Effect of a Nanoparticle on Wettability Alteration and Wettability Retainment of Carbonate Reservoirs

Yue Shi, Xuezhen Wang, and Kishore Mohanty*, The University of Texas at Austin

Abstract

The oil recovery in many carbonate reservoirs is low due to oil-wetness and heterogeneity. In this study, nanoparticles are evaluated for altering the wettability of oil-wet limestones and their properties are compared with those of an anionic surfactant. A surface-modified silica nanoparticle (SiNP) with a negative zeta potential was found to be aqueous stable in brines. Wettability studies showed that the SiNP cannot change the wettability of an initially oil-wet calcite plate, but SiNP treated calcite surface can remain water-wet after aging in oil. Spontaneous imbibition tests confirmed the observations of wettability tests and showed that a SiNP treated carbonate core retained its water-wettability during oil injection and aging. The imbibition into a SiNP treated and oil aged core was comparable to that in a water-wet core. However, SiNP was not able to remove the oil layers in initially oil-wet cores and imbibe water into these cores. In contrast, the anionic surfactant could alter the oil-wet carbonate rocks to a more water-wet condition, but failed to prevent the water-wet surface from getting oil-wet during oil-aging. The results suggest that the SiNP can be injected into wettability-altered (water-wet) reservoirs/regions to help retain the water-wettability during the long-term oil production. The 0.5 wt% SiNP dispersions transported through 18 mD limestone cores without any plugging. The SiNP retention was measured to be 2.5 mg/m^2, much higher than that of the anionic surfactant.

Keywords: Silica nanoparticle, wettability retainment, anionic surfactant, wettability alteration

*Corresponding Author: Kishore K. Mohanty, The University of Texas at Austin, mohanty@mail.utexas.edu

1. Introduction

Carbonate reservoirs contain more than half of world's oil reserves. Oil recovery by waterflooding is normally less than 20% OOIP (original oil in place) due to high heterogeneity and oil/mixed-wettability. Injected water mostly flows through high permeability fractures/regions and bypasses the tight oil-wet matrix. To invade into the oil-bearing tight matrix, fluid must overcome the negative capillary pressure. Surfactant treatment has been proposed to direct injected water into the matrix by altering the rock wettability and/or reducing interfacial tension. Standnes and Austad (2000) have shown that quaternary ammonium cationic surfactants, C_nTAB, alter wettability and recover oil in imbibition tests (>60% of OOIP) in carbonate cores. Standnes et al. (2002) attributed the wettability alteration by cationic surfactant to the formation of a strong ion pair between the surfactants and adsorbed organic acids. Our previous work (Shi et al. 2021) showed that cationic surfactants (CTAC and DTAB) have high wettability alteration potential for a West Texas carbonate reservoir among 37 surfactants tested. Anionic surfactants have also been proposed to lower the IFT and improve spontaneous imbibition from carbonate rocks (Seethepalli et al. 2004; Zhang et al. 2006). A sulfonated anionic surfactant, Calimulse AOS, also changes the oil-wet West Texas carbonate reservoir rock to an intermediate-wet condition and produce additional 45% oil compared to brine imbibition (Shi et al. 2021). Other anionic surfactants as well as nonionic and zwitterionic surfactants have also been identified to be effective in interfacial tension reduction and wettability alteration in carbonates (Vijapurapu et al. 2004; Xie et al. 2005; Gupta and Mohanty 2011).

It has been experimentally demonstrated that nanoparticles (NPs) can also be used to improve oil recovery. NPs can reduce interfacial tension between oleic and aqueous phases to improve oil recovery (Shahrabadi et al. 2012; Hendraningrat et al. 2013; Zaid et al. 2013). Suleimanov et al. (2011) evaluated the performance of a light non-ferrous metal NP with particle size of 90-110 nm. Addition of the NPs into the anionic sulphonate solution showed no significant effect on contact angle reduction, but decreased the interfacial tension. Compared to surfactant flooding, NPs aided surfactant flooding recovered approximately 10% additional oil from the sandpack. Luo et al. (2016) designed and formulated a nanofluid with graphene-based amphiphilic nanosheets, which is stable and effective in a high salinity brine (4 wt% NaCl and 1 wt% $CaCl_2$). The nanosheets tended to adsorb at the oil/water interface and reduced interfacial tension. Oil displacement tests were performed in high permeability sandstones; low concentrations of nanofluid (0.01 wt%) produced up to 15% incremental oil recovery.

NPs have also been proposed for wettability alteration in porous rocks. Many studies have shown the effectiveness of NPs in altering wettability of sandstone surfaces (Shahrabadi et al. 2012; Hendraningrat et al. 2013; Roustaei et al. 2013; Hendraningrat and Torsæter, 2015; Yuan et al. 2021). Wasan and Nikolov (2003) proposed that nanoparticles can form a wedge-shaped film at the three-phase contact region. Structural disjoining pressure is applied to the vertex of the film which continuously drives the nanoparticles at the vertex to move forward. Zhang et al. (2014) presented an in-house silica nanofluid which was designed for high salinity and high temperature conditions. Compared to brine, the nanofluid decreased contact angle of the crude oil droplet on a glass substrate from 74° to 1.2° and reduced interfacial tension from 16 mN/m to 1.4 mN/m. Spontaneous imbibition with Berea sandstones showed the oil recovery was enhanced from less than 5% to 55% by adding nanofluid into the brine. Ehtesabi et al. (2014) showed improved recovery of heavy oil from sandstone cores by altering the wettability from oil-wet to water-wet by TiO_2 NP. Scanning electron microscopy revealed a homogeneous deposition of nanoparticles onto the core surface, which is proposed to be responsible for the wettability alteration. Kuang et al. (2018) studied the synergistic effect of nanoparticles and surfactants for enhanced oil recovery. Compared to nonionic surfactants alone, Al_2O_3 NP aided nonionic surfactant showed better performance (with around 4% incremental oil recovery) in sandstone cores.

Some studies have also been conducted to evaluate wettability alteration potential of NPs in carbonates (Esfandyari et al. 2014; Dehghan-Manfared et al. 2016; Alzobaidi et al. 2021). Karimi et al. (2012) reported an experimental study on effect of a ZrO_2-based NP on the wettability alteration of carbonates. High NP concentration ($\geq$5 wt%) was used and the contact angle on carbonate surface was reduced from 90° to 35° by the addition of NP. However, the calcite surface was only aged in n-heptane for oil-wetness without the presence of organic acid components prevalent in crude oils. Esfandyari et al. (2014) performed a comprehensive study on EOR potential of three metal oxide NPs (Al_2O_3, TiO_2 and SiO_2) in carbonates. At room temperature, contact angle in presence of Al_2O_3, TiO_2 and SiO_2 was reduced to 71°, 57° and 26° from the contact angle of 90° in brine. Displacement tests in high-permeability (>2 Darcy) limestones revealed EOR potentials of 2% - 10% incremental oil recovery after waterflood. The carbonate rock was not aged with the crude oil properly in this work (>80 °C, a week for plates and a month for cores). Dehghan-Manfared et al. (2016) evaluated the stability and wettability alteration potential of the unmodified ultrapure silica NP. 500 ppm of silica NP (SiNP) can remain stable in NaCl brine with salinity up to 4 wt% at the room temperature. The calcite surface was treated with a model oil (n-heptane with 0.018 M of steric acid). Contact angle measurements showed that NP could effectively reduce contact angle from 150° to 50° and contact angles decreased with the increase of NP concentration. The partial release of hydrophobic organic groups from the oil-wet surface in presence of NP was suggested as the wettability alteration mechanism.

Jang et al. (2018) used silica NPs modified with a silane coupling agent, (3-Glycidoxypropyl)trimethoxysilane, which can be tolerant of high salinity (up to 20 wt%) and high temperature (90°C) reservoir conditions. The NPs could alter the originally kerosene-wet dolomite and limestone to neutral-wet/water-wet. Jafarbeigi et al. (2020) synthesized a surface modified nano-graphene oxide (NGO) and showed its effectiveness in wettability alteration. The synthesized NGO fluid could reduce IFT from 19.34 mN/m to 10.8 mN/m and decrease the contact angle from 166° to 40° at a low concentration of 500 ppm, but the oil-aging details were not obvious in the publication. NGO particles could achieve 15% incremental oil after waterflood from carbonate cores. Naghizadeh et al. (2020) applied a fluorine modified silica NP to alter the carbonate surfaces from liquid-wetting to intermediate gas-wetting for the application of condensate removal. Coreflood tests showed that the nanoparticle-treated cores can achieve approximately 10% more condensate recovery by injecting gas compared to untreated cores. A recent work done by Alzobaidi et al. (2021) compared the performance of NPs modified by cationic, nonionic and anionic ligands. Cationic ligand modified NP was found to be effective in reducing contact angles at low temperatures, but those with anionic and nonionic ligands. Han et al. (2022) utilized nanoparticles as additives in low salinity water (LSW) flood for EOR from carbonates. The results suggest that LSW can reduce the contact angle due to the charge screening effect and enhance the NP adsorption on the rock. Silica NPs were found to be effective in contact angle reduction by electrostatic attraction with carbonate rock, but not in IFT reduction. In contrast, Al_2O_3 NPs have relatively weak hydrophilicity than SiO_2, so that they tend to migrate to oleic phase and reduced IFT. The oil phase was decane with no organic acids in this study. In many of the studies cited here, the oil was not a crude oil and the oil-aging was not conducted rigorously. The wettability alteration is evaluated for an oil-wet rock in this study with a nanoparticle.

