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Laboratory Investigation of Hybrid Nanoparticles Injection for Enhanced Oil Recovery Process

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Abstract - Nanoparticles due to their unique characteristics are gaining attraction for enhanced oil recovery (EOR) applications. Nanoparticles during the EOR process may activate many mechanisms, particularly wettability alteration, and thus improve the recovery factor. Silica nanoparticle has been largely testified for EOR. The effect of alumina nanoparticles for EOR is also being investigated recently. Their combination may enhance their performance in wettability alteration. In this research, we studied the wettability alteration and recovery performance of the hybrid nanoparticles. A series of experiments were conducted starting from zeta potential and contact angle measurement to determine optimum concentrations of silica, alumina, and hybrid nanoparticles. After dispersing nanoparticles (alone and hybrid), solutions were homogenized using ultrasonic homogenizer. The zeta potential results showed that the silica nanofluid could stay stable for at least 3 days without the need for a stabilizer. However, a stabilizer (SDBS) is required to prepare stable alumina and hybrid nanofluid. Baseline experiments were conducted with the stabilizer to quantify the performance of the stabilizer. Later, contact angles were measured (at room temperature and 80 °C) to analyze the effect of the nanofluid on rock/oil/brine systems and to determine the optimal nanofluid concentration. The results of contact angle experiments prove that, for both temperatures (room and 80 °C), maximum alteration in wettability was shown by the hybrid nanoparticle mixture (0.1wt%silica+0.05wt%Alumina), 29° and 33°, respectively. Finally, coreflooding tests were conducted to study the performance of the optimal nanofluid in enhancing oil recovery. The coreflood experiment was conducted with optimum hybrid nanofluid at 80 °C. The recovery factor recorded with Caspian Seawater was 42%, and silica nanofluid improved the recovery to 46%. The injection was followed by a hybrid nanofluid, which increased the recovery factor to 73%. The results presented in this study prove that hybrid nanoparticle injection improves the performance as compared to standalone nanoparticles.

***Keywords*:** Chemical Enhanced Oil Recovery, Nanoparticle flooding, Wettability alteration, Hybrid Enhanced Oil Recovery

1. Introduction

Carbonate reservoirs account for more than 50% of global conventional oil reserves, and only 20-40 percent of original oil in place (OOIP) can be produced through primary and secondary recovery processes [1]. The main reason for low recovery in carbonate reservoirs is the complexity and wettability of carbonate. The enhanced oil recovery (EOR) methods are becoming a critical way to improve oil production, mainly after the secondary recovery process. Chemical EOR is one of the important EOR techniques which is practically implemented in China and around the world. Chemical EOR can be mainly classified into alkaline flooding, surfactant flooding, and polymer flooding. The main mechanisms of chemical EOR are mobility control by using polymer and interfacial tension (IFT) reduction by using a surfactant.

Nano-assisted EOR is one of the newest chemical EOR techniques. Nanotechnology deals with nanoparticles that have size on the order of a nanometer [2]. Because of their small size, nanoparticles possess some unique features than other materials, such as a relatively high surface to volume ratio, which will be very helpful to enlarge the contact area between nanoparticles and rock surfaces [3]. Nanoparticles have been proved to enhance oil recovery for carbonate reservoirs at a laboratory scale, and the most acceptable mechanism proposed by the researchers is wettability alteration [4].

Various researchers have reported that several possible mechanisms may take place individually or simultaneously during the implementation of nanofluid EOR [5, 6]. Those mechanisms include but are not limited to, altering the wettability from oil-wet to water-wet, reducing IFT, changing the structural disjoining pressure, mobility control by increasing the viscosity of displacing fluid (nanofluid), and log-jamming effect [5, 6]. Consequently, the oil trapped in the pores will be pushed to move and consequently decreases residual oil saturation.

The silica nanoparticle is one of the most commonly used nanoparticles [7-10]. On the other hand, alumina nanoparticles have also been shown to improve oil recovery [11, 12]. However, there is little research on combining silica and alumina nanoparticles for EOR in carbonate reservoirs. This study provides a comparison of the performance of the silica nanoparticles and hybrid nanoparticles as an EOR method for carbonate reservoirs.

2. Materials and Methods

This section provides details of the materials and methodology used in this study.

