

EXPERIMENTAL INVESTIGATIONS OF WETTABILITY ALTERATION DUE TO VARIOUS NANOPARTICLES: AN EOR IMPLICATION WITH NANOFUIDS

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ABSTRACT

This study investigates the dynamic interactions of fluid-rock through wettability modifications among cores and quartz plate solid-phases with crude oil as an oleic-phase and various hydrophilic nanoparticles dispersed in a synthetic seawater as an aqueous-phase to reveal its role during flooding as a novel enhanced oil recovery method. Two solid substrates were employed (quartz glass plates and Berea sandstone outcrops) with different initial wettability properties (water-wet and oil-wet). Several parameters were evaluated, including water salinity, ionic composition, different types and concentration of nanoparticles, initial medium wettability, solid system, soaking time and stabilizer presence. These parameters dramatically alter the substrate wettability with time. The incorporation of hydrophilic nanoparticles caused the media to become more water-wet in all wettability systems. In addition, soaking time with nanoparticles significantly altered the wettability of the porous medium. These results demonstrate that wettability can be altered as a possible displacement mechanism when using nanoparticles in flooding processes.

INTRODUCTION

Understanding the relationships among wettability, capillary pressure and the distribution of oil and water in pore spaces is critical for optimizing oil recovery and is a necessary, difficult step in quantifying wettability and its relation to oil recovery (Morrow, 1990). These relationships are complex within crude oil/brine/rock (COBR) systems because of the complexity of pore structures and reservoir rocks mineralogy (Morrow, 1990). The aim of this study is to reveal possible oil displacement mechanisms for enhanced oil recovery with NPs (Nano-EOR). This paper investigates various types of hydrophilic nanoparticles (NPs) that may affect wettability when they are dispersed in a synthetic seawater (SSW) as model formation brine. The dynamic wettability modification due to the hydrophilic nanoparticles was monitored by contact angle measurement under ambient conditions. Several parameters were evaluated during fluid-rock interactions, including salt concentration, water salinity, different types of NPs, initial medium wettability, concentration, solid system, soaking time and stabilizer presence.

EXPERIMENTAL

In this study, several types and sizes of hydrophilic NPs from Evonik Degussa were employed, including silica (SiO₂), alumina (Al₂O₃) and titania (TiO₂). Table 1 summarizes the NPs properties.

Table 1. Nanoparticles properties

Properties	SiO ₂	Al ₂ O ₃	TiO ₂
Specific surface area, BET (m ² /g)	300±30	65±10	50±15
Declared primary particle size (nm)	7	17	21
Bulk density (g/L)	50	50	130
pH (4-5% in dispersion)	3.7-4.7	4.5-6.0	3.5-4.5

Their fluid properties are shown in Table 2. The salinity is a measure of the total dissolved salt but is often used interchangeably with total dissolved solid (TDS), which is defined as the amount of all inorganic and organic non-particulate material (Houston, 2007). Based on representative sea water composition analyses from sedimentary basins around the world (reported by Houston in 2007), the major salt components are Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, HCO₃⁻ and SO₄²⁻, with pH ranging from 5.73 to 6.70 and TDSs ranging from hundreds to 300,000 ppm. In this study, sodium chloride (NaCl) at 3.0 wt.% (TDS approx. 30,000 ppm) and de-ionized water were used as the base SSW. The other SSW with compositions/salinities from 3,000 to 100,000 ppm were mixed with NPs.

Table 2. Synthetic seawater (SSW) properties

SSW type	Composition	TDS, ppm	Density, g/cm ³	Viscosity, cP	pH	Surface Conductivity, mV
A	NaCl 3.0 wt. %	30,000	1.02	1.00	6.76	14.2
B	NaCl 0.3 wt. %	3,000	1.00	1.00	5.94	44.2
C	NaCl 10 wt. %	100,000	1.07	1.06	6.90	14
D	KCl 3.0 wt. %	30,000	1.02	1.06	5.60	63
E	NaCl (2.7%) + CaCl ₂ .2H ₂ O (0.57 wt. %)	30,000	1.02	1.05	6.03	38
F	NaCl (2.7%) + MgCl ₂ .6H ₂ O (1.01 wt. %)	30,000	1.02	1.05	6.00	38.9