During wettability alteration floods in reservoirs, the wettability altering chemical slug is followed by a brine drive. It is important that the wettability of the rock does not revert back to the original wettability after the passage of the chemical slug. The organic components from oil could attach to the carbonate surfaces after the chemical slug and make it oil-wet again. It is of great importance to keep the wettability-altered carbonate rock water-wet; this is termed wettability retainment. SEM-EDS and AFM analysis performed by Al-Anssari et al. (2016) showed that SiNP can irreversibly adsorb onto the calcite surfaces and prevent oil-wetness.

In this study, the wettability alteration and wettability retainment potentials of a surface modified negatively charged SiNP were evaluated on calcite plates and carbonate cores. Similar experiments were also conducted for an anionic surfactant because they both carry negative charge. The target reservoir is a carbonate reservoir from West Texas with the reservoir temperature of 35 ºC. The plates and cores were aged with the reservoir oil and brine at 85 ºC to make them oil-wet before the treatment with chemicals. The wettability alteration of the calcite plates was monitored and the spontaneous imbibition of brine was measured. The transport and retention of the chemicals in limestone cores were also studied.

2. Methodology

2.1 Materials

In this study, both calcite mineral plates, Texas Cream limestone and Silurian dolomite outcrop cores were used. The outcrop cores were obtained from Kocurek Industries. Calcite mineral plates were provided by Fisher Scientific, with purity of >99%. Fluid samples were obtained from a West Texas reservoir. **Table 1** shows the oil properties. The oil density was measured to be 0.84 g/cm^3 at 24°C. The viscosity of oil is 7.46 cP at the reservoir temperature (35°C), which was measured with an ARES-G2 rheometer. The acid number, base number, molecular weights, and saturates/aromatics/resin/asphaltenes (SARA) analysis were conducted by SGC North America Inc.

Table 1 Oil analysis results

Property	Value

Density @25°C (g/cm^3)	0.84
Viscosity @35°C (cP)	7.46
Molecular Weight (g/mol)	213
Acid Number (mg KOH/g)	0.26
Base Number (mg KOH/g)	1.0
Saturate (wt%)	50.8
Aromatic (wt%)	16.5
Resin (wt%)	32.5
Asphaltene (wt%)	0.1

Table 2 shows the composition of the brine. The recent produced water (PW) has a salinity of 40,393 ppm. In our previous study, 16-times dilution of PW (PW/16) brine was found to be effective in enhanced oil recovery. In this study, PW/16 brine was used.

Table 2 Brine composition

Composition	Produced Water (PW)	16-times Diluted PW (PW/16)
Na^+	11.14 g/L	0.70 g/L
K^+	0.52 g/L	0.03 g/L
Ca^{2+}	1.61 g/L	0.10 g/L
Mg^{2+}	0.63 g/L	0.04 g/L
Cl^-	22.02 g/L	1.38 g/L
SO_4^{2-}	4.13 g/L	0.26 g/L
TDS	40,393 ppm	2,524 ppm
pH	7.74	7.72

An anionic surfactant, Calimulse AOS, provided by Pilot Chemicals was used in this study. The main component of Calimulse AOS is sodium C_{14}-C_{16} olefin sulfonate. It has a pH of 8.0 and density of 1.04 g/cm^3. The molecular weight ranges from 298-322 g/mol; it was supplied as a 40% solution in water. Our previous study (Shi et al., 2021) found that Calimulse AOS solution (0.5 wt% prepared in PW/16) can change the oil-wet carbonate rock surface to a more water-wet condition and result in more than 40% incremental oil recovery in imbibition tests.

DP9711 is a surface modified SiNP used in this study. It was obtained from Nyacol Nano Technologies. The surface modification with an organic compound increases the aqueous stability of the SiNP in brines. It was about 20 nm in diameter. DP 9711 was supplied as pre-dispersed in water with a concentration of 30 wt%.

2.2 Silica Nanoparticle Characterization

Beckman Particle Analyzer instrument (Delsa Nano C) was used to measure the dynamic light scattering (DLS) size and zeta potential of SiNP using a diluted nanoparticle suspension in DI water. Transmission electron microscope (TEM) Joel 2010F was used to acquire SiNP morphology. To prepare the sample for transmission electron microscopy analysis, SiNP was well dispersed in DI water before loading onto a 400 Mesh carbon-coated copper TEM grid.

2.3 Aqueous Stability Test

Surfactant and SiNP were tested for aqueous stability in PW/16 brine. 0.1 wt%, 0.5 wt% and 1 wt% were used for SiNP solutions and 0.5 wt% was used for the surfactant solution. The test solutions were visually inspected to determine the aqueous stability with and without presence of oil under 35°C.

2.4 Wettability Analysis

The calcite mineral plates were used in the wettability analysis, which consisted of wettability alteration tests and wettability retainment tests. In wettability alteration tests, the plate was first conditioned in PW/16 brine for 24 hours at 35°C. Then, the plate was aged in crude oil for over 7 days at 85°C to obtain oil-wetness. Next, the oil-aged plate was immersed in the test solution for 7 days and the surface was monitored to evaluate the wettability altering performance of the test solution.

In a second type of wettability test termed “wettability retainment tests”, the mineral plate was first immersed in the 80 mL of test solution at 35°C. During this step, negatively charged surfactant or SiNP would adsorb onto the positively charged plate surface. Then, the treated plate was carefully rinsed with PW/16 brine to remove excess test solutions. Next, the plate was aged in crude oil for over 7 days at 85°C. Finally, the plate was placed into PW/16 brine to evaluate the wettability state of the plate.

2.5 Porous Media Tests

A 1-ft long Texas Cream limestone outcrop core was used in the porous media tests. The outcrop core was cut into two 5.5” short cores, one was used to evaluate anionic surfactant and the other was used to test SiNP. **Figure 1** shows the workflow of the porous media tests. Before the test, the outcrop core was assembled vertically into a Hassler-type core holder with confining pressure of 800 psi. Three cycles of CO_2 saturation and vacuum were performed to purge all the air in the core. The core was first fully saturated with PW/16 brine to determine liquid porosity ϕ_L. Then, PW/16 brine was injected through the core to determine initial absolute permeability K_{L1}. The brine injection was followed by the test solution injection (0.5 wt% surfactant or SiNP prepared in PW/16). More than 2 PV of test solution was injected at a slow injection rate (0.1 ft/day). To assure the equilibrium was reached, the core was left in the core holder under 35°C for a week after the test solution injection. Next, post PW/16 brine injection (at injection rate of 1 ft/day) was performed to 1) recover excess test solution and 2) determine final absolute permeability K_{L2}. More than 3 PV of PW/16 brine was injected until chemical concentration of the effluent reached zero. Crude oil was then injected from the top side of the core until no water production. Oil relative permeability before aging (K_{ro1}^{o}) was measured when residual water saturation was achieved. Over 2 PV of crude oil was slowly injected (<0.1 ft/day) through the core, and the oil saturated core was then aged in the coreholder for 1 month under 85°C. Oil relative permeability after aging (K_{ro2}^{o}) was also measured by flooding oil though the core. Finally, spontaneous imbibition tests were performed to evaluate wettability state of the oil-aged outcrop cores. The core was immersed in PW/16 brine in an Amott cell and oil production was monitored. The imbibition tests were performed under 35°C.