2.1. Core samples

Indiana limestone rock samples were used in this research work. The core sample is first cut into 3-inch-long core plugs and then the pellets are cut into a semicircle shape with a radius of 1.5 cm and a thickness of around 0.5 cm from these cores and is shown in Figure 1. Figure 2 presents the energy dispersive spectroscopy (EDS) analysis of the rock sample showing the elemental composition of the rock, which coincides with the limestone. Absolute permeability and porosity of the core plugs vary between 45-55 mD and 14.5 -15.1%, respectively.

Fig. 1: Core pellets used in this study for contact angle measurement

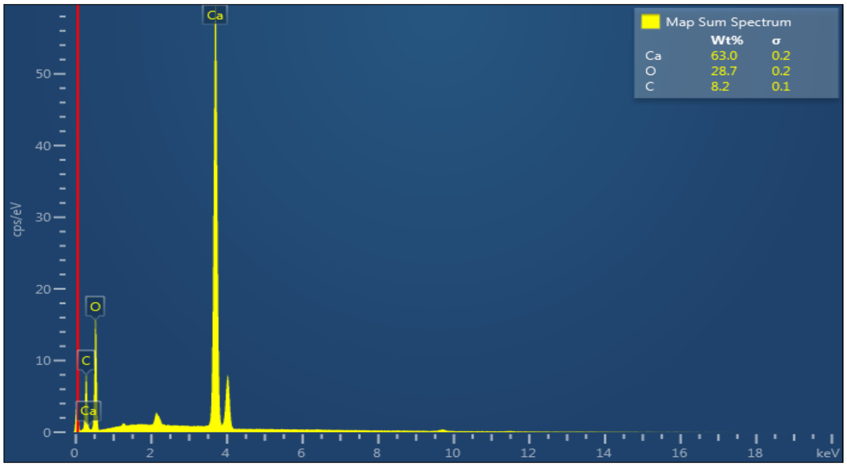

Fig. 2: Elemental composition of core samples

2.2. Crude Oil

The crude oil sample is received from one of the oilfields in Kazakhstan in the Caspian Sea region. The oil is filtered to remove solid particles. The properties of the oil are the same as those presented in one of our previous studies [7].

2.3. Nanoparticles

Two nanoparticles, Al_2O_3 and SiO_2, were studied in this research. Both nanoparticles were purchased from Sky Spring Nanomaterials, Inc. Table 1 presents the physical properties of these two nanoparticles.

Table 1: Types of nanoparticles

Nanoparticles	**Type**	**Size**	**purity**
SiO_2	porous	10-20nm	99.5%
Al_2O_3	alpha	40nm	99.0%

2.4. Brines

Distilled water (DW) is used as the base fluid for dissolving both nanoparticles used in the experiment. Caspian Sea water (CSW) with a salinity of 13000 ppm is used as injection brine while formation water (FW) with a salinity of 182980 ppm is used as formation brine in this experiment. The ionic composition of CSW and FW is presented in Table 2.

Table 2: Ionic composition of CSW and FW

Ions	**CSW (ppm)**	**FW (ppm)**
Na+, K+	3240	81600
Ca2+	350	1470
Mg2+	740	9540
Cl-	5440	90370
SO42-	3010	0
HCO3-	220	0
TDS	13000	182980

2.5. Nanofluid Preparation

To screen and prepare stable nanofluid, the related parameters: the type of base fluid, the weight concentration of nanoparticles in the solution, the stirring time as well as the stirring speed of the magnetic stirrer, the homogenization time as well as the power range of the ultrasonic homogenizer, etc. were optimized. However, despite varying all these parameters the alumina nanoparticles prepared in CSW precipitated, thus CSW failed to be used as a base fluid for dispersing nanoparticles. Therefore, DW was used to disperse nanoparticles and was proven to be more appropriate for use as the base fluid. Different weight concentrations (0.05%, 0.1%, 0.3%, 0.5%) of nanofluid were prepared. The weight of the nanoparticles was weighed on the electronic weight balance. The nanofluid is first stirred on the magnetic stirrer for 30 minutes at 650rpm. Then the nanoparticles are dispersed in the ultrasonic homogenizer for 45 minutes at a 70% power rate with a frequency of 20-25 Hz using a 6mm probe.

2.6. Zeta Potential Test

The zeta potential measurements were conducted to investigate colloid-electrolyte interactions and to test the stability of the nanofluid using the Malvern Zeta sizer. The zeta potential values determine the various stability regions of the nanofluids, as presented in our previous research paper [7].

