

Article

# Enhancing oil recovery with hydrophilic polymer-coated silica nanoparticles

Alberto Bila <sup>1,2,\*</sup> and Ole Torsæter <sup>3</sup>

<sup>1</sup> Department of Chemical Engineering, Eduardo Mondlane University (EMU), Maputo – Mozambique

<sup>2</sup> Centre of Studies in Oil and Gas Engineering and Technology, Eduardo Mondlane University (EMU), Maputo – Mozambique

<sup>3</sup> PoreLab Research Centre, Department of Geoscience and Petroleum, Norwegian University of Science and Technology, Trondheim – Norway; ole.torsater@ntnu.no

\* Correspondence: alberto.bila@uemep.uem.mz

**Abstract:** Nanoparticles have been proposed for enhanced oil recovery (EOR). The research has demonstrated marvelous effort to understand the mechanisms of nanoparticles-EOR. Nevertheless, gaps still exist in terms of understanding the improved fluids and fluid-rock interactions by nanoparticles, which are the key driving forces for oil mobilization. This paper investigates four types of polymer-coated silica nanoparticles as additives for water flooding oil recovery in water-wet reservoirs. A series of flooding experiments were performed with nanoparticles at 0.1 wt.% in seawater at ambient conditions. The dynamics of fluids, fluid-rock interface interactions and fluid flow behavior were characterized in order to understand oil recovery mechanisms of nanoparticles. Experimental results showed an increase in oil recovery up to 14.8%-point with nanofluid injection compared to an average of 40% of the original oil in place (OOIP) obtained from control water flood test. Moreover, the nanoparticles mobilized residual oil and incremented oil recovery up to 9.2% of the OOIP. Displacement studies show that no single mechanism could account for the EOR effect with the application of nanoparticles. Instead, the mobilization of oil seemed to occur through a combination of reduced oil/water IFT, change in the rock surface roughness and wettability to more water-wet, and microscopic flow diversion due to clogging of the pores.

**Keywords:** Polymer-coated nanoparticles, Crude oil recovery, Interfacial tension, Wettability alteration, flow diversion.

## 1. Introduction

Oil companies are facing a decline in production rates due to reduced efficiency in oil recovery from the technologies used today. Such technologies as thermal recovery, injection of chemicals, etc. are hampered by the high costs of preparing and transporting fluids, especially to offshore fields. Furthermore, the discoveries of new oil fields have been scarce [1, 2] and/or require more intricate technologies for the production and maximization of crude oil recovery [3]. Small reservoir pores or thief zones are responsible for trapping a significant amount of residual oil during oil production process. These areas are also responsible for trapping of injection fluids, leading to reduced reservoir permeability and increased economics of oil-recovery flooding operations [4]. Nanotechnology, which uses nanoparticles, has been able to improve the oil recovery factor on a laboratory scale. The application of NPs has also proven to be a solution to some of the problems faced by old techniques in the upstream oil industry. Nanoparticles are materials with diameter size from 1 to 100 nm. The size is the key reason behind the enormous EOR potential of nanoparticles. Owing to nanoscale size and shape, NPs can improve the flooding potential through the porous media with little effect on reservoir permeability and increase recovery from thief zones [1, 3, 5]. With reduced size, NPs have a large surface area and, therefore, a large contact area in the swept areas [3]. The chemical reactivity of NPs increases in the contacted areas of a reservoir; thus, the probability of NPs altering the properties of fluids and rocks to the most favorable conditions for oil recovery also increases. The

research shows that silica NPs are the most researched nanomaterials additives for water flooding oil recovery. The wide spread use of silica NPs is due to their natural occurrence in sandstone formations in the form of quartz; they can be synthesized with some degree of ease, and their properties can be manipulated or tailored with different surface coatings materials for the desired applications [5-7].

Bera and Belhaj [8] pointed out that 5 to 15% of the OOIP can be achieved with the application of NPs on a laboratory scale. A recent statistical research on nanoparticle core flooding data conducted by Ding, et al. [9] revealed that incremental recovery can be as high as 30% of the OOIP with NPs injection, but the most frequent range is 5% of the OOIP. Despite this achievement, the major challenge is still the formulation of stable nanofluid dispersion especially for oil harsh reservoirs environments, this is, high pressure, high temperature, and high salinity, particularly when divalent ions are present [10, 11].

Functionalization/coating of the NP surface layer with polymer molecules or other additive materials is a novel-active area of scientific research; the technique has been wished-for improving dispersion stability, stabilization of emulsion, decrease the amount of NP retention on the rock surface, and improving NP transport through porous media. The use of polymer-coated silica nanoparticles to improve displacement efficiency on a micro-scale was investigated by Omran, et al. [12]. These types of NPs were found to perform more efficiently in water-wet glass micromodels than in intermediate and oil-wet rock models. The displacement efficiency was attributed to the ability of NPs to promote better clusterization of oil, thus leaving small and less connected oil drops trapped in the pores of the micromodel [12]. Saigal, et al. [13] reported that silica NPs covalently grafted with polymer chains (2-(dimethylamino)ethyl methacrylate) were extremely efficient emulsifier agents at low NP concentrations. Qi, et al. [14] applied interfacially active, pH responsive polymer-coated silica NPs for EOR. The results indicated that NPs can significantly stabilize heavy oil-in-water emulsion and increase recovery by 10 wt.% of the heavy oil-in-place at concentrations of NP as low as 0.1 wt.%.