Various types of NPs were dispersed in various SSW at 0.05 wt.% for the base nanofluid concentration with SiO₂ NPs. This concentration was selected based on our previous concentration optimization study using silica NPs (Hendraningrat et al., 2013). The nanofluid was synthesized using high-speed magnetic stirring and agitated with ultra-sonication at 60-100% amplitude (output power 90-100 Watt). A stabilizer, polyvinylpyrrolidone (PVP), was used at 1.0 wt.% to avoid early aggregation (Hendraningrat et al., 2014). The nanofluid properties are presented in Table 3. Berea core specimens and rectangular transparent plates of quartz were employed in this study as solid substrates. Several core specimens and quartz plates were initially rinsed with methanol and then distilled water, and dried in a heating cabinet at 50-60 °C for several days. Each measurement used a new solid substrate. Hendraningrat et al. (2013) reported that the original wettability of quartz plates and Berea cores can be observed by measuring the contact angle in crude oil/brine/rock (COBR) systems, which are considered to be strong water-wet (SWW). Energy-dispersive X-ray (EDX) and X-ray diffraction (XRD) were performed for the mineralogical identification of the Berea cores. Similar results have been reported by Hendraningrat and Torsæter (2014) that demonstrate that the cores are composed primarily of quartz (83-93 wt.%) with minor minerals, such as alkali feldspar (max 8 wt.%) and pyroxene (<1 wt.%). Therefore, it is assumed that our initial mineralogy data are representative of the entire core specimens studied in this work. For oil-wetting measurement, a chemical mixture of 70% (V/V) pentane (C₅-H₁₂) and 30% (V/V) SurfasilTM (C₈-H₂₄-Cl₂-O₃-Si₄) was prepared to alter the quartz plate wettability from SWW to oil-wet (I_w ranged from -0.5 to -0.6). This process took

approximately 6 days at room conditions, which was similar to the core aging from other studies.

Table 3. Nanofluid properties under ambient conditions

Nanofluid	Composition	Density, g/cm ³	Viscosity, cP	pH	Surface Conductivity, mV
A	SSW-A + SiO ₂ 0.05 wt.%	1.02	1.01	6.16	48.2
B	SSW-B + SiO ₂ 0.05 wt.%	1.00	0.96	5.24	82.1
C	SSW-C + SiO ₂ 0.05 wt.%	1.07	1.11	5.57	57.2
D	SSW-D + SiO ₂ 0.05 wt.%	1.02	0.90	4.87	103.5
E	SSW-E + SiO ₂ 0.05 wt.%	1.02	1.03	5.39	69.9
F	SSW-F + SiO ₂ 0.05 wt.%	1.01	0.99	5.66	56.5
G	SSW-A + PVP 1 wt.%	1.02	1.23	3.64	168.4
H	SSW-A + Al ₂ O ₃ 0.05 wt.% + PVP 1 wt.%	1.02	1.09	4.07	170.5
I	SSW-A + TiO ₂ 0.05 wt.% + PVP 1 wt.%	1.02	1.09	4.36	152.6
J	SSW-A + SiO ₂ 0.05 wt.% + PVP 1 wt.%	1.02	1.03	3.65	168.3
K	SSW-A + SiO ₂ 0.10 wt.%	1.02	1.05	5.25	81.8
L	SSW-A + SiO ₂ 0.10 wt.% + PVP 1 wt.%	1.02	1.06	3.46	167.5

The contact angle of the COBR system was measured directly on solid substrates (quartz plate and Berea core specimen) using a Goniometry KSV CAM instrument under ambient conditions for 3-6 hours, as shown in Figure 1. The system consists of a quartz plate/Berea core specimen as the solid substrate, crude oil as the oleic-phase and a nanofluid as the aqueous-phase. The contact angle is measured using a formula as follow:

$$\theta_{wo} = \cos^{-1} \left(\frac{\sigma_{so} - \sigma_{sw}}{\sigma_{wo}} \right) \quad (1)$$

where σ describes the interfacial tension components of phase, indices s, o and w stand for solid, oleic and water phases and θ is the contact angle.