2.7. Contact Angle Measurement

The cleaned core pellets were saturated with oil and were aged in oil to achieve oil wet conditions. After obtaining the initial oil-wet condition of the pellets, the pellets were aged in nanofluids, and contact angle measurements were carried out using OCA-25 to determine the optimal concentration of nanofluid. The captive bubble method was used to measure the contact angle to avoid the gravity effect. The oil drop was injected using a special bent needle beneath the pellet; thus, the drop is attached to the lower surface of the pellet. Once the equilibrium is achieved, the contact angle was measured. Later, the contact angle was subtracted from 180°, to report the data in the conventional form.

2.8. Rheology Measurement

The rheology of optimal nanofluid was measured at different shear rates at 80°C by using Anton Paar Modular Compact Rheometer 302. The viscosity of both nanofluids does not change much with the shear rate at 80 °C, indicating that they are all Newtonian fluids. In addition, the viscosity of both nanofluids is closer to water viscosity. The viscosity values of the nanofluids are presented in Table 3.

Table 3: Viscosity of nanofluids

Nanofluid	**Viscosity, mPa.s**
Optimal SiO2 nanofluid	1.474
Optimal hybrid nanofluid	1.292

2.9. Coreflooding Experiment

A conventional coreflooding system was used to conduct the experiment. The schematic of the system is presented in our previous research paper [7]. The core plug was firstly dried in the oven for 24 hours at a temperature of 80 ℃ and then saturated with FW for another 24 hours at 1100 psi. Subsequently, the core plug was flooded with FW to measure the absolute permeability. The core plugs were then flooded with crude oil to measure effective permeability and irreducible water saturation and initial oil saturation. Finally, the core plugs were aged in the oven for four weeks at 80 ℃ to obtain strong oil-wet condition.

After aging, the core plugs were loaded again in the core holder and was then flooded with CSW to mimic secondary recovery process at various rates. Once there was no oil production, 0.1wt.% SiO_2 nanofluid was injected for enhanced oil recovery. Finally, the optimal hybrid (0.1wt.% SiO_2+0.05wt.% Al_2O_3) nanofluid was injected for ultimate oil recovery. Injection rates were designed at 0.5 cc/m, 2 cc/m, 5 cc/m, and 7 cc/m to overcome the capillary end effects. The recovered oil volume in each stage was measured for volumetric calculations and analysis.

3. Results and Discussion

This section provides the results and a discussion of the results obtained in this study.

3.1. Nanofluid Stability

The first thing was to prepare a stable nanofluid. Visual observation and zeta potential tests were conducted to study the stability of nanofluid. First, four times diluted CSW (4dCSW) was used as a base fluid to prepare nanofluids. For Al_2O_3 nanofluid, 0.05wt.%, 0.1wt.%, 0.3wt.% and 0.5wt.% concentrations were prepared. However, it was noticed by visual inspection that the nanoparticles precipitated quickly in 10 minutes in 4dCSW. Therefore, the zeta potential of the nanofluids prepared in 4dCSW was not measured. To avoid the nanoparticle precipitation, we used distilled water as the base fluid for preparing both silica and alumina nanofluids because we finally needed to prepare the hybrid nanofluid.

For the SiO_2 nanofluid, we previously determined the optimum concentration and found that it was 0.1% by weight; the details are presented in our previous research [13]. We also noted that the silica nanofluid is very stable and thus does not require any stabilizer. In this study, we prepared silica nanofluid (0.1 wt%) in distilled water, and it also proved to be stable. The measured zeta potentials of silica nanofluids as a function of time are presented in Figure 2.

For Al_2O_3 nanofluid, it is recommended in the literature to use SDBS surfactant that improves the stability of Al_2O_3 nanofluid [14]. However, before using SDBS, we tested the pH adjustment method to improve stability at various pH values (pH=3, pH=5, pH=9, pH=10, and pH=11). It was noticed that for pH=3, pH=5 and pH=9, nanoparticles precipitated immediately right after homogenization. At pH=10 and pH=11, although the zeta potential value is in the stable zone, the nanoparticles precipitated fully in one day. At pH=6, which is the condition without pH adjustment, the nanoparticles precipitated 10 minutes after homogenization. Therefore, we conclude that the pH adjustment method does not enhance the stability of the alumina nanofluid.