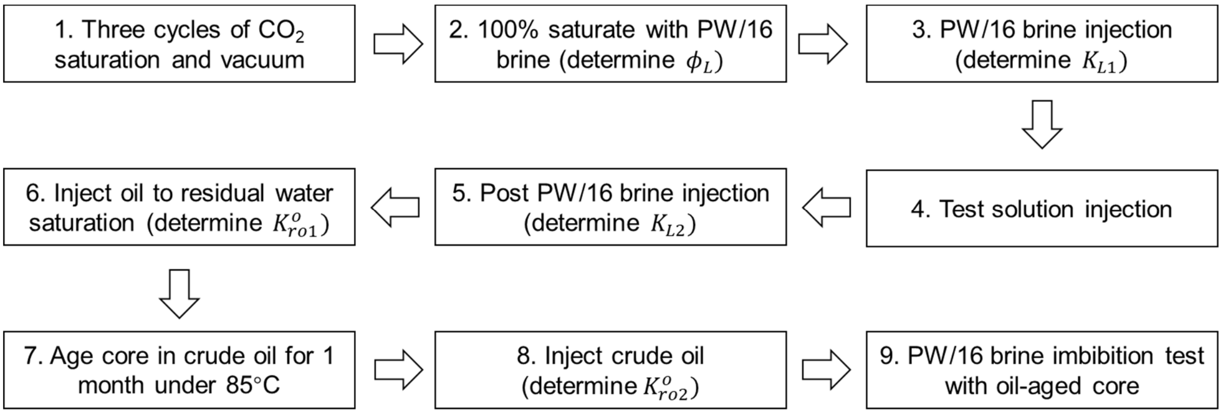


Figure 1. Workflow of the porous media tests

To confirm the wettability altering potentials of SiNP and Calimulse AOS, another set of imbibition test was conducted in Silurian dolomite cores. The cores were 100% oil saturated and aged at an elevated temperature over a month to obtain oil-wetness. Then the cores were immersed in either the SiNP solution or in the surfactant solution and the spontaneous imbibition was studied.

2.6 Retention Measurement

The chemical retention was calculated by subtracting chemicals produced from chemicals injected. Effluent samples from the porous media tests were analyzed for chemical concentration to calculate surfactant and SiNP retentions. Surfactant concentration was analyzed using a two-phase titration method using UV-Vis spectroscopy. The method is based on formation of a dye-surfactant complex. The absorbance of the complex measured by UV-Vis spectroscopy is linearly correlated to the surfactant concentration. The dye used here is Methylene blue. The procedure of this titration method was detailed in the work by Miller et al. (2020).

Thermal gravimetric analysis (TGA) was used to quantify SiNP concentration. Pure silica NP has high thermal stability, which makes it hard to be analyzed with TGA. SiNP used here, DP 9711, has a certain amount of organic compound coated on the surface, which would be completely decomposed when temperature rises up to 600°C. In this study, the proportion of organic compound was measured by TGA and used to estimate SiNP concentration. Before the TGA measurement, all the samples were heated at 100°C for 24 hours to get rid of free water maximally. Pure SiNP powder was tested in TGA to obtain the mass fraction of coated organic compound in SiNP. Effluent samples were also heated at 100°C for 24 hours to obtain the precipitated solid, which is a mixture of salts and SiNP. Then the mixture was tested in TGA. Mettler Thermogravimetric Analyzer (Model TGA/DSC 1) was used in this test. For each measurement, around 3-mg of solid sample was analyzed. N_2 flows at rate of 50 mL/min during the measurement. Temperature ramped from 35°C to 800°C at a constant ramping rate of 5°C/min.

2.7 Surface Area Measurement

The specific surface area of the Texas Cream outcrop sample was analyzed with a Micromeritics 3Flex Adsorption Analyzer. The outcrop sample was first pulverized and sieved to obtain rock powder with particle size of 0.2-1 mm. Then, the powder was placed in 105°C oven for 12 hours to get rid of moisture. Next, around 1 g of powder sample was loaded into the sample tube and N_2 was injected into the tube to degas. Finally, the sample tube was assembled onto the adsorption analyzer and the sample was analyzed over N_2 pressure range from 0.74 to 742 mmHg. The data within relative pressure range of 0.05 to 0.35 was used to compute specific surface area according to Brunauer-Emmett-Teller (BET) theory.

3. Results

3.1 Silica Nanoparticle Characterization

SiNP was characterized to better understand the size, surface charge and morphology. **Figure 2** shows the particle size distribution of SiNP prepared in DI water and brine (PW/16) using DLS. The average size of SiNP in DI was measured to be 21.2±13.5 nm, while the average size of SiNP in PW/16 increased to 38.9±13.7 nm. The majority of SiNP have diameter less than 100 nm, which is less than the minimum pore throat diameter of the tested rock sample according to MICP data. The transport of the SiNP is not expected to be an issue. TEM image of SiNP in **Figure 3** confirmed the size distribution measured by DLS. The SiNP was spherical in shape and relatively uniform in size. The zeta potential of the SiNP was measured to be -16.9±0.5 mV, indicating SiNP is negatively charged.

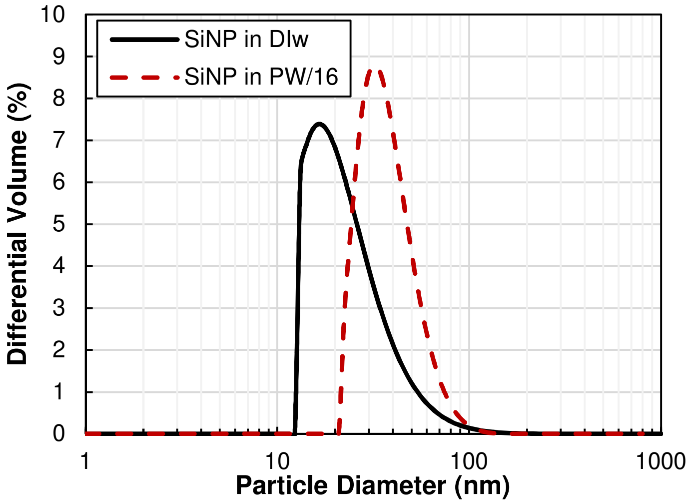


Figure 2. Particle size distribution of SiNP prepared in DI water and PW/16 brine

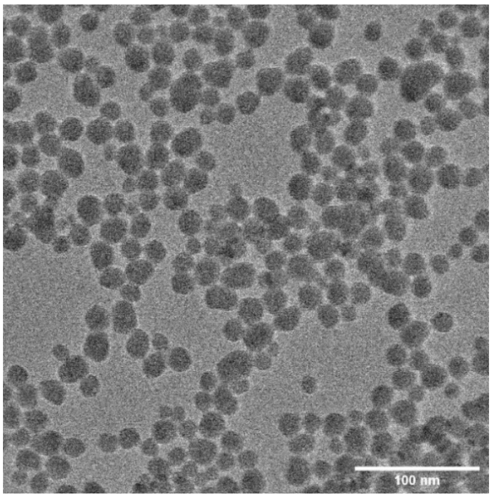
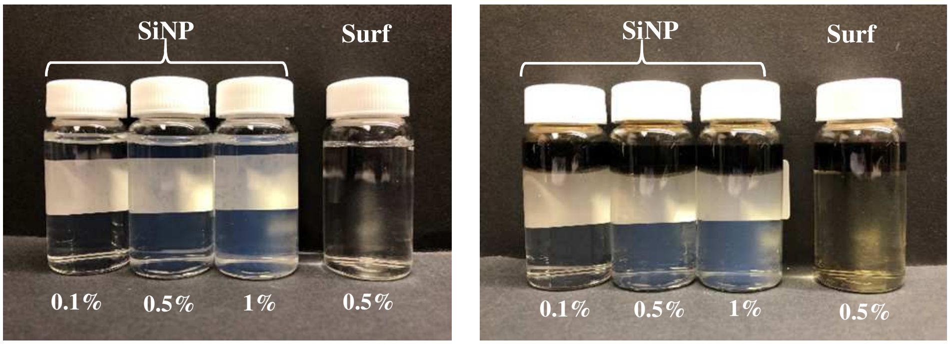


Figure 3. TEM image of silica nanoparticle used in this study.

3.2 Aqueous Stability

Figure 4 shows the aqueous stability of SiNP and Calimulse AOS solutions. SiNP was prepared in PW/16 brine with concentrations of 0.1 wt%, 0.5 wt% and 1wt%. 0.5% Calimulse AOS was also prepared in PW/16 brine. Both SiNP and anionic surfactant solutions remained stable at 35°C for at least 7 days. The solutions were then mixed with crude oil and placed in a 35°C oven for 7 days. As shown in **Figure 4**, SiNP solutions showed good aqueous stability without and with the presence of oil. The surfactant solution developed a brownish color after mixing with oil, which indicates the oil solubilization in the aqueous phase by surfactant micelles.