Ponnapati, et al. [15] reported an incremental recovery of 7.9% of the OOIP by injecting a stable suspension of polymer-functionalized silica NPs in Berea sandstone. Hendraningrat and Torsæter [13] used a water-soluble polymer, polyvinylpyrrolidone (PVP), to stabilize silica-based nanofluids. Their flooding experiments revealed an increment of 2% of the OOIP. A series of flooding experiments for EOR by means of polymer-coated silica NPs dispersed in seawater to 0.1wt.% were recently carried out by Bila, et al. [16] and Bila, et al. [17]. They reported an increase in oil recovery of about 14% of the OOIP in water-wet Berea core plugs and 5% of the OOIP in neutral-wet cores, respectively. Many studies have demonstrated marvelous effort to understand the mechanisms associated with NPs injection and their interactions with oilfield constituents in order to explain the EOR effect. Wettability alteration to increasingly water-wet and reduction in interfacial tension (IFT) are the two most proposed EOR mechanisms of NPs [9, 18]. Interfacial tension and wettability are the most important physical properties that characterizes fluid-fluid and fluid-rock interfaces, respectively. Both properties control the distribution and mobility of reservoir fluids within pore spaces. In oil displacement processes by nanofluid flooding, interfacial tension is expected to decrease during the partitioning of NPs at the oil/water interface from the aqueous solution; this process is governed by the size of the NPs and wettability [19, 20]. On the other side, NPs can also adhere to the rock surface because of the attractive forces originating from dipole-dipole interactions [21, 22] and/or driven by physical interactions due to the external forces. This process results in the change of the rock surface roughness. A synergistic interaction effect of IFT reduction and wettability change creates unfavorable conditions for the oil to reside within pores, leading to its removal from the pores to the production wells. Besides, oil displacement mechanisms may be functioning during silica-based nanofluid flooding process. Such mechanisms may include (i) creation and stabilization of emulsions *in-situ* [23-25], (ii) structuring disjoining pressure [26, 27] and (iii) microscopic flow diversion due to clogging of the pores [28-31]. Despite this achievement/knowledge, gaps still exist in terms of understanding the effect of different types of NPs, their binding effect with surface additive materials and the resulting interactions with oil reservoir and its constituents, which act as propellants for the mobilization of mobile and residual oil, increasing oil recovery. From the various research works, it appears that no single mechanism of nanoparticle-EOR can be adopted for all kinds

of formations due to variable characteristics of reservoir formations, i.e., different rock type and mineralogy, composition of crude oil and brine, and injection EOR fluids, etc. Therefore, despite the widespread use of nanotechnology, a large-scale field application of NPs in the oil and gas industry has not been reported, except for some small-scale field trials [21]. Obviously, this calls for more studies to expand the knowledge of nanoparticle technology so that can be applied with less risk in the oil industry. This work demonstrates the applicability of polymer-coated silica NPs for the recovery of crude oil and proposes potential oil displacement mechanisms of nanoparticles.

## 2. Materials and Methods

### 2.1. Silica nanoparticles and injection seawater

Four types of nanostructured particles stabilized by methacrylate-based polymer molecules were used in this work. Additionally, the polymer shells on the particle surface were intended to decrease the hydrophilicity of silica particles. The nanostructured particles were comprised of silicon dioxide (SiO<sub>2</sub>), aluminum dioxide (Al<sub>2</sub>O<sub>3</sub>) and mixed oxides (MOX). They were spherical and amorphous silica products marketed under AEROSIL® trade name from Evonik Industries. The nanoparticles were supplied to us for EOR testing as special research and development (R&D) products AERODISP®, which are AEROSIL® particles in liquid solution. Selected properties of NPs in solution or concentrated solutions are given in Table 1. The concentrated solutions were diluted with synthetic seawater to 0.1% wt.%, then used in all experiments. Synthetic water was prepared

**Table 1.** Properties of concentrated solutions of silica NPs in distilled water.

Nanofluid (NF)	Basis	Modification	Concentration (wt.%)	Size (nm)
1	SiO <sub>2</sub> (sol-gel cationic)	Polymer	38.6	107
2	SiO <sub>2</sub> (sol-gel anionic)	Polymer	26.0	32
3	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /MOX	Polymer	21.6	218
4	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /MOX	Polymer	25.5	145

under laboratory conditions, dissolving certain amount of salts in distilled water. **Table 2** shows the composition of the prepared seawater. The total dissolved salts were 38,318 ppm.

**Table 2.** Composition of synthetic sea water in 1-little bottle.

Salts	NaCl	KCl	NaHCO <sub>3</sub>	Na <sub>2</sub> SO <sub>4</sub>	CaCl <sub>2</sub> ·6H <sub>2</sub> O	MgCl <sub>2</sub> ·6H <sub>2</sub> O	Sr <sub>2</sub> ·6H <sub>2</sub> O
wt.%	25.50	0.72	0.22	4.06	1.62	3.16	0.02

The density of water was 1.024 g/cm<sup>3</sup> and viscosity of 1.025 cP. With added NPs to the injection seawater, the new density and viscosity were 1.023 – 1.028 g/cm<sup>3</sup>, and 1.023 to 1.058 cP, respectively. This shows a negligible effect of NPs on the initial properties of the injection water. All properties were measured at room conditions (21 °C) using Anton Paar Density meter and Anton Paar Rheometer for density and viscosity, respectively. The pH of water solution was 7.96 and with added NPs a minimal change was observed and was between 7.53-8.10.

### 2.2. Crude oil and normal decane

The crude oil was obtained from a field in the North Sea. Its viscosity was 33 cP and the gravity 28 °API at room conditions (21 °C). The characterization of the degassed crude oil in terms of SARA (Saturates, Aromatics, Resins, Asphaltenes) analysis is provided in Figure 1. It is a light oil with asphaltenes content of 0.18 wt.%. Before use, the crude oil was filtered twice through a 5-µm Millipore to remove any suspended particles or other impurities that can affect its composition and flooding experiments [11]. The crude oil was used in all experiments. However, normal decane was used for wettability tests. The decane had a density of 0.73 g/cm<sup>3</sup> and viscosity of 0.92 cP at 20 °C.

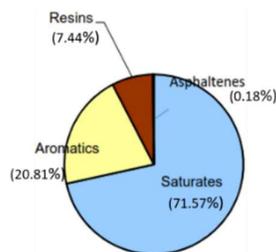


Figure 1. SARA analysis for crude oil.

### 2.3. Type of porous media

Oil recovery experiments were conducted using originally water-wet Berea sandstone rocks. The mineral composition of the rocks was characterized with X-ray diffraction (XRD) on five rock samples. The cores were nearly homogeneous and composed of 93.7 Vol.% quartz, 5.0 vol.% of Microcline (Alkali feldspar), and Diopside (1.3 vol.%), on average. For flooding experiments, cylindrical core samples were prepared with standardized dimensions: diameter of 3.75 cm, the length varied from 4.5 to 6 cm. The cores were cleaned with methanol using Soxhlet extraction and dried in the oven at 60 °C for three days. Then they were evacuated for 2 hours and saturated with water using a vacuum container. The porosity was determined via Helium porosimeter and ranged from 16.7 – 19%. The core absolute permeability varied between 277 – 400 mD and was measured using a constant head permeameter with nitrogen gas then corrected for the Klinkenberg effect.