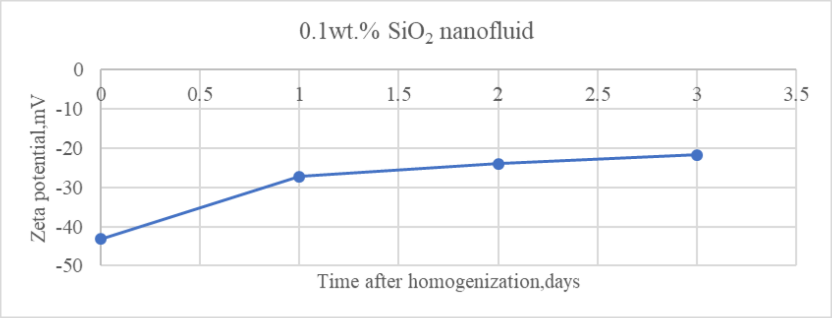

Figure 3 Zeta potential values of 0.1 wt% SiO2 as a function of time

Table 4: Zeta potential values of SDBS and Alumina nanofluids as a function of time

SDBS concentration(wt.)	**Zeta Potential (mV)**		**Al_2O_3 concentration (wt. %)**	**Zeta Potential (mV)**	
	t=0 days	**t=3 days**		**t=0 days**	**t=3 days**
0.01%	-37.1	-37.2	0.05	-50	-48
0.03%	-52.5	-47.8	0.1	-51.1	-52.2
0.05	-48.9	-49.7	0.3	-45.9	-40.7
0.08%	-54.4	-51.6	0.5	-39.8	-35.8
0.1%	-56.2	-54.1			

After failing to achieve stable alumina nanofluid through pH adjustment method, surfactant SDBS was used to attain the stability of nanofluid. First, the alumina concentration was fixed at 0.05wt.%, to determine the optimal concentration of SDBS. As it can be observed from the result shown in Table 4, the 0.05 wt.% SDBS concentration was found to be the optimum concentration. Subsequently, at a fixed SDBS concentration (0.05 wt.%), nanofluids with varying concentrations of alumina were prepared. The zeta potential values measured for all alumina nanofluids are presented in Table 4. As can be observed by the data presented in Table 4, the use of SDBS stabilized the nanofluids for all alumina concentrations.

3.2. Contact Angle (Wettability Alteration)

In order to study the performance of alumina nanoparticles on the wettability of carbonate rocks, and to determine the optimal concentration of alumina nanofluid, pellets are aged in alumina nanofluid (0.05wt.%,0.1wt.%,0.3wt.%, and 0.5wt.%), at fixed SDBS=0.05%, for one week at 20°C and 80°C. The contact angles measured for all alumina concentrations and for both temperatures are presented in Figure 4 (a). It can be observed from the data presented in Figure 4 (b) all concentrations of alumina studied in this research has a very weak effect on wettability alteration for both temperatures, even after soaking pellets in nanofluids for one week. The maximum contact angle difference was shown by 0.05% by weight of alumina for both temperatures. For 20 °C, the contact angle change was found to be 11.3°, while for 80 °C, the contact angle change was 4.4°. Although the alumina nanofluid failed to considerably alter the wettability from oil wet conditions to water wet conditions, however, the maximum alteration in wettability is shown by 0.05 wt.%, therefore, it was selected as an optimum concentration to study further for hybrid method. It is worth mentioning that a base line with only SDBS was also established, and it was noted that change in contact angle was negligible.