(a) (b)

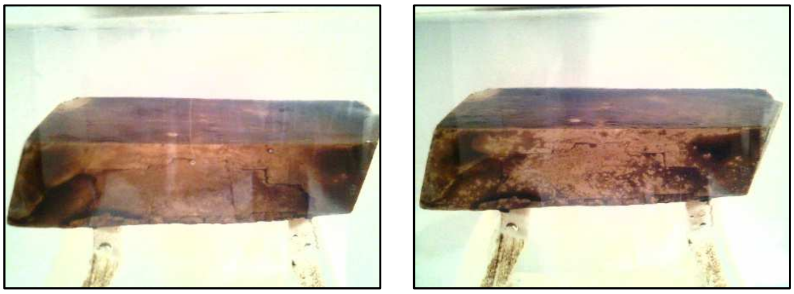
Figure 4. SiNP solutions (left) and Calimulse AOS surfactant solution (right) (a) without any oil and (b) with oil under 35°C after 7 days.

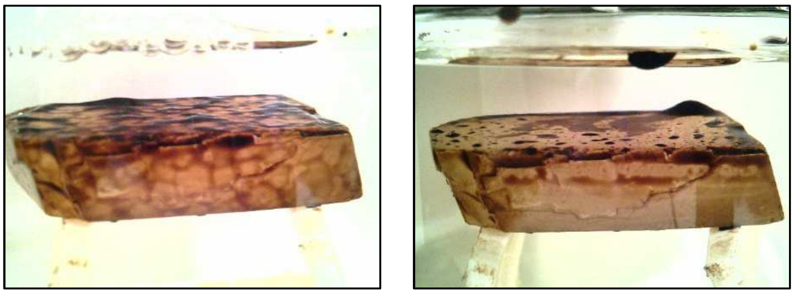
3.3 Wettability Tests

In wettability alteration tests, oil-aged calcite plates were placed in SiNP and Calimulse AOS solutions to evaluate their wettability alteration potentials. **Figure 5** shows the surface of the oil-aged plates in test solutions after 0 hour and 24 hours of immersion under 35°C. The fate of the surface oil was monitored over a week; no obvious change was observed after 24 hours. For the plate in SiNP solution, oil was smeared and surface of plate remained oil-wet after 24 hours of immersion, which indicates SiNP is not effective in altering wettability of calcite surface. The interfacial tension between SiNP solution and crude oil was measured to be 27.8 mN/m which is close to that between brine and crude oil (28 mN/m). Both the SiNP and the oil-water interface are negatively charged and repel each other. Since the solid surface is covered with oil and the IFT is large, the nanoparticles do not get a chance to contact the solid surface.

The lack of wettability alteration observed in these nanoparticle experiments is consistent with the results of Alzobaidi et al. (2021) who found that cationically modified nanoparticles could change the wettability to water-wet, but not anionically modified nanoparticles. The nanoparticles used in our work had a negative zeta potential and are anionic. However, these results are different from the results of other previous experiments on carbonate rocks, discussed in the introduction section. The primary reason is the lack of rigorous aging of the mineral plate with crude oil prior to treatment with nanoparticles in the other studies. Esfandyari et al. (2014) did not age the limestone plates in crude oil. They aged the plate in the nanofluids and then placed a drop of oil on the surface. This experiment indicates that nanoparticles retain the water-wettability, but does not imply that nanoparticles alter the wettability of originally oil-wet limestone. Dehghan-Manfared et al. (2016) did not work with crude oil. They worked with a model oil (heptane with stearic acid), brine with no divalent ions and aged the calcite plates in the model oil for only one day. The calcite plate was then washed with heptane and deionized water. Then a drop of model oil was placed on the calcite plate to measure a contact angle. This process does not resemble displacement of oil by a nanofluid in a reservoir. In our experiment and those by Alzobaidi et al. (2021), the calcite plates were aged in crude oil properly (for a week at >80 °C) and then placed directly in the nanofluid. Our method mimics in situ displacement processes and indicates if the nanoparticles are capable of wettability alteration.

Calimulse AOS solution had a different effect on oil-aged calcite plate than the SiNP dispersion; some parts of the plate surface got clear and free of dark oil after 24 hours immersion in Calimulse AOS solution. Calimulse AOS can alter the oil-wet carbonate surface to an intermediate-wet condition with a post-treatment contact angle of 120°-140°, as shown in **Figure 6**. In post-treatment contact angle measurement, the chemical treated carbonate plate was carefully rinsed with brine, and then immersed in brine. Several oil droplets were injected via a U-shaped needle onto the bottom side of the carbonate plate. The contact angle of the droplets was captured and analyzed with a goniometer. The interfacial tension was reduced from 28 mN/m to 0.87 mN/m by adding Calimulse AOS into the PW/16 brine, which also helped in detaching crude oil from the calcite surface. In contrast, the interfacial tension between SiNP solution and crude oil was measured to be 27.8 mN/m, which is close to that between brine and crude oil.




(a) (b)

(c) (d)

Figure 5. Oil-aged calcite plate in 0.5 wt% SiNP solution after (a) 0 hour and (b) 24 hours; Oil-aged plate in 0.5 wt% Calimulse AOS solution after (c) 0 hour and (d) 24 hours.

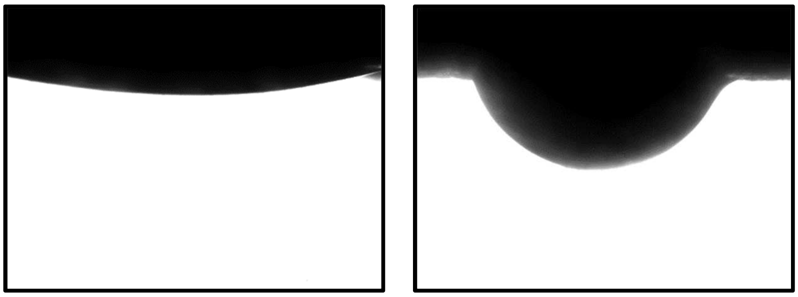

(a) **(b)**

Figure 6. Post contact angle on (a) oil-wet carbonate plate and (b) Calimulse AOS treated carbonate plate

In wettability retainment tests, one calcite plate was first treated with 0.5 wt% Calimulse AOS solution for 7 days. Then the sample was carefully rinsed with PW/16 and aged in crude oil for over 7 days at elevated temperature (85°C). **Figure 7** shows the oil-aged plate in PW/16 brine after 24 hours immersion. Oil smeared on the surface of the plate and the surface rendered a strong affinity towards oil. It suggests that the surfactant treated calcite surface cannot remain water-wet after a long-time exposure to oil at high temperature.


Figure 7. Oil-aged calcite plate in PW/16 after 24 hours. The plate was treated by 0.5 wt% Calimulse AOS solution for 7 days before aging in oil.

SiNP was then evaluated for wettability retainment potentials. The plates were first treated by SiNP solutions with concentrations of 1 wt%, 0.5 wt% and 0.1 wt%. For each concentration, treatment time varied from 1 day to 3 days. Then, the treated plates were carefully rinsed with PW/16 brine to remove the excess test suspension and aged in crude oil for 7 days at an elevated temperature (85°C). **Figure 8** shows the images taken right after immersing the oil-aged plates in PW/16 brine. In general, if an enough treatment time (> 3 days) was given, surface of the plate can be fairly clean and free of dark oil, which indicates the surface remained water-wet even after aging in oil. The adsorption of the SiNP onto the calcite surface is considered to be strong and mostly irreversible (Al-Anssari et al., 2016).

Figure 8 reveals that the solution with a higher concentration of SiNP needs less treatment time to be effective in wettability retainment. Specifically, the plate treated by 1 wt% SiNP solution for 1 day remained water-wet and the most of the surface was free of dark oil. In contrast, it would take up to 3 days for 0.1 wt% SiNP solution to be effective in wettability retainment. To keep the calcite surface free of organic acids, a certain surface concentration of adsorbed NP might be required. Higher concentration of NP would have higher adsorption kinetics and would take less time to satisfy the required surface concentration. The ratio of solution volume to rock surface area in this test is much higher than that in actual reservoirs; so a longer treatment time might be required in a reservoir rock, when low concentration NP (<0.1 wt%) is used.