### 2.4. Interfacial tension measurement

Interfacial tension (IFT) is an important parameter for oil recovery. It provides a qualitative measure of the movement and distribution of fluids in porous spaces. In this work, IFT was measured using pendant drop technique. We used a J-syringe needle with inner diameter of 1.0047 mm to dose crude oil drops in the bulk phase. While the oil drop was hanging from a needle within the continuous phase, IFT was measured every 20 seconds until equilibrium was reached. All measurements were carried out at room temperature.

### 2.5. Rock wettability tests

Wettability of a reservoir affects the location, the flow and distribution of fluids in porous media [32]. Together with IFT, wettability plays a great role in all stages of oil recovery. Wettability of a reservoir can change during oil production stages. In petroleum engineering, wettability of reservoir rocks is widely characterized by Amott test. The test combines spontaneous and forced displacements of fluids to measure the average wetting condition of a reservoir rock sample [32]. The Amott test was used in this work to assess the wettability of the rocks before and after nanofluid-injection. The spontaneous imbibition/drainage tests were performed using Amott cells; An Amott cell is a visual glass with a graduation tube on top [33]. For the spontaneous imbibition (SI) tests, an oil-saturated core plug is placed in an Amott cell filled with water. The oil displaced from the core is collected and read step by step through the graduation tube until the equilibrium is reached. For the spontaneous drainage, the difference lies in the fact that a water-saturated core is placed in oil-filled cell to measure the displacement of water by oil. At the end of each spontaneous imbibition/drainage tests, the forced displacement was conducted with core plug inserted in a Hassler-core holder. Figure 2 shows wettability indexes proposed by Cuiec [34] for the categorization of different rock wettability.

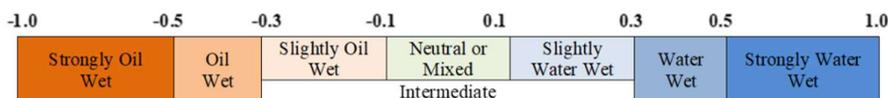


Figure 2. Categorization of rock wettability based on wettability index.

### 2.5. Rock core flooding experiments

Core flooding tests are widely used to study how well fluids flow through porous media and oil recovery. Figure 3 illustrates a schematic diagram of core flooding set up. The system consists of individual fluid holding cylinders, containing crude oil, water and nanofluid. All cylinders were mounted vertically inside a temperature-controlled oven. The core block consists of a Hassler type core holder in which the core is loaded and oriented horizontally. The core block is supported by a customized stand, the core was confined with an overburden pressure held within 18 – 22 bars. Designated fluid was injected into the core with aid of the hydraulic fluid; fluid flow through rock pores was studied via pressure sensors connected to the inlet and outlet of the core holder.

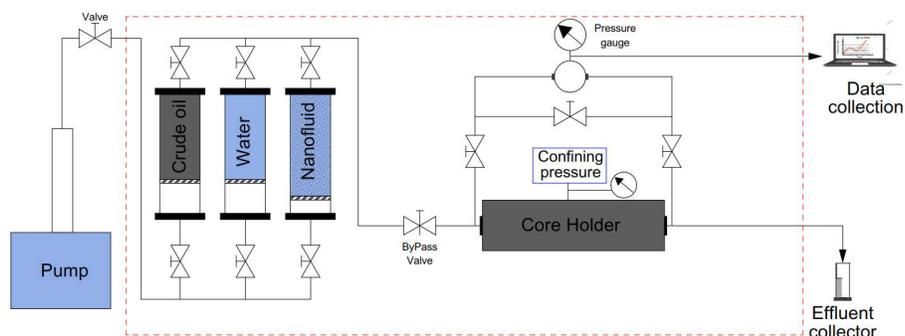


Figure 3. Schematic diagram of the core flooding system.

To simulate oil production of a reservoir: (i) a water-saturated core loaded in the core holder was injected with crude oil. Three different flowrates (0.5, 1.5 and 3 ml/min) were used until the displacement of water reached initial water saturation ( $S_{wi}$ ). The sequential increase in injection flow rate mitigated/reduced zones of capillary end-effects [35, 36], while the injection of crude oil at both core ends even the distribution of fluids within the core. (ii) to mimic secondary EOR operation, the nanofluid was injected at a constant rate (0.2 ml/min) until there was no oil production for approximately 3-pore volumes (PVs). Finally, (iii) in the tertiary EOR operation, nanofluid was injected after secondary water flood using the same flowrate until there was no more oil production at core outlet. The effluent was collected in 5 ml vials; an automated camera was used to record oil production during slow oil production stage. The experiments were done at ambient conditions; two nearly identical core plugs were used to determine experimental repeatability and reduce errors.

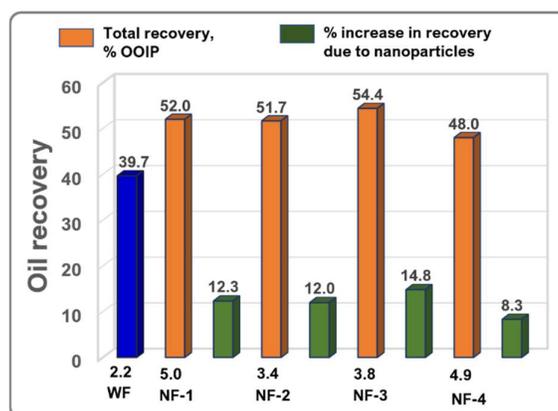
## 3. Results and discussion

### 3.1. Nanoparticle oil recovery performance

For most oil reservoirs, water flood (WF) is the most chosen technique for pressurizing the reservoir after primary depletion and for displacing a portion of the remaining oil to production wells. Availability of water, high recovery rates and low costs for execution make this technique the primary choice for oil companies [2, 37, 38]. EOR fluids can mobilize both mobile oil and residual oil, so they can be applied after the primary oil production stage, as a secondary recovery fluid. In this case, the displacement efficiency must be better than the water flooding [39]. This hypothesis was also studied in this work.