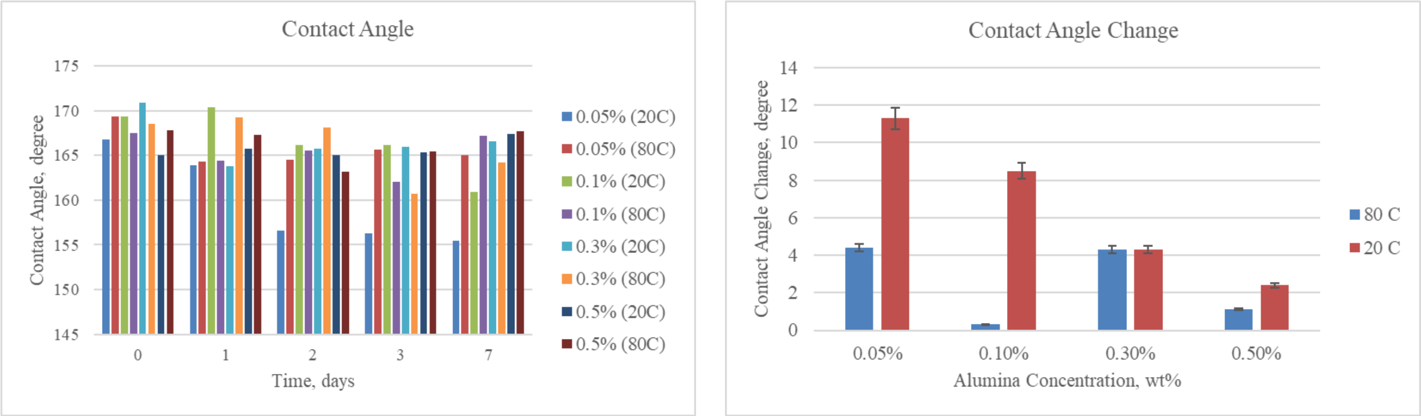

Fig. 4. a) Contact angle as a function of time for various alumina concentrations, b) Change in contact angle after one week

On the other hand, silica nanofluid showed a promising trend for wettability alteration, for both temperatures. The pellets were soaked in 0.1 wt.% silica nanofluids for one week and the change in contact angle was found to be 22.5° and 44.3° for 20 °C and 80 °C, respectively, as presented in Figure 5 (a). The wettability alteration was more prominent for higher temperature and shifted the wettability of pellets from strongly oil wet to intermediate wet conditions.

In order to prepare hybrid nanofluid and to determine the effectiveness of hybrid nanofluid, optimum concentrations of alumina (0.05 wt.%) and silica (0.1 wt.%), determined from the standalone experiments were mixed. The pellets were aged in hybrid nanofluid and contact angles were measured at different times for both temperatures. The effect of hybrid nanofluid on the contact angle is presented in Figure 5 (b). As can be seen from Figure 5 (b), contact angle decreased in all cases after aging in hybrid nanofluid for one week. It is worth mentioning that the change in contact angle is found to be 29.1° and 33.6° for room and elevated temperatures, respectively, indicating no temperature's catalyst effect on wettability alteration, consequently the final state of the pellets was close to intermediate-wet conditions.

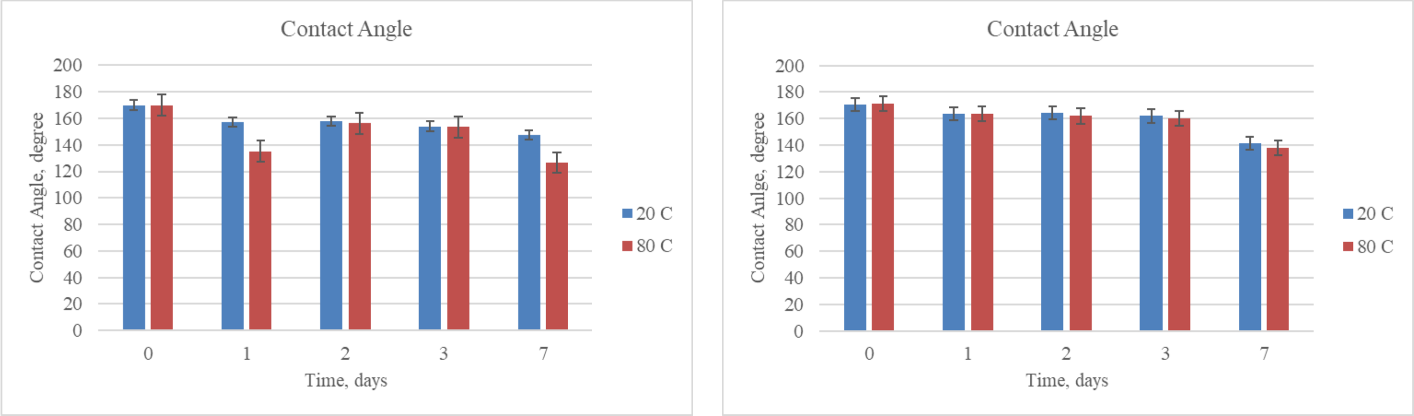

Fig. 5. a) Contact angle as a function of time for various silica concentrations, b) Contact angle as a function of time for hybrid nanofluid