Treiber et al. (1971) defined the contact angle in a 3-phase system (water, oil and rock) as follows: water-wet in a range from 0° to 75°, intermediate/neutral-wet from 75° to 105° and oil-wet from 105° to 180°. A contact angle of 0° represents that a denser fluid is completely wetting the solid.

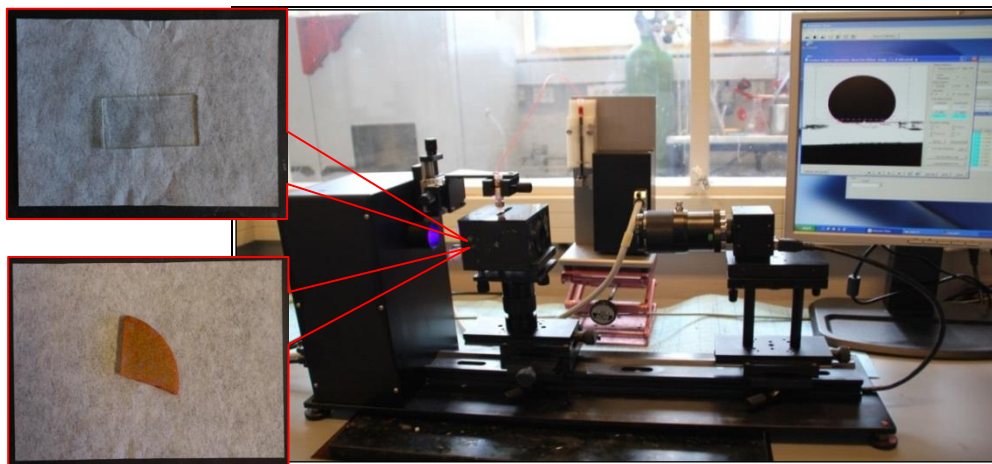


Fig. 1—Contact angle measurements using the Goniometry KSV CAM instrument

RESULTS AND DISCUSSION

The dynamic wettability modification, as assessed by contact angle measurement under ambient conditions, is shown from Figure 2 to Figure 5. Several parameters were evaluated during the fluid-rock interaction, such as the salt concentration, water salinity, different types of NPs, initial medium wettability, concentration, solid system, soaking time and stabilizer presence. There are several essential findings within this particular study.

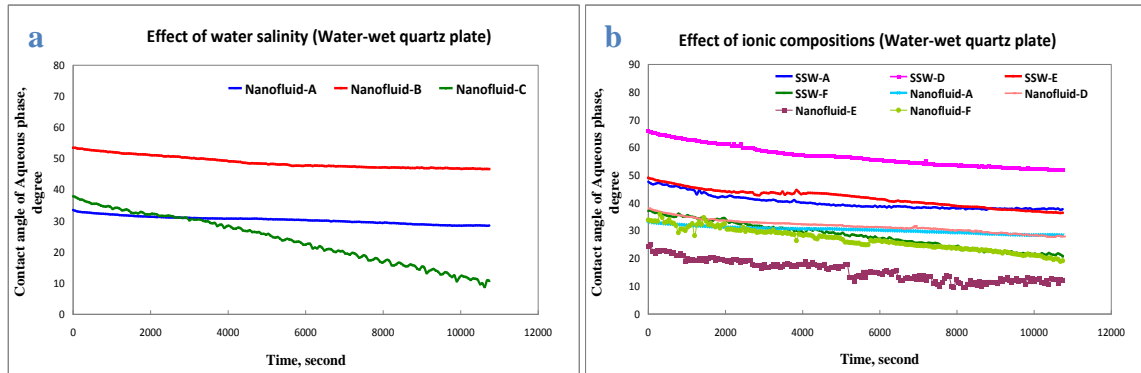


Figure 2 Wettability alteration was determined by contact angle measurements on water-wet quartz plates. Effects of water salinity and ionic compositions