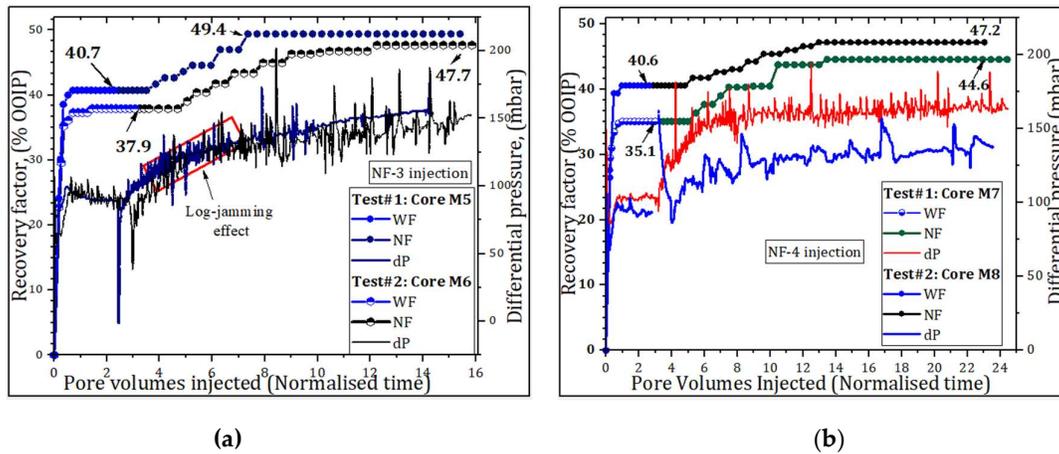
The results of sixteen core flood experiments proved the EOR potential of silica-based nanofluids. As secondary EOR fluids, the NPs show the ability to retard the breakthrough time compared to the plain water injection. Accordingly, higher ultimate recoveries were achieved by nanofluids than the injection of the water. This is likely to happen because water flood suffers from viscous fingering, causing an earlier water breakthrough, poor sweep efficiency and excessive water production (conformance problems). Viscous fingering results from the displaced phase (crude oil) having higher viscosity than oil-recovery displacing fluid (water) [40]. Although, the NPs did not

show a tangible effect on the viscosity of water, they delayed the breakthrough time. This behavior is attributed to the structuring of NPs and plugging of some pores. As explained by Wang, et al. [41] the existence of NPs, either attracting or repelling water molecules, changes the pressure distribution of fluids, and thus modifying the capillary and viscous forces. Accordingly, the water flow pathway becomes more tortuous, delaying breakthrough time [42]. In this work, the experiments were stopped after the injection of about 10-PVs, when there was no production. Under the experimental conditions, the injected PVs may be enough to support the long-range structuring of NPs within pores; this allowed the nanofluids to perform better, achieving higher ultimate recovery than reference water flood. Figure 4 shows results of ultimate recovery versus injected number of PVs. Our experiments revealed that the oil can be produced to a certain extent with the injection of nanofluids, after that, little or no oil is recovered with the continuous injection of nanofluids. This indicates that NPs can become trapped in the thief zones and form nano-layers reducing reservoir permeability. It is therefore expedient that nanofluid is designed to trigger physical and chemical interactions as soon as possible, when in contact with the reservoir and its constituents. Furthermore, the range or optimum concentration of nanoparticles should be estimated for oil recovery process. The average recoveries of water and nanofluid-flood as a function average pore volume for maximum oil recovery are summarized in **Error! Reference source not found.**. The recovery by water flood was 39.7% of OOIP (average of eight tests, see Table 3). Two tests were performed for each nanofluid type. The oil displacement by nanofluids gave higher recoveries than the use of plain water. The recovery rates varied from 48% to 54.4% of the OOIP, or the nanofluids increased recovery by factors between 8.3 to 14.8%-point.



**Figure 4.** Secondary oil recoveries from various nanofluids compared to reference water flood. The numbers on X-axis show average pore volumes injected to reached ultimate oil production.

Additional eight tests were conducted with nanofluids as tertiary EOR fluids, using 6 cm core at ambient conditions. It was observed that for the nanofluid to mobilize residual oil and form a producible oil bank, a minimum of 1-PV must be injected. While most cores failed to mobilize residual oil to the core outlet at 1-PV, one core had a recovery of 3.3% of the OOIP with nanofluid (NF-1) injection. Probably, the core properties, PVs injected during water flood stage and oil accumulated at core outlet due to capillary end-effect can explain this deviation. Figure 5 presents oil recovery profiles for selected samples. A summary of all recoveries from all nanofluids is given by Table 3.



**Figure 5.** Influence of nanofluid on oil recovery and differential pressure across the core against injection pore volume: (a) WF oil recovery in cores M5 and M6 were 40.7 and 35.9% OOIP, respectively; After nanofluid "NF-3", the recovery was 49.4% and 47.7% OOIP. (b) In cores M7 and M8, WF recoveries were 35.1 and 40.6% OOIP, respectively; after nanofluid "NF-4" injection, it increased to 44.6 and 47.2% OOIP, respectively.

After water flood ceased production, oil recoveries varied from 35.1% to 43.1% of the OOIP (see Table 3). Silica nanoparticles at concentration as low as 0.1 wt.% could increase water flood oil recoveries. The total recoveries ranged from 44.6% to 49.4% of the OOIP. Moreover, the displacement efficiency ( $E_D$ ) evaluated using equation 1, in Table 3, varying between 8.11 to 20.71% proves the ability of silica NPs to improve the microscopic sweep of water flooding.

$$E_D = \left[ 1 - \left( \frac{S_{or2}}{S_{or1}} \right) \right] \times 100\% \quad 2$$

Here,  $S_{or1}$  and  $S_{or2}$  represent residual oil saturation after water- and nanofluid-flooding, respectively.

**Table 3.** Summary of oil recovery factors (expressed as % of OOIP) and residual oil saturation achieved at the end flood tests.