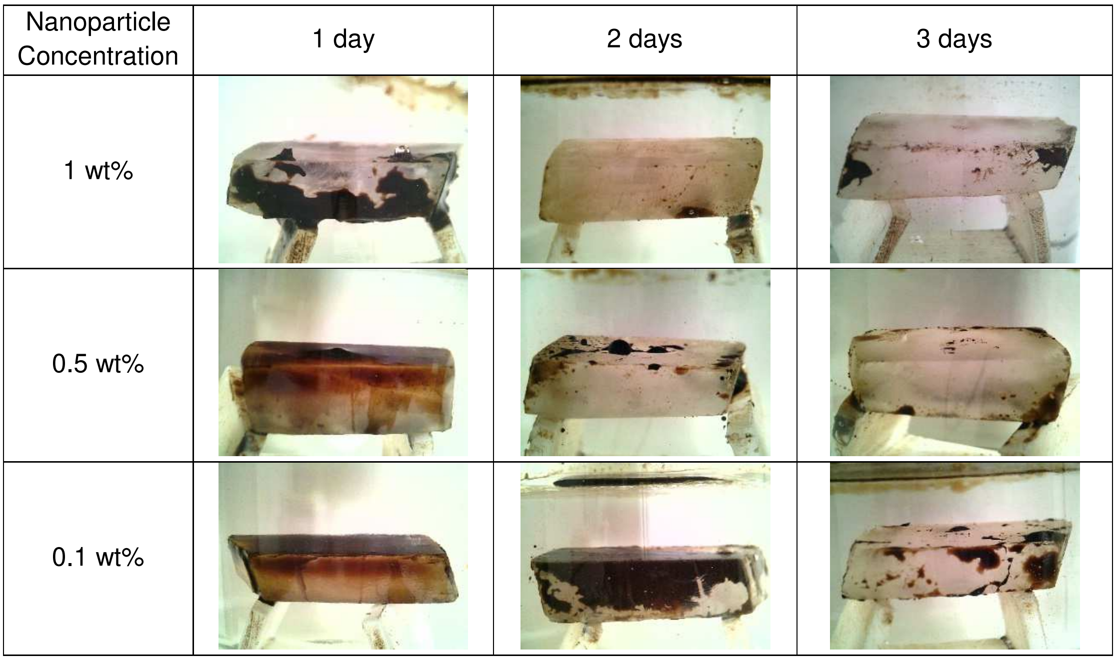


Figure 8. Oil-aged calcite plates in PW/16. The plates were treated by SiNP solutions with different concentrations and treatment times before aging in oil.

As schematically illustrated in **Figure 9**, negatively charged surfactants can adsorb onto the calcite surface exposing the hydrophobic tail of the adsorbed surfactant which can attract organic acid once oil is introduced. The organic acids can also adsorb on the calcite surface and displace anionic surfactants. On the contrary, when the SiNP particles (with multiple negative charges) adsorb on the calcite surface, the negative charges of the SiNPs are displayed. This surface repels the negatively charged organic acids and oil does not attach to the calcite surface. Thus, the SiNP treated calcite mineral retains its water-wetness in the presence of oil.

The zeta potentials of the carbonate rock powder were measured before and after treatment with the chemicals. The zeta potential on carbonate rock powder in PW/16 brine was measured to be 8.2 mV. When this powder was treated with 0.5 wt% surfactant in PW/16, the zeta potential decreased to 4.5 mV, still positive. On the other hand, the zeta potential of the 0.5 wt% SiNP-treated powder in PW/16 brine was -3.5 mV. This negative surface charge keeps the oil (which is itself negatively charged) away from the mineral surface. These zeta potential measurements support the mechanisms illustrated in **Figure 9**.

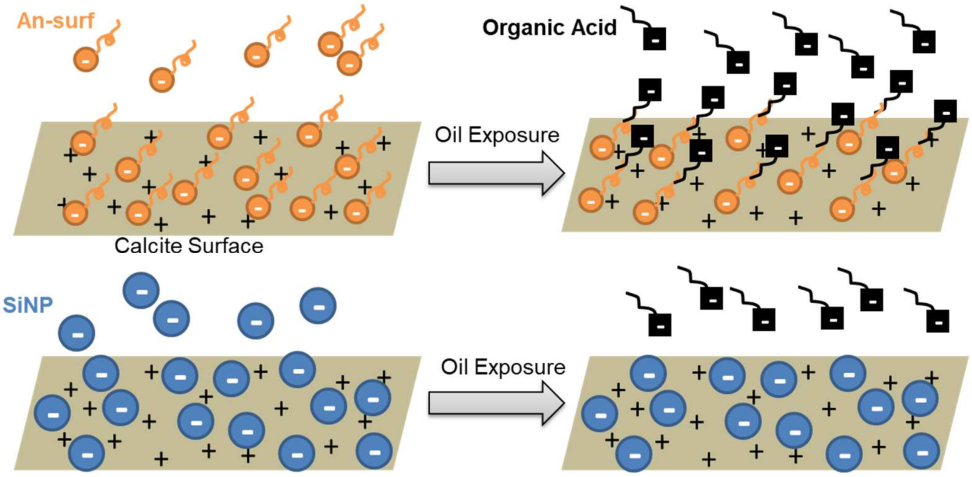


Figure 9. Schematic of anionic surfactant (An-surf) and studied nanoparticle (SiNP) treated calcite surfaces before and after exposing to oil.

3.4 Porous Media Tests

Table 3 summarizes the rock properties, displacement parameters, and results of the porous media tests. A ft-long Texas Cream limestone outcrop was used in this study. Two 5.5”-long cores were cut from a 1 ft-long core, named as TxCream_1 and TxCream_2. The rest of the rock material was pulverized into powder for the surface area measurement. TxCream_1 and TxCream_2 were used to test SiNP and Calimulse AOS solutions, respectively. The two cores shared similar brine permeability ($\boldsymbol{K_{L1}}$ is around 18 mD) and porosity (33%). The surface area of the tested rock sample was measured to be 0.63 m^2/g-rock by BET adsorption.

The cores were first 100% saturated with brine followed by the test solution injection. After the test solution equilibrated with the cores, brine (“post-brine”) was injected to displace the test solutions. A second permeability, $\boldsymbol{K_{L2}}$ was measured to evaluate the transport of the test solutions. $\boldsymbol{K_{L2}}$ was close to $\boldsymbol{K_{L1}}$ for both TxCream_1 and TxCream_2, which suggests that both test solutions have no/negligible plugging issue in the studied porous medium. Oil was then injected into the rock samples to achieve a residual water saturation. Residual water saturations of TxCream_1 and TxCream_2 were measured to be 0.35 and 0.32, respectively. When water production ceased and pressure drop stabilized, an oil relative permeability $\boldsymbol{K_{ro1}^{o}}$ was measured. The oil-saturated cores were then aged in oil for a month at an elevated temperature. After oil-aging, the oil relative permeability, $\boldsymbol{K_{ro2}^{o}}$ was measured. For TxCream_1, $\boldsymbol{K_{ro2}^{o}}$ was close to $\boldsymbol{K_{ro1}^{o}}$, which proved that SiNP can firmly adsorb onto the core surface and cannot be removed during post-brine and oil injection. The adsorbed nanoparticles retained the water-wetness of the rock surface. Zhang et al. (2015) used the theory proposed by Burdick et al. (2005) to estimate the minimum flow rate to move the attached SiNP on a rough surface. According to their calculation, if an asperity height of 0.5 nm was assumed, the velocity must be higher than 5×10^4 ft/day to move a 20-nm SiNP, which is several orders of magnitude larger than the test injection rate (~ 1 ft/day). The irreversible NP adsorption effectively retained the rock water-wetness during the oil aging. In contrast, $\boldsymbol{K_{ro}^{o}}$ of TxCream_2 decreased from 0.61 to 0.39 during the oil-aging period. This is an indication of the change in rock wettability state from water-wet to a more oil-wet condition.

Table 3. Rock properties, displacement parameters, and results of the porous media tests

Core ID		**TxCream_1**	**TxCream_2**
Core Properties	Initial mass (g)	303.01	308.28
	Length (cm)	13.65	13.97
	Diameter (cm)	3.78	3.78
	Pore volume (cm^3)	50.39	52.03
	Porosity (fraction)	0.33	0.33
	Grain density (g/cm^3)	2.94	2.93
	Absolute permeability K_{L1} (mD)	17.97	17.75
	Specific surface area (m^2/g-rock)	0.63	0.63
Test Solution Injection	Test solutions	0.5 wt% SiNP in PW/16	0.5 wt% anionic surfactant in PW/16
	Pore volume of injection	2.63	2.01
	Injection rate (cm^3/min)	0.02	0.02
	Soaking time after injection (days)	7	7
Post-PW/16 Injection	Pore volume of injection	2.09	4.43
	Final absolute permeability K_{L2} (mD)	17.75	17.77
Oil Saturation	Residual water saturation	0.35	0.32
	Oil relative permeability before oil aging K_{ro1}^{o}	0.56	0.61
Oil Aging	Time of aging (days)	30	30
	Oil relative permeability after oil aging K_{ro2}^{o}	0.54	0.39

3.4.1 Surfactant Retention

Figure 10 shows the surfactant concentration of the effluents analyzed by UV-Vis spectroscopy. Surfactant solution was injected after 2 PV of PW/16 injection. After 2 PV of surfactant injection, the core was left in the core holder for 1 week. Then, more than 4 PV of PW/16 was injected until surfactant concentration in the effluent reached zero. As shown in **Table 4**, 523.9 mg of surfactant was injected into the core while 337.37 mg of surfactant was produced by analyzing the data in **Figure 10**. The surfactant retention was measured to be 0.61 mg/g-rock (0.96 mg/m^2).