We show on Fig. 2a that increasing salinity (sodium chloride) of the water with 0.05 wt.% NPs from 3,000 to 100,000 ppm is effective at altering the wettability toward a more water-wet system. Based on the contact angle measurements on Fig. 2b, both monovalent and divalent cations can increase the degree of water-wetness of the system. The changes in contact angle with the presence of monovalent cations (Na^+ and K^+) and NPs exhibit similar potential for modifying the rock wettability. Meanwhile, divalent cations ions, such as Ca^{2+} and Mg^{2+} , have greater effects on the rock surface and alter the rock wettability. These observations are in accordance with Jabbar et al. (2013) in carbonate rocks. Active divalent ions, such as Ca^{2+} , Mg^{2+} and SO_4^{2-} , more effectively decrease the charged density. Consequently, more divalent ions can contact the grain surface and alter the wettability (Austad, 2013). These changes might occur due to the adsorption of NPs, involving physicochemical interactions during transport through the porous medium, resulting in wettability alteration (Zhang et al., 2013).

The different types of NPs also provided different responses to wettability modification in water- and oil-wet systems as shown in Fig. 3a and 3b, respectively. In water-wet systems, once the hydrophilic metal oxide (with PVP) is introduced into the brine, the contact angle is further reduced, which means that the metal oxide-based nanofluids render the quartz plate more water-wet. The greatest reduction in contact angle was achieved with the TiO_2 -based nanofluid. Meanwhile, different initial wettability systems had different impacts on the wettability. Unlike in water-wet systems, silica-based nanofluids were more effective than aluminum-based nanofluids at altering the system toward a weaker oil-wet condition. Unfortunately, due to the poor clarity of the TiO_2 -based nanofluid in the oil-wet system, the measurements could not be performed. However, Ehtesabi et al. (2014) observed that rock wettability changes from oil- to water-wet after treatment with TiO_2 nanoparticles. Hence, the selection of NPs type should consider the initial wetting condition of the rock to achieve effective wettability alteration.

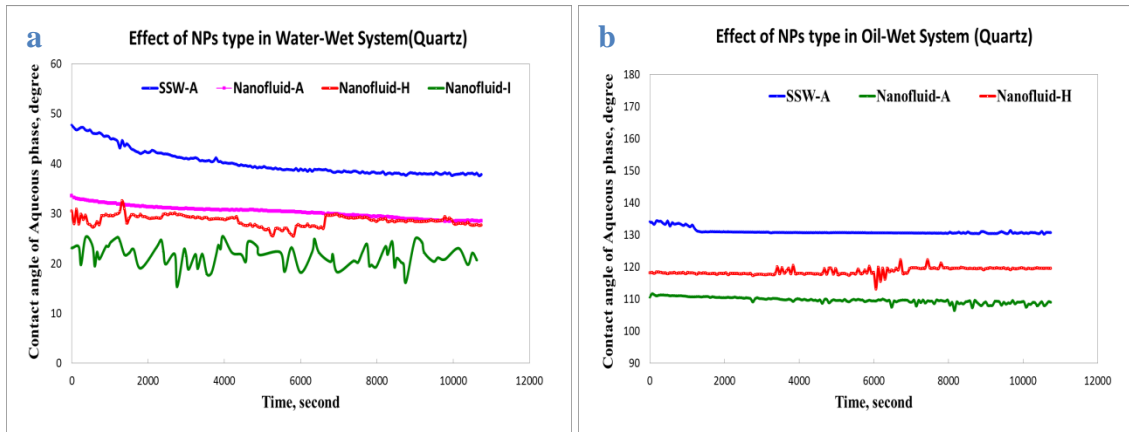


Figure 3 Wettability alteration was determined by contact angle measurements on quartz plates. Effects of nanoparticles type in water- and oil-wet systems

The use of different substrates (Fig. 4a) and soaking times (Fig. 4b) also affected the wettability effect of the NPs. However, as reported by Morrow (1990), data from quartz plates are limited in value because quartz is a single mineral. If any other minerals are present, the fluid-rock interactions might be more complex. The trend showed that longer soaking time altered the system to become more water-wet. Thus, NPs have the ability to modify the wettability of substrates as a function of their interaction/contact time.

