice surfaces;
- Contact angle is first decreased by increasing γ-Al_2O_3 nanoparticles weight fraction, reaches a minimum, and then increases. However, there is a significant difference between the secondary contact angle and the primary contact angle at the all concentrations of nanoparticles;
- By injecting γ-Al_2O_3 nanofluid as a tertiary recovery, oil recovery increased by 11.25% through changing the wettability of carbonate rock surface.

Nomenclature

cP	: Centipoise
ppm	: Part per million
SEM	: Scanning electron microscopy
TEM	: Transmission electron microscopy

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