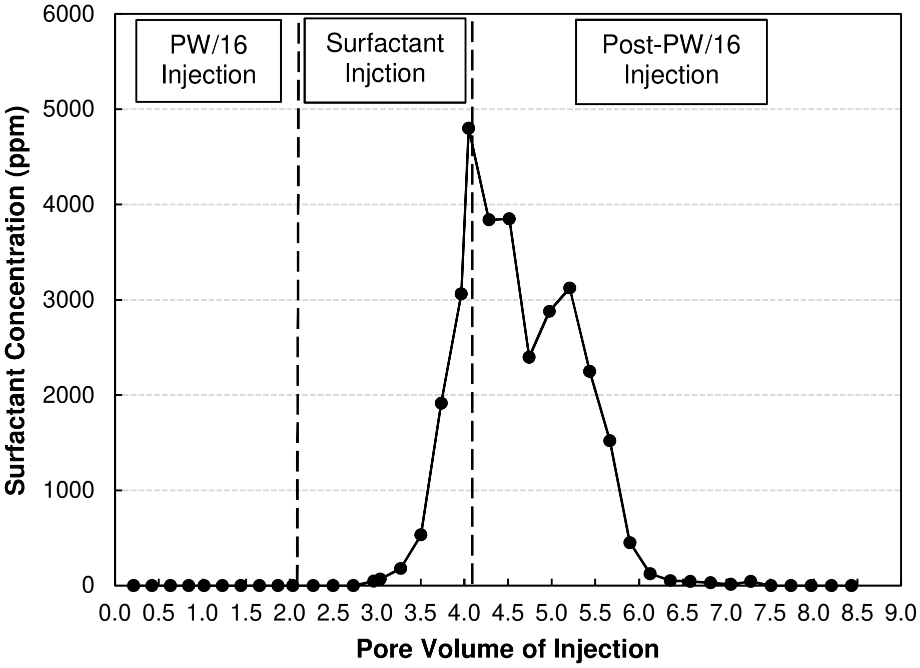


Figure 10. Surfactant concentration of effluent samples

Table 4. Surfactant retention calculation.

Total injected surfactant (mg)	523.90
Total recovered surfactant (mg)	337.37
Retained surfactant (mg)	186.53
Mass of rock sample (g)	308.28
Surfactant retention (mg/g-rock)	0.61
Surfactant retention (mg/m^2)	0.96

3.4.2 Nanoparticle Retention

Nanoparticle retention measurement was conducted similar to the surfactant retention. The SiNP dispersion in PW/16 was injected into the core followed by PW/16 brine injection. TGA was used to determine nanoparticle concentrations in effluent samples. **Figure 11** shows TGA results of nanoparticle samples and effluent samples. Pristine silica NP without any surface modification has good thermal stability (blue curve in **Figure 11**); the mass of the Pristine silica NP showed negligible change for the temperature above 100°C after free water was lost. For pure SiNP (black curve in **Figure 11**), a steep mass loss (around 3.78 wt%) occurred in the temperature range of 400°C to 600°C. The mass loss in this range is mainly caused by decomposition of the organic surface functionalized compounds. For effluent samples, due to the low concentration, all the effluent samples were mixed into one container to obtain one average effluent sample. The yellow curve in **Figure 11** showed the mass loss of the average effluent sample. To minimize the mass loss induced by salts (especially $MgCl_2$), the temperature ramped from 35°C to 350°C, then stayed at 350°C for 6 hours before resuming the temperature ramping. That is the reason why the yellow curve in **Figure 11** has a shock at 350°C. The mass loss within 400°C to 600°C for the yellow curve was due to the decomposition organic compound from SiNP surface, and used to calculate the SiNP concentration in effluent samples.

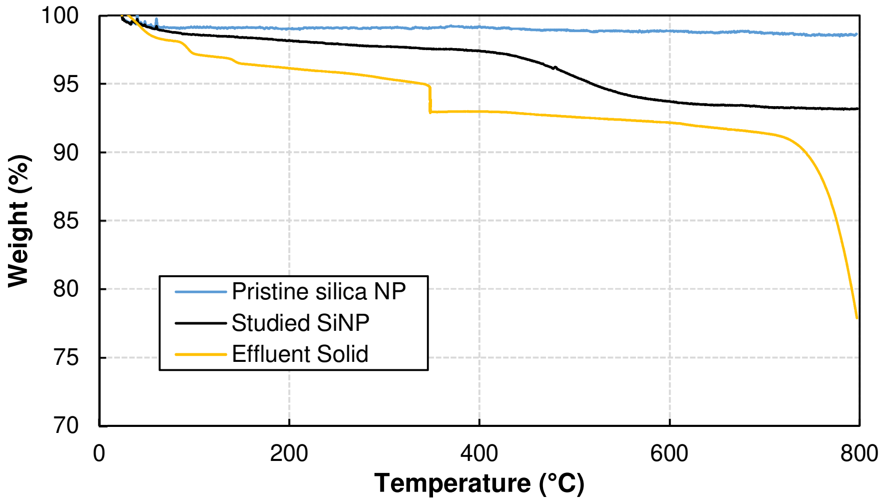


Figure 11. TGA results of pure Pristine silica NP, studied SiNP solid and effluent solid sample

Table 5 shows the data used to calculate SiNP retention. The retention was calculated by subtracting produced SiNP from the injected SiNP. The SiNP retention was calculated to be 1.58 mg/g-rock (2.50 mg/m^2). Zhang et al (2015) performed a series of Silica NP retention tests with using sandstone sand packs. NP retention ranges from 10^{-5} to 10 mg/g-rock and increases as NP concentration increases. 0.5 wt% SiNP dispersion was used in this work. Less SiNP retention could be achieved by reducing the injection concentration of the NP; more work is needed to optimize the NP concentration. It is worth noting that SiNP may not necessarily be applied to the whole reservoir. In the regions which are adjacent to producers, rock is more prone to become oil-wet due to long-term exposure to produced oil. The SiNP can be injected through the producers to treat the near-wellbore regions for wettability retainment.

Table 5. Nanoparticle retention calculation

Total Injected SiNP solution (mL)	132.50
Total Injected mass of NP (mg)	662.50
Mass loss for pure NP within 400°C - 600°C (100%)	3.69
Mass loss for effluent solid within 400°C - 600°C (100%)	0.86
Salt concentration in effluent (ppm)	2524.56
Calculated NP concentration in effluent (ppm)	767.18
Total volume of effluent been analyzed (mL)	237.70
Total recovered mass of NP (mg)	182.36
Mass of NP retained in rock sample (mg)	480.14
Nanoparticle retention (mg/g-rock)	1.58
Nanoparticle retention (mg/m2)	2.50

3.4.3 Spontaneous Imbibition Test

Spontaneous imbibition tests were performed to evaluate the wettability behavior of the TxCream_1 (first treated with the SiNP solution) and TxCream_2 (first treated with the surfactant solution) cores after oil aging. **Figure 12** shows the spontaneous imbibition results. After the oil relative permeability measurement (after oil aging), the two cores were first immersed in PW/16 brine. For SiNP treated TxCream_1, a fast oil production rate (equivalently water imbibition rate) was observed and approximately 59% OOIP was recovered within the first week, which indicates the strong water-wetness of the rock. The rock surface was relatively clean and oil droplets beaded up at the top and side faces of the rock. To further confirm the water-wetness of the TxCream_1, another Texas Cream limestone outcrop which shared similar porosity and permeability (0.35 and 19.8 mD) was used as a blank case. The core was first 100% brine saturated, then oil was injected into the core to achieve residual water saturation of 0.36. Right after oil saturation, the core was placed in an Amott cell with PW/16 for imbibition without oil aging. The black curve in **Figure 12** showed the oil recovery from this water-wet (WW) core is very consistent with that from TxCream_1, which demonstrated that the SiNP treated core retained water wettability during oil aging.