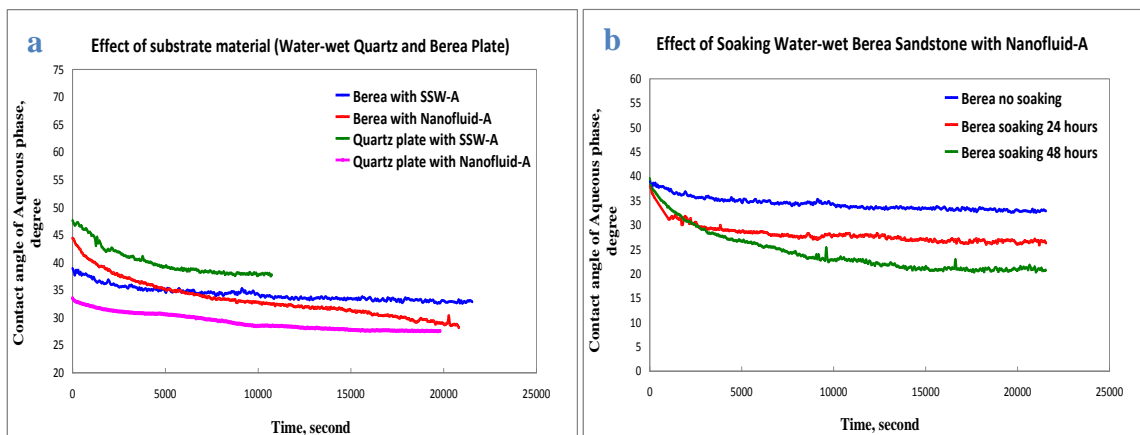


Figure 4 Wettability alteration was determined by contact angle measurements on water-wet quartz plates and Berea sandstones. Effects of substrate material and soaking duration

Stabilizers were added to avoid the early aggregation of the NPs and provided better stability over longer periods. PVP (1 wt.%) dispersed with the model formation brine caused the quartz plate to become more weakly water-wet as shown in Fig. 5a. Increasing the nanofluid concentration further decreases the aqueous contact angle, making the system more water-wet (Fig. 5b). Therefore, the NPs concentration also affects the degree of wettability modification of the COBR system.

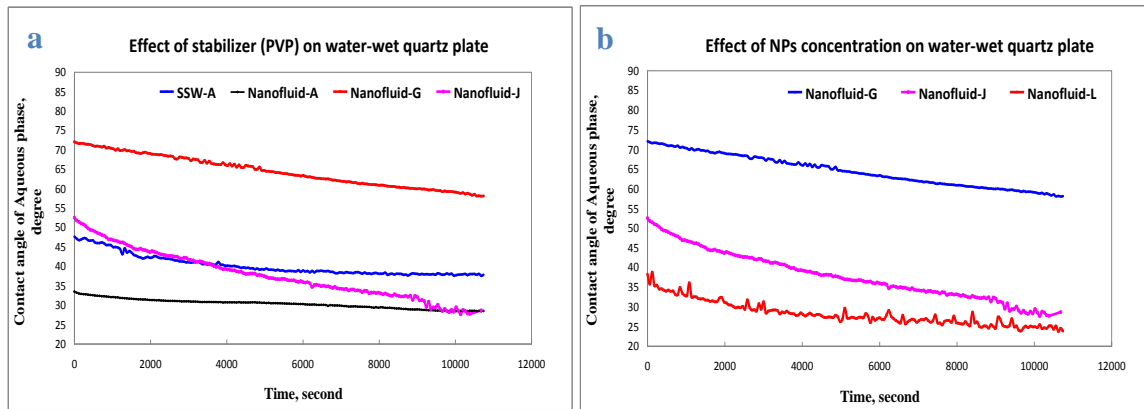


Figure 5 Wettability alteration was determined by contact angle measurements on water-wet quartz plates . Effects of substrate material and soaking duration

CONCLUSION

We revealed that hydrophilic nanoparticles (NPs) can modify the wettability of media. These alterations in wettability depend on the NPs type and concentration, degree of water salinity, ionic composition, initial porous medium wettability, solid system, and duration of NP interaction in the fluid-rock system. Based on this particular study, the use of PVP as a stabilizer did not influence the wettability. Our results demonstrate that NPs wettability alteration is a possible displacement mechanism for flooding processes.

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