NF	Core #	PV (ml)	$S_{wi}$ (%)	Water flood		Nanofluid flood			$E_D$ (%)	Total RF (%)
				RF (%)	$S_{or1}$ (%)	RF (%)	$\overline{RF}$ (%)	$S_{or2}$ (%)		
NF-1	M1	11.8	33.93	43.1	37.61	4.6	5.9	35.55	8.11	47.7
	M2	12.0	24.22	38.9	46.29	7.3		40.83	11.79	46.2
NF-2	M3	11.7	24.68	41.7	43.91	7.4	7.2	38.36	12.67	49.1
	M4	12.2	20.68	39.4	48.05	7.0		42.52	11.50	46.4
NF-3	M5	11.4	20.78	40.7	43.07	8.7	9.2	36.78	14.63	49.4
	M6	11.1	20.73	37.9	49.22	9.8		41.47	15.74	47.7
NF-4	M7	8.1	23.97	35.1	49.35	9.5	8.1	42.14	20.71	44.6
	M8	8.3	18.40	40.6	48.48	6.6		43.09	11.14	47.2
Average				39.7	45.75			40.00		

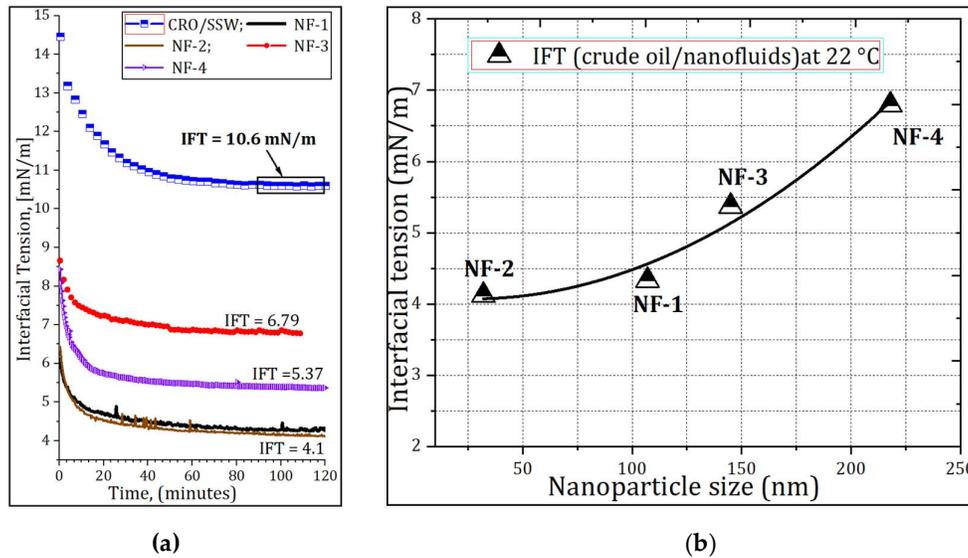
The average incremental recovery varied between 5.9 to 9.2% of the OOIP. Inspection of the results presented in Figure 4 and Table 3 show higher total recoveries in secondary mode than in tertiary mode. The current results may support the notion that, for practical applications, NPs are preferable/efficient as secondary EOR fluids. Similar results were reported by Torsater, et al. [43]. Moreover, in tertiary mode many pore volumes of nanofluids are needed to increase recovery factor compared to secondary injection. In this regard, tertiary operation may also raise concerns about the

cost of nanomaterials. Besides the surface activity of NPs, the recovery potential of nanofluids relies mostly on the time-dependent physicochemical interactions with the rock system. For instance, the gradual increase in oil recovery seen in Figure 5, during nanofluid injection, evidences the effect of long range structural disjoining mechanism in enhancing oil recovery. The longer the time the nanofluids are in contact with the rock system, the better the oil recovery [44]. In summary, the polymer-coated silica NPs revealed a good EOR potential in water-wet rocks. Additional flood tests are recommended at conditions of high temperature and high pressure to best mimic oil field conditions. This should include the application of a bump flood at the end of low rate injection is recommended to mitigate the capillary end effect and establish true water flood residual oil saturation prior to the implementation of the EOR fluid injection.

### *3.1. Evaluation of nanoparticle oil recovery mechanisms*

#### *3.1.1. Interfacial tension analysis*

The interfacial tension (IFT) between the aqueous solution of NPs and crude oil phases was evaluated at room conditions with pendant drop method. Figure 6(a) shows the dynamic measurement of the IFT versus time. The reference tension (crude oil/water) was 10.6 mN/m; it was measured in our previous work [17]. Figure 6(a) indicates that the reference tension reduced to a range of 6.8 – 4.1 mN/m in the presence of NPs in the aqueous phase. Moreover, Figure 6(b) proves that the reduction in IFT depends on the size of the NPs in the aqueous solution, which is in agreement with earlier findings [19, 20]. Typically, small diameter NPs have a high-affinity adsorption capacity at the oil/water interface, allowing them to contact a large surface area and decrease the tension than the large particles. Behera and Sangwai [45] explain that smaller sizes of NPs can increase repulsive forces within NPs. This induces a higher disjoining pressure, which is responsible for the reduction of IFT between the two phases. On the other hand, this phenomenon can be, in part, attributed to the surface-active polymer shells bonded to the NP surface, intended to enhance steric repulsive forces and stabilization of NPs. However, one of the challenging issues in nanoparticle-EOR is understanding the individual contribution of NPs and surface coating agents. We argue that the physicochemical interactions resulting from the bonding of silica NPs with surface coated polymers, such as improved surface reactivity, stability, etc., play a role in reducing IFT and, therefore, in the efficient microscopic displacement of the oil. A reduction in IFT, even below the critical value for the onset of oil mobilization, is regarded crucial for oil recovery, as it can change the microscopic distribution of the oil in porous spaces [46]. Additionally, polymer-coated NPs can stabilize oil droplet emulsions [47], paving the way for their efficient mobilization towards production wells and increase oil recovery. We confirmed experimentally that nanofluids NF-1 and NF-2 could generate oil-water-emulsions by increasing injection rate at the end of low rate injection. Potentially, oil was recovered as an emulsion in water phase. This observation is well related to its small size and the ability to reduce IFT compared to samples NF-3 and NF-4, which did not share the same behavior. It has also been claimed that NPs emulsification ability is, in part, attributed to the surface activity of the polymer molecules [13]; the polymer molecules can enter the oil/water interface, decrease surface energy and interfacial tension.