3.3. Coreflooding Experiment

This coreflooding experiment has two aims: firstly, to investigate whether pure 0.1wt.% silica nanofluid and optimal hybrid(0.1wt.%silica+0.05wt.%alumina) nanofluid will enhance oil recovery in oil-wet carbonate rocks; secondly, to compare the performance of pure silica nanoparticles and hybrid nanoparticles as an EOR process. Figure 6 presents the results for the recovery from the coreflood test as a function of the pore volume injected, together with the pressure profile.

As shown in Figure 6, the recovery factor from CSW was found to be 41.8% of OOIP, whereas the injection of optimal SiO2 nanofluid increased recovery to 45.9% of OOIP. However, the injection of an optimized hybrid nanofluid enhanced oil recovery resulted in an incremental recovery of 27.2 %, corresponding to 73.1% OOIP. The pressure profile indicates that the pressure gradient increased by 3 times during the nanofluid injection. Since the viscosity of nanofluid is similar to the brine, it indicates the adsorption of hybrid nanoparticles on the rock, thus promoting the wettability alteration process and resulting increment in oil recovery. Therefore, this experiment showed a very positive result: both 0.1wt.% SiO2 nanofluid and the optimal hybrid nanofluid can enhance oil recovery in oil-wet carbonate reservoirs; the optimal hybrid nanofluid is much stronger than the pure optimal silica nanofluid in EOR in oil-wet carbonate rocks.

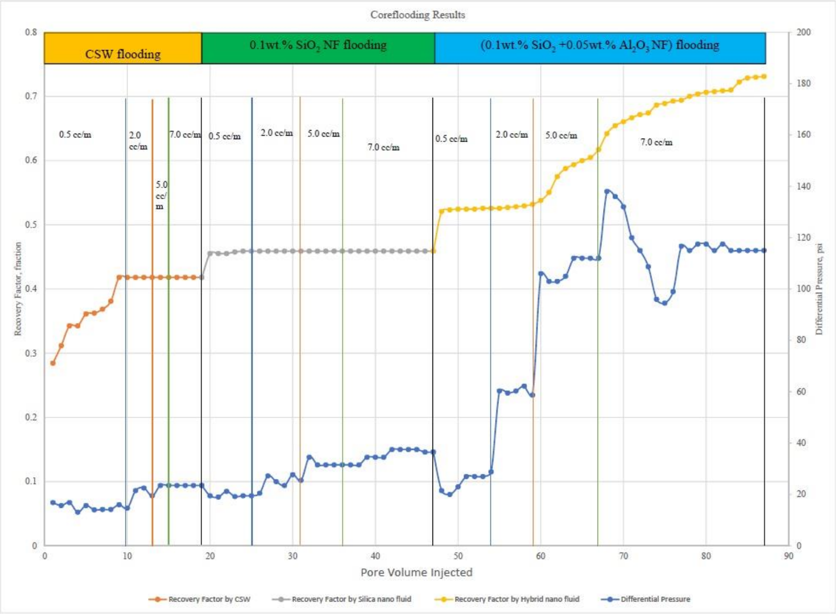

Fig. 6. Coreflooding results for CSW, silica and hybrid nanofluid

4. Conclusions

Although silica and alumina nanoparticles have been widely used for EOR process, there is little research on combining these two nanoparticles for EOR application. This research investigated and compared the performance of the standalone silica and alumina nanoparticles as well as hybrid nanoparticles as an EOR process in carbonate rocks by studying the wettability alteration mechanism. The following conclusions are drawn from this research:

(1) Compared with alumina nanoparticles, silica nanoparticles are more adapted to the saline environment. However, alumina nanoparticles can only remain stable with the help of surfactant SDBS.

(2) Silica nanoparticles showed a better result than alumina nanoparticles for wettability alteration in carbonate reservoirs. However, the silica nanoparticles altered the wettability of pellets from a strong oil-wet state to intermediate wet conditions.

(3) Both silica nanoparticles and hybrid nanoparticles showed the capability to improve oil recovery in oil-wet carbonate rocks. Furthermore, the optimal hybrid nanofluid improved oil recovery more than the optimal silica nanofluid, increasing around 27%.

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