In contrast, the Calimulse AOS treated TxCream_2 core showed a much slower oil production rate during PW/16 imbibition and only achieved 19% OOIP oil recovery after 21 days. The strong oil affinity of TxCream_2 was also evidenced by a relatively dark rock surface on which the oil was smeared. To confirm the oil-wetness of the TxCream_2, one 5.2-inch Texas Cream limestone outcrop with comparable porosity and permeability (0.30 and 12.4 mD) was used as a blank case. The core was first 100% brine saturated, then residual water saturation of 0.35 was achieved by injecting oil. Upon aging in oil over one month at 85°C, the oil-aged core was placed in an Amott cell with PW/16 for imbibition. **Figure 12** showed the oil recovery profile of this oil-wet (OW) core is comparable to that of the TxCream_2, suggesting the Calimulse AOS treated core can not retain water-wetness during oil aging.

After an equilibrium was reached, TxCream_2 was immersed into the surfactant solution (0.5 wt% Calimulse AOS solution in PW/16) and incremental oil recovery was monitored. After 12 days of immersion, surfactant recovered additional 34% oil, possibly due to lowering interfacial tension and altering the oil-wet rock surface to a more water-wet condition. Upon the equilibrium of surfactant imbibition, the synergistic effect between surfactant and SiNP was evaluated by adding 0.5 wt% DP9711 SiNP into the surfactant solution. No incremental oil recovery was observed after addition of SiNP, which suggests the studied SiNP has no wettability altering ability in this testing condition, and no synergistic effect between the studied surfactant and SiNP.

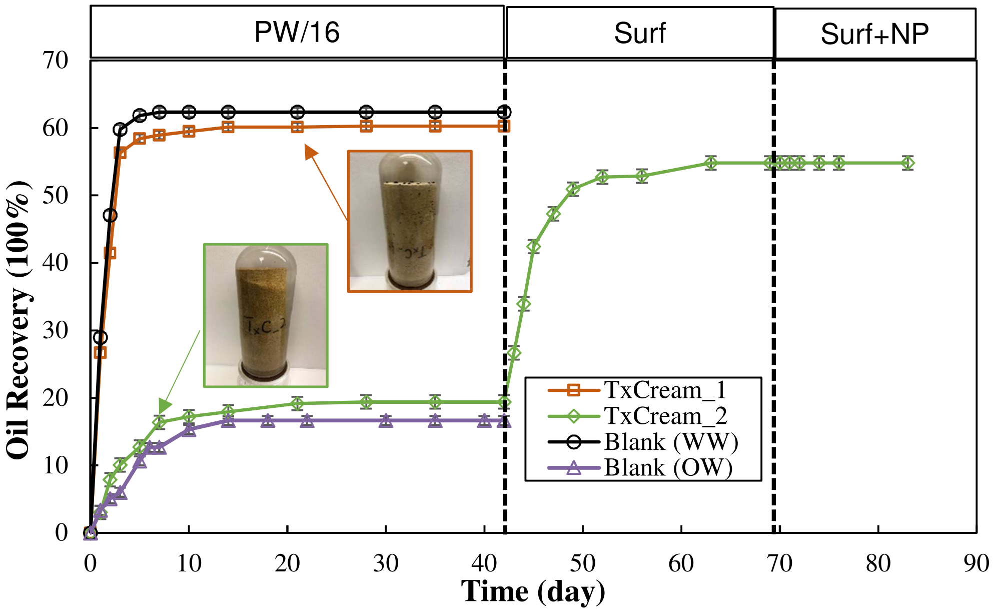


Figure 12. Spontaneous imbibition in SiNP pretreated TxCream_1 and surfactant pretreated TxCream_2 cores (Surf: 0.5 wt% Calimulse AOS in PW/16; Surf+NP: 0.5 wt% Calimulse AOS+0.5 wt% DP9711 in PW/16)

Overall, the oil recovery rate by PW/16 from SiNP treated TxCream core (59%) was much higher than that from Calimulse AOS treated TxCream core (19%). The oil recovery rate from SiNP treated core was comparable to that from a referenced water-wet core. However, the post-treatment by adding SiNP to surfactant solution did not improve oil recovery. The surface modified SiNP was not able to alter the core surface from oil-wet to more water-wet. The SiNP failed to remove the oil layer from the calcite surface and adsorb onto the calcite surface. Hence, the adsorption of SiNP is more likely to happen when core is water-wet. The irreversible adsorption of nanoparticle on the rock surface helped with retaining the rock water-wettability after being exposed to crude oil. For field applications, wettability retaining SiNP should be used only after the reservoir has been treated and the rock surface has become water-wet.

To further confirm the wettability altering potentials of SiNP and Calimulse AOS, another set of imbibition test was conducted. Silurian dolomite cores with similar permeabilities (length of 3-in., diameter of 1.5-in., porosity of 0.14 and permeability of 13 mD) were used. The cores were 100% oil saturated and aged at an elevated temperature over a month to obtain oil-wetness. Then the cores were immersed in either the SiNP solution or in the surfactant solution. **Figure 13** shows the imbibition test results. Immersion of an oil-wet core in the SiNP solution results in slow oil production rate and low final oil recovery (6.2% of OOIP), which is very similar to that of the PW/16 brine alone. This observation confirmed that SiNP is not effective in altering the wettability of the oil-wet rock surface to a more water-wet condition. On the contrary, Calimulse AOS solution shows a fast oil production and a high final oil recovery (of 50.5% OOIP) by spontaneous imbibition, an indication of wettability alteration to a water-wet condition. Thus, the SiNP can adsorb on an initially water-wet carbonate core and keep it water-wet, but it cannot alter the wettability of an initially oil-wet carbonate core.

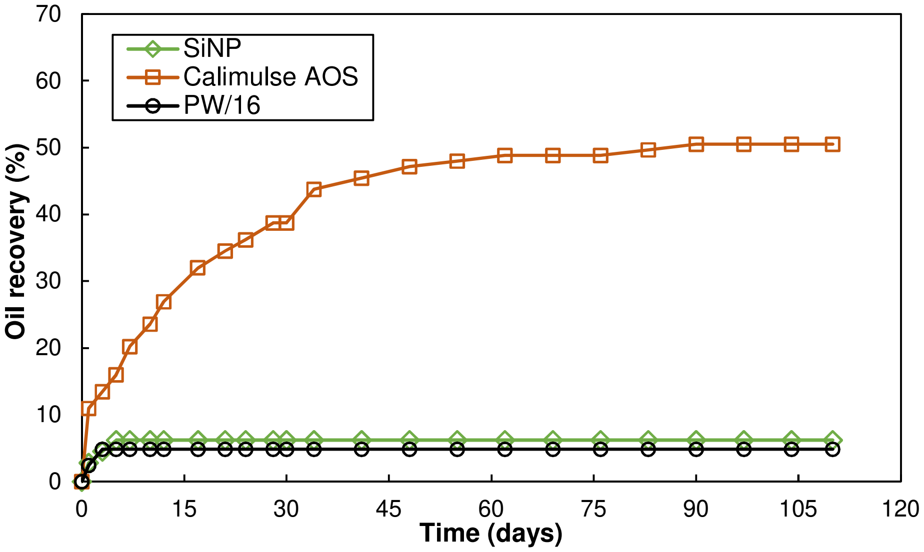


Figure 13. Spontaneous imbibition of SiNP solution (0.5% in PW/16), Calimulse AOS solution (0.5% in PW/16) and PW/16 into oil-wet carbonate cores

4. Conclusions

The role of nanoparticles in wettability alteration (oil-wet to water-wet) and wettability retainment (prevent water-wet surface from becoming oil-wet during a long-term exposure to oil) in carbonate rocks was studied in this work. A surface modified silica nanoparticle (SiNP) with a negative zeta potential and an anionic sulfonate surfactant (Calimulse AOS) were tested. Surface analysis (on calcite chips) and porous media tests (in Texas Cream and Silurian Dolomite outcrops) were performed. The conclusions of this work are summarized as follows:

- The surface-modified negatively charged SiNP showed excellent aqueous stability in the presence of divalent cations at 35°C. The organic coating provides steric stabilization for SiNP to form a stable colloidal dispersion in brine.
- Wettability analysis showed that SiNP treated calcite surface can remain water-wet after a long-time exposure to crude oil; however, the negatively charged SiNP cannot change wettability from oil-wet to water-wet.
- Imbibition studies also showed that the SiNP can adsorb on an initially water-wet carbonate core and keep it water-wet, but it cannot alter the wettability of an initially oil-wet carbonate core. In contrast, the anionic surfactant can alter oil-wet calcite surfaces to a more water-wet condition, but failed to prevent the water-wet surface from getting oil-wet during oil-aging.
- Comparison of oil relative permeabilities before and after oil-aging further demonstrated the excellent wettability retainment potential of the SiNP. SiNP can irreversibly adsorb onto water-wet carbonate surfaces and help with maintaining the rock water-wetness.