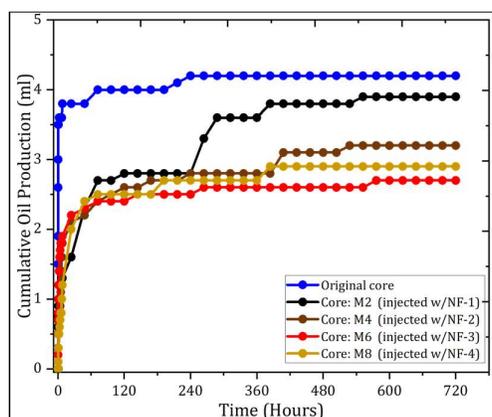


**Figure 6.** (a) Dynamic measurement of IFT between crude oil (CRO) and nanofluids at 22 °C, and (b) Variation of IFT with particle size.

Although there is a correlation between IFT reduction and the size of the NPs, the same does not apply for oil recovery. For instance, NF-2 with the smallest particle size and therefore the largest IFT reduction (4.1 mN/m) had an incremental recovery of 7.2% of the OOIP, while the largest particle size sample NF-3, with the highest IFT value, recorded the highest incremental recovery of 9.2% of the OOIP. As the IFT does not change dramatically when adding polymer-coated silica NPs to water, it is therefore not a primary mechanism responsible for the EOR effect. We speculate that the surface coating polymers molecules left insufficient accessible surface sites for the NPs adsorption, thus impeding them to play their role at the interfaces. Further studies should be conducted in order to determine the ideal conditions for NP surface coating to achieve the lowest IFT and, at the same time, be efficient in providing high stability for NP dispersion during the EOR operation.

### 3.1.2. Spontaneous imbibition tests

In previous section, we examined the influence of NPs on fluid-fluid properties. Next, the effect of NPs on the fluid-rock interface is evaluated by spontaneous imbibition (SI). It should be noted that SI tests were performed after nanofluid flood oil recovery experiments. The core with residual crude oil saturation was injected with decane and then placed in an Amott cell. Figure 7 shows spontaneous oil recovery versus time. The highest cumulative oil production was achieved in the core previously not contacted by the NPs, i.e. reference/original core plug. Initially, the SI rate seems to follow the same oil recovery profile up to a point where it decreased and oil production stopped for a while, in the case of the core plugs contacted by the nanoparticles. Meanwhile, water continued to imbibe and increased oil recovery in the reference core plug, indicating a strongly water-wet condition. The core plugs, previously injected with NPs, exhibited a gradual production of oil after a stagnant period. This behavior can be attributed to the reduced IFT and the dynamic change in core wettability induced by NP and rock interactions.



**Figure 7.** Oil recovery by spontaneous imbibition versus time.

From Figure 7, the main observation is that cumulative oil production is inversely related to the reduction of IFT and the size of NPs. In other words, the core plugs injected with small size NPs displayed better capillary water-intake and high recovery by SI, showing an agreement with the results presented in Figure 6(b). The Amott water index ( $I_w$ ) varied from 0.54 to 0.78; the wettability index from reference core plug was measured in our previous work and was 0.86 [30]. The rate of SI and  $I_w$  indicate that the core plugs remained more water-wet after being injected with hydrophilic nanoparticles. In the absence of attractive forces between the NPs and rock surface, Wasan and Nikolov [26] and Chengara, et al. [27] explain that the layering and structuring arrangement of NPs in the pores causes the disjoining pressure and the development of new hydrophilic surfaces; this detaches oil from surface and increases the recovery of oil. In this case, wettability alteration by hydrophilic NPs seems minimal and cannot account for a significant oil recovery.

### 3.1.2. Injection pressure profile

The existence of nanoparticles, either attracting or repelling water molecules, can change the pressure distribution of fluids, which can modify the capillary and viscous forces, and resulting in different displacement velocity and efficiency [41]. Hence, the differential pressure over the core can be used to interpret the oil displacement mechanisms of nanofluid injection.

Examples of differential pressure profiles recorded during the injection of nanofluid are presented in Figure 5. In the water flooding stage, the injection pressure stabilizes after the breakthrough point, because the oil ceased production. Then, the pressure increases above the reference water flood pressure with nanofluid injection; however, little or no entrainment of oil at this stage occurred with the injection of nanofluids. With the progress of the injection, NPs caused pressure fluctuations and was noticeable during the injection of NF-3 and NF-4 (probably due to their large particle size). Additionally, the fluctuations in pressure can be caused by the pore blockage, pore-opening and mobilization of residual oil [42]. The square in Figure 5 illustrates zones of jammed NPs in some parts of the core plug and potential zones of reduced permeability. In order to provide new flow paths and reduces excess inner pore-pressure in the jammed zones, the pressure was redistributed, and the water flow redirected to the adjacent pore channels. The zones of sudden increase in pressure (in Figure 5) can be related to oil droplets that squeeze through the constricted pores, followed by breakage and, therefore, pressure release and oil entrainment [42]. As a result, oil recovery is increased at microscopic level [28, 29]. In Table 3 one can see that large size NPs had high oil displacement efficiency; following Section 3.1.1, it was noted that large size NPs had the least influence on the IFT reduction. Hence, the interpretation of the pressure profile suggests that not only the log jamming effect, but also the straining occurred during the oil mobilization. The challenge here is to determine the contribution of increased pressure for the oil mobilization; the difficulty is the pressure remaining unstable for the duration of the nanoparticle injection.

The reduction in core permeability ranged from 7 to 24% of initial values. As expected, the large diameter NPs had the largest influence on initial permeability of the cores. However, this pressure variance in the cores reflects small changes in the initial values of permeability of the cores. This implies that the polymer molecules attached to the particle's surface played some role in inhibiting the retention of NPs on the surface of Berea sandstone while enhancing oil recovery.

## 5. Conclusions

In this paper, we investigated the potential of silica nanoparticles as water flood additives for oil recovery, as well as the underlying oil recovery mechanisms. The results showed that NPs at a concentration of 0.1 wt.% in seawater can enhance oil recovery in water-wet reservoirs. Having examined the possible displacement mechanisms of silica nanoparticles, we conclude that different mechanisms, such as IFT reduction, modification of the surface roughness due to structuring of nanoparticles in the rock pores and wettability change to more water-wet, and log-jamming effect can explain the nanoparticle-EOR effect in water-wet reservoirs. Additional findings include:

- The NPs at 0.1wt.% had a minor effect on the viscosity of the injection water; however, showed an ability to retard the breakthrough time, resulting in a high recovery compared to the control test.
- Hydrophilic silica nanoparticles (polymer-coated  $\text{SiO}_2$ ) seemed to be more effective in enhancing oil recovery as secondary EOR fluids in Berea sandstone.
- Hydrophilic silica nanoparticles are capable of gradually changing the microscopic distribution of fluids due to deposition on the surface, changes in the surface roughness and wettability of the rock to more water-wet condition, which could be an important mechanism for long injection periods expected in a field scale.
- Generation of in-situ oil emulsions droplets in water phase could be influencing factor on the recovery of oil for some of small size nanoparticles.

**Funding:** This research was funded Norwegian Research Council for the financial support through PoreLab, Centre of Excellence, project number 262644.

**Acknowledgments:** The authors are grateful to Evonik Industries for providing the nanoparticles and for the fruitful discussions.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Sun, X.; Zhang, Y.; Chen, G.; Gai, Z., Application of Nanoparticles in Enhanced Oil Recovery: A Critical Review of Recent Progress. *Energies* **2017**, *10*, (3).
2. Muggerridge, A.; Cockin, A.; Webb, K.; Frampton, H.; Collins, I.; Moulds, T.; Salino, P., Recovery rates, enhanced oil recovery and technological limits. *Philosophical transactions. Series A, Mathematical, physical, and engineering sciences* **2014**, *372*, (2006), 20120320-20120320.
3. Sandeep, R.; Jain, S.; Agrawal, A., Application of Nanoparticles-Based Technologies in the Oil and Gas Industry. In *Nanotechnology for Energy and Environmental Engineering*, Springer: 2020; pp 257-277.
4. Ahmadi, M.; Habibi, A.; Pourafshari, P.; Ayatollahi, S., Zeta Potential Investigation and Mathematical Modeling of Nanoparticles Deposited on the Rock Surface to Reduce Fine Migration. In *SPE Middle East Oil and Gas Show and Conference*, Society of Petroleum Engineers: Manama, Bahrain, 2011; p 14.
5. Bennetzen, M. V.; Mogensen, K., Novel Applications of Nanoparticles for Future Enhanced Oil Recovery. In *International Petroleum Technology Conference*, International Petroleum Technology Conference: Kuala Lumpur, Malaysia, 2014; p 14.

6. Negin, C.; Ali, S.; Xie, Q., Application of nanotechnology for enhancing oil recovery—A review. *Petroleum* **2016**, *2*, (4), 324-333.
7. Miranda, C. R.; Lara, L. S. d.; Tonetto, B. C., Stability and Mobility of Functionalized Silica Nanoparticles for Enhanced Oil Recovery Applications. In *SPE International Oilfield Nanotechnology Conference and Exhibition*, Society of Petroleum Engineers: Noordwijk, The Netherlands, 2012; p 11.
8. Bera, A.; Belhaj, H., Application of nanotechnology by means of nanoparticles and nanodispersions in oil recovery-A comprehensive review. *Journal of Natural Gas Science and Engineering* **2016**, *34*, 1284-1309.
9. Ding, H.; Zhang, N.; Zhang, Y.; Wei, M.; Bai, B., Experimental Data Analysis of Nanoparticles for Enhanced Oil Recovery. *Industrial & Engineering Chemistry Research* **2019**, *58*, (27), 12438-12450.
10. Zhou, Y.; Wu, X.; Zhong, X.; Reagen, S.; Zhang, S.; Sun, W.; Pu, H.; Zhao, J. X., Polymer nanoparticles based nano-fluid for enhanced oil recovery at harsh formation conditions. *Fuel* **2020**, *267*, 117251.
11. Bila, A. L., Experimental investigation of surface-functionalised silica nanoparticles for enhanced oil recovery. *PhD. Thesis* **2020**.
12. Omran, M.; Akarri, S.; Torsaeter, O., The Effect of Wettability and Flow Rate on Oil Displacement Using Polymer-Coated Silica Nanoparticles: A Microfluidic Study. *Processes* **2020**, *8*, (8).
13. Saigal, T.; Dong, H.; Matyjaszewski, K.; Tilton, R. D., Pickering emulsions stabilized by nanoparticles with thermally responsive grafted polymer brushes. *Langmuir* **2010**, *26*, (19), 15200-15209.
14. Qi, L.; Song, C.; Wang, T.; Li, Q.; Hirasaki, G. J.; Verduzco, R., Polymer-coated nanoparticles for reversible emulsification and recovery of heavy oil. *Langmuir* **2018**, *34*, (22), 6522-6528.
15. Ponnappati, R.; Karazincir, O.; Dao, E.; Ng, R.; Mohanty, K. K.; Krishnamoorti, R., Polymer-functionalized nanoparticles for improving waterflood sweep efficiency: Characterization and transport properties. *Industrial & Engineering Chemistry Research* **2011**, *50*, (23), 13030-13036.
16. Bila, A.; Åge Stensen, J.; Torsæter, O., Polymer-functionalized silica nanoparticles for improving water flood sweep efficiency in Berea sandstones. *E3S Web Conf.* **2020**, *146*, 02001.
17. Bila, A.; Stensen, Å. J.; Torsæter, O., Experimental Investigation of Polymer-Coated Silica Nanoparticles for Enhanced Oil Recovery. *Nanomaterials* **2019**, *9*, (6).
18. Aziz, H.; Tunio, S. Q., Enhancing oil recovery using nanoparticles—a review. *Advances in Natural Sciences: Nanoscience and Nanotechnology* **2019**, *10*, (3), 033001.
19. Tangparitkul, S.; Charpentier, T. V. J.; Pradilla, D.; Harbottle, D., Interfacial and colloidal forces governing oil droplet displacement: Implications for enhanced oil recovery. *Colloids and Interfaces* **2018**, *2*, (3), 30.
20. Chevalier, Y.; Bolzinger, M.-A., Emulsions stabilized with solid nanoparticles: Pickering emulsions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2013**, *439*, 23-34.
21. Afolabi, R. O.; Yusuf, E. O., Nanotechnology and global energy demand: challenges and prospects for a paradigm shift in the oil and gas industry. *Journal of Petroleum Exploration and Production Technology* **2019**, *9*, (2), 1423-1441.
22. Roustaei, A.; Saffarzadeh, S.; Mohammadi, M., An evaluation of modified silica nanoparticles' efficiency in enhancing oil recovery of light and intermediate oil reservoirs. *Egyptian Journal of Petroleum* **2013**, *22*, (3), 427-433.
23. Zhang, T.; Davidson, D.; Bryant, S. L.; Huh, C., Nanoparticle-Stabilized Emulsions for Applications in Enhanced Oil Recovery. In *SPE Improved Oil Recovery Symposium*, Society of Petroleum Engineers: Tulsa, Oklahoma, USA, 2010; p 18.
24. Adil, M.; Lee, K.; Zaid, H. M.; Latiff, N. R. A.; Alnarabiji, M. S., Experimental study on electromagnetic-assisted ZnO nanofluid flooding for enhanced oil recovery (EOR). *PloS one* **2018**, *13*, (2), e0193518.