- Porous media analysis showed that SiNP dispersion (0.5 wt%) transports well in tight limestone cores with permeability of 18 mD with no/negligible plugging tendency.
- SiNP retention was measured to be 2.5 mg/m^2 in the limestone cores, which is more than twice that of anionic surfactant retention (0.96 mg/m^2).

Acknowledgements

The authors thank the US Department of Energy-NETL (Grant # DE-FE0031791) for partially funding this research.

References

Al-Anssari, S., Barifcani, A., Wang, S., Maxim, L., Iglauer, S. (2016). Wettability alteration of oil-wet carbonate by silica nanofluid. *Journal of Colloid and Interface Science*, 461, 435-442.

Alzobaidi, S., Wu, P., Da, C., Zhang, X., Hackbarth, J., Angeles, T., Rabat-Torki, N.J., MacAuliffe,S., Panja, S., Johnston, K. P. (2021). Effect of surface chemistry of silica nanoparticles on contact angle of oil on calcite surfaces in concentrated brine with divalent ions. *Journal of Colloid and Interface Science*, 581, 656-668.

Burdick, G.M., Berman, N.S., Bourdoin, S.P. (2005). Hydrodynamic Particle Removal from Surfaces. *Thin Solid Films*, 488, 116-123.

Dehghan Monfared, A., Ghazanfari, M. H., Jamialahmadi, M., Helalizadeh, A. (2016). Potential application of silica nanoparticles for wettability alteration of oil–wet calcite: a mechanistic study. *Energy & Fuels*, 30(5), 3947-3961.

Ehtesabi, H., Ahadian, M. M., Taghikhani, V., Ghazanfari, M. H. (2014). Enhanced heavy oil recovery in sandstone cores using TiO2 nanofluids. *Energy & Fuels*, 28(1), 423-430.

Esfandyari Bayat, A., Junin, R., Samsuri, A., Piroozian, A., Hokmabadi, M. (2014). Impact of metal oxide nanoparticles on enhanced oil recovery from limestone media at several temperatures. *Energy & fuels*, 28(10), 6255-6266.

Jafarbeigi, E., Kamari, E., Salimi, F., & Mohammadidoust, A. (2020). Experimental study of the effects of a novel nanoparticle on enhanced oil recovery in carbonate porous media. *Journal of Petroleum Science and Engineering*, 195, 107602.

Jang, H., Lee, W., & Lee, J. (2018). Nanoparticle dispersion with surface-modified silica nanoparticles and its effect on the wettability alteration of carbonate rocks. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 554, 261-271.

Gupta, R. A., & Mohanty, K. K. (2011). Wettability alteration mechanism for oil recovery from fractured carbonate rocks. *Transport in Porous Media*, 87(2), 635-652.

Han, S., Han, J., Kim, J. W., & Lee, Y. (2022). Changes to interfacial characteristics by low salinity water/nanoparticle flooding in carbonate reservoir. *Journal of Petroleum Science and Engineering*, 208, 109711.

Hendraningrat, L., Li, S., & Torsæter, O. (2013). A coreflood investigation of nanofluid enhanced oil recovery. *Journal of Petroleum Science and Engineering*, 111, 128-138.

Hendraningrat, L., Torsæter, O. (2015). Metal oxide-based nanoparticles: revealing their potential to enhance oil recovery in different wettability systems. *Applied Nanoscience*, 5(2), 181-199.

Karimi, A., Fakhroueian, Z., Bahramian, A., Pour Khiabani, N., Darabad, J. B., Azin, R., Arya, S. (2012). Wettability alteration in carbonates using zirconium oxide nanofluids: EOR implications. *Energy & Fuels*, 26(2), 1028-1036.

Kuang, W., Saraji, S., Piri, M. (2018). A systematic experimental investigation on the synergistic effects of aqueous nanofluids on interfacial properties and their implications for enhanced oil recovery. *Fuel*, 220, 849-870.

Luo, D., Wang, F., Zhu, J., Cao, F., Liu, Y., Li, X., Ren, Z. (2016). Nanofluid of graphene-based amphiphilic Janus nanosheets for tertiary or enhanced oil recovery: High performance at low concentration. *Proceedings of the National Academy of Sciences*, 113(28), 7711-7716.

Miller, C., Bageri, B.S., Zeng, T., Patil, S., Mohanty, K.K. (2020). Modified Two-Phase Titration Methods to Quantify Surfactant Concentrations in Chemical Enhanced Oil Recovery Applications," *J. of Surfactants & Detergents*, 23 (6), 1159-1167.

Naghizadeh, A., Azin, R., Osfouri, S., & Fatehi, R. (2020). Wettability alteration of calcite and dolomite carbonates using silica nanoparticles coated with fluorine groups. *Journal of Petroleum Science and Engineering*, 188, 106915.

Roustaei, A., Saffarzadeh, S., Mohammadi, M. (2013). An evaluation of modified silica nanoparticles' efficiency in enhancing oil recovery of light and intermediate oil reservoirs. *Egyptian Journal of Petroleum*, 22(3), 427-433.

Seethepalli, A., Adibhatla, B. & Mohanty, K. K. (2004). Physicochemical Interactions During Surfactant Flooding of Carbonate Reservoirs. *SPE Journal*, 9 (4), 411-418.

Shahrabadi, A., Bagherzadeh, H., Roustaei, A., Golghanddashti, H. (2012, June). Experimental investigation of HLP nanofluid potential to enhance oil recovery: A mechanistic approach. *SPE International Oilfield Nanotechnology Conference and Exhibition*. doi: 10.2118/156642-MS

Shi, Y., Miller, C., & Mohanty, K. (2021). Surfactant-Aided Low-Salinity Waterflooding for Low-Temperature Carbonate Reservoirs. *SPE Journal*, 1-17.

Standnes, D. C., Austad, T. (2000). Wettability alteration in chalk: 2. Mechanism for wettability alteration from oil-wet to water-wet using surfactants. *Journal of Petroleum Science and Engineering*, 28(3), 123-143.

Standnes, D. C., Nogaret, L. A., Chen, H. L., Austad, T. (2002). An evaluation of spontaneous imbibition of water into oil-wet carbonate reservoir cores using a nonionic and a cationic surfactant. *Energy & Fuels*, 16(6), 1557-1564.

Suleimanov, B. A., Ismailov, F. S., Veliyev, E. F. (2011). Nanofluid for enhanced oil recovery. *Journal of Petroleum Science and Engineering*, 78(2), 431-437.

Vijapurapu, C. S., Rao, D. N. (2004). Compositional effects of fluids on spreading, adhesion and wettability in porous media. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 241(1-3), 335-342.

Wasan, D. T., & Nikolov, A. D. (2003). Spreading of nanofluids on solids. Nature, 423(6936), 156-159.

Xie, X., Weiss, W. W., Tong, Z., Morrow, N. R. (2004, April). Improved oil recovery from carbonate reservoirs by chemical stimulation. *SPE/DOE Symposium on Improved Oil Recovery*. doi: 10.2118/89424-PA

Yuan, L., Zhang, Y., Dehghanpour, H. (2021). A Theoretical Explanation for Wettability Alteration by Adding Nanoparticles in Oil-Water-Tight Rock Systems. *Energy & Fuels*, 35(9), 7787-7798.

Zaid, H. M., Yahya, N., Latiff, N. R. A. (2013). The effect of nanoparticles crystallite size on the recovery efficiency in dielectric nanofluid flooding. *Journal of Nano Research* (Vol. 21, pp. 103-108). Trans Tech Publications Ltd.

Zhang, D. L., Liu, S., Puerto, M., Miller, C. A., Hirasaki, G. J. (2006). Wettability alteration and spontaneous imbibition in oil-wet carbonate formations. *Journal of Petroleum Science and Engineering*, 52(1-4), 213-226.

Zhang, H., Nikolov, A., Wasan, D. (2014). Enhanced oil recovery (EOR) using nanoparticle dispersions: underlying mechanism and imbibition experiments. *Energy & Fuels*, 28(5), 3002-3009.

Zhang T, Murphy MJ, Yu H, Bagaria HG, Yoon KY, Neilson BM, Bielawski CW, Johnston KP, Huh C, Bryant SL. (2015). Investigation of nanoparticle adsorption during transport in porous media. *SPE Journal*, 20(04), 667-677.