25. Kim, I.; Worthen, A. J.; Johnston, K. P.; DiCarlo, D. A.; Huh, C., Size-dependent properties of silica nanoparticles for Pickering stabilization of emulsions and foams. *Journal of Nanoparticle Research* **2016**, *18*, (4), 82.
26. Wasan, D. T.; Nikolov, A. D., Spreading of nanofluids on solids. *Nature* **2003**, *423*, (6936), 156-159.
27. Chengara, A.; Nikolov, A. D.; Wasan, D. T.; Trokhymchuk, A.; Henderson, D., Spreading of nanofluids driven by the structural disjoining pressure gradient. *Journal of colloid and interface science* **2004**, *280*, (1), 192-201.
28. Spildo, K.; Skauge, A.; Aarra, M. G.; Tweheyo, M. T., A New Polymer Application for North Sea Reservoirs. *SPE Reservoir Evaluation & Engineering* **2009**, *12*, (03), 427-432.
29. Skauge, T.; Spildo, K.; Skauge, A., Nano-sized Particles For EOR. In *SPE Improved Oil Recovery Symposium*, Society of Petroleum Engineers: Tulsa, Oklahoma, USA, 2010; p 10.
30. Bila, A.; Stensen, J. Å.; Torsæter, O., Experimental Evaluation of Oil Recovery Mechanisms Using a Variety of Surface-Modified Silica Nanoparticles in the Injection Water. In *SPE Norway One Day Seminar*, Society of Petroleum Engineers: Bergen, Norway, 2019; p 19.
31. Kokubun, M. A. E.; Radu, F. A.; Keilegavlen, E.; Kumar, K.; Spildo, K., Transport of Polymer Particles in Oil-Water Flow in Porous Media: Enhancing Oil Recovery. *Transport in Porous Media* **2019**, *126*, (2), 501-519.
32. Anderson, W. G., Wettability Literature Survey Part 5: The Effects of Wettability on Relative Permeability. *Journal of Petroleum Technology* **1987**, *39*, (11), 1453-1468.
33. Nazari Moghaddam, R.; Bahramian, A.; Fakhroueian, Z.; Karimi, A.; Arya, S., Comparative Study of Using Nanoparticles for Enhanced Oil Recovery: Wettability Alteration of Carbonate Rocks. *Energy & Fuels* **2015**, *29*, (4), 2111-2119.
34. Cuiec, L., Rock/Crude-Oil Interactions and Wettability: An Attempt To Understand Their Interrelation. In *SPE Annual Technical Conference and Exhibition*, Society of Petroleum Engineers: Houston, Texas, 1984; p 14.
35. Ramakrishnan, T. S.; Cappiello, A., A new technique to measure static and dynamic properties of a partially saturated porous medium. *Chemical engineering science* **1991**, *46*, (4), 1157-1163.
36. Heaviside, J.; Black, C. J. J., Fundamentals of Relative Permeability: Experimental and Theoretical Considerations. In *SPE Annual Technical Conference and Exhibition*, Society of Petroleum Engineers: San Francisco, California, 1983; p 17.
37. Youssif, M. I.; El-Maghraby, R. M.; Saleh, S. M.; Elgibaly, A., Silica nanofluid flooding for enhanced oil recovery in sandstone rocks. *Egyptian Journal of Petroleum* **2018**, *27*, (1), 105-110.
38. Satter, A.; Iqbal, G. M., 7-Reservoir Life Cycle and Role of Industry Professionals. *Reservoir Engineering; Gulf Professional Publishing: Boston* **2016**, 127-136.
39. Green, D. W.; Willhite, G. P., *Enhanced oil recovery*. Henry L. Doherty Memorial Fund of AIME, Society of Petroleum Engineers ...: 1998; Vol. 6.
40. Sydansk, R. D.; Romero-Zeron, L., *Reservoir conformance improvement*. Society of Petroleum Engineers Richardson, TX: 2011.
41. Wang, X.; Xiao, S.; Zhang, Z.; He, J., Displacement of nanofluids in silica nanopores: influenced by wettability of nanoparticles and oil components. *Environmental Science: Nano* **2018**, *5*, (11), 2641-2650.
42. Rezaei, N.; Firoozabadi, A., Macro-and Microscale Waterflooding Performances of Crudes which form w/o Emulsions upon Mixing with Brines. *Energy & fuels* **2014**, *28*, (3), 2092-2103.
43. Torsater, O.; Engeset, B.; Hendraningrat, L.; Suwarno, S., Improved Oil Recovery by Nanofluids Flooding: An Experimental Study. In *SPE Kuwait International Petroleum Conference and Exhibition*, Society of Petroleum Engineers: Kuwait City, Kuwait, 2012; p 9.

44. Zhang, H.; Ramakrishnan, T. S.; Nikolov, A.; Wasan, D., Enhanced oil recovery driven by nanofilm structural disjoining pressure: flooding experiments and microvisualization. *Energy & Fuels* **2016**, 30, (4), 2771-2779.
45. Behera, U. S.; Sangwai, J. S., Interaction of Nanoparticles with Reservoir Fluids and Rocks for Enhanced Oil Recovery. In *Nanotechnology for Energy and Environmental Engineering*, Springer: 2020; pp 299-328.
46. Chatzis, I.; Kuntamukkula, M. S.; Morrow, N. R., Effect of capillary number on the microstructure of residual oil in strongly water-wet sandstones. *SPE Reservoir Engineering* **1988**, 3, (03), 902-912.
47. ShamsiJazeyi, H.; Miller, C. A.; Wong, M. S.; Tour, J. M.; Verduzco, R., Polymer-coated nanoparticles for enhanced oil recovery. *J Appl Polym Sci* **2014**, 131, (15).