# Heavy oil mobilization with nanoparticle-stabilized water-external emulsions

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## Abstract

In-situ oil-in-water emulsion generation, using modified silica hydrophilic nanoparticles as emulsifier, has been proposed as an enhanced oil recovery process. The nanoparticles are injected as an aqueous dispersion; its hydrophilic character allows emulsifying the immobile heavy oil, and transports it out of the reservoir as a low viscosity fluid. Generating the emulsions in the reservoir was suggested because it offers numerous advantages. The first advantage is low injectivity pressures due to the low dispersion viscosity. Also, the size of nanoparticles (5 nm) yields a better emulsion stability.

Twelve nanoparticle dispersions were created using nanoparticle concentrations of 0.5, 2.0 and 5.0 wt%, deionized water or brine made with 0.5 wt% of Sodium Chloride. These dispersions were tested to investigate their ability to generate oil-in-water emulsions. Emulsion generation experiments included interfacial tension measurements, microscopy and emulsion viscosity measurements. Results obtained indicated that the nanoparticles lead to a reduction of the interfacial tension of the heavy oil and the dispersion.

Six core flooding experiments were conducted to study the effect of the nanoparticle dispersion flooding on the final recovery under different settings. Two types of core plugs with permeabilities of 150 md and 2,300 md, and two heavy oils with viscosities of 600 cp and 3500 cp were combined to establish the original experiment conditions. Tertiary heavy oil recoveries obtained ranged from 20% to 64 % of OOIP. The results throughout these experiments suggest that if the reservoir conditions (e.g. permeability, porosity and oil viscosity) are adequate, the nanoparticle dispersion flooding may be a reliable alternative to the thermal recovery processes.

**Keywords:** Heavy oil, emulsifier, nanoparticle, hydrophilic.

# Movilización de crudo pesado a través de la generación de emulsiones con el uso de nanopartículas

## Resumen

La generación de emulsiones agua-aceite en sitio, usando nanopartículas hidrófilas como emulsionante, ha sido propuesta en este trabajo como un proceso de recuperación mejorada. Las nanopartículas son inyectadas en forma de dispersión acuosa y su carácter hidrófilo permite emulsificar el crudo inmóvil y transportarlo fuera del yacimiento como un fluido de baja viscosidad. La generación de emulsiones dentro del yacimiento fue propuesta debido a que ofrece numerosas ventajas. La primera es la baja presión de inyección debido a que la dispersión es de baja viscosidad; así mismo, el tamaño de las nanopartículas (5nm) permite una mejor estabilidad de las emulsiones.

Doce dispersiones fueron generadas usando concentraciones de 0.5, 2.0 y 5.0 p/p de nanopartículas y salmuera a 0.5 p/p de cloruro de sodio y/o agua desionizada. Las dispersiones fueron probadas con la finalidad de investigar su capacidad de generar emulsiones agua-aceite. Las pruebas de laboratorio incluyeron medición de la tensión interfacial crudo-dispersión, imágenes microscópicas y medición de viscosidades. Los resultados obtenidos indicaron que las nanopartículas tienden a bajar la tensión interfacial facilitando la emulsificación.

Seis pruebas de desplazamiento en núcleos fueron llevadas a cabo para estudiar el efecto de la inyección de la dispersión de nanopartículas en el factor de recuperación final bajo diferentes condiciones. Se utilizaron dos tipos de núcleos con permeabilidades de 150 mD y 2,300 mD, así como, dos tipos de crudos pesados de 600 cP y 3,500 cP que combinados sirvieron para establecer las condiciones originales de los experimentos. Las recuperaciones obtenidas después de la inyección de agua fueron desde 20% hasta un 60% del aceite original en sitio. Los resultados sugieren, que si las condiciones de los yacimientos (permeabilidad, porosidad y viscosidad el crudo) son adecuadas, la inyección de nanopartículas puede considerarse como un proceso fiable y alterno a los procesos térmicos de recuperación.

**Palabras clave:** Crudo pesado, emulsiones, nanopartículas, hidrófilas.

## Introduction

Fossil fuels have been the principle source of energy in the world in the last century. However, due to accelerated population growth and decline of conventional hydrocarbon production, it is necessary to develop new energy sources to supply the high demand of countries such as the United States or China. To address this problem, the oil industry has turned to unconventional resources. Every unconventional reservoir has its own unique characteristics and challenges. This work will focus on heavy oil reservoirs since they are a vast source of hydrocarbons. According to the International Energy Agency (IEA), such reservoirs hold more than 70% of the oil resources.

Heavy oil is not as valuable as light oil; in addition to this, it is more difficult to extract, refine and transport because of its high density and high viscosity. However, oil companies have realized that the volume of heavy oil in place is very significant, more than 9 trillion barrels in place (Alboudwarej et al. 2006). Therefore, the oil industry sees in heavy oil reservoirs an opportunity to generate profit by investing early in methods and techniques to enhance recovery.

Primary heavy oil recovery methods are being applied widely in Canada and Venezuela. For example, cold heavy oil production with sand (CHOPS) in Canada currently contributes to more than 500,000 bpd (Dusseault and Baoci 2011). Other techniques involve very complex well geometry, e.g. the Orinoco heavy oil Belt wells in Venezuela. Nevertheless, thermal enhanced oil recovery (EOR) methods have demonstrated to be more efficient since they are able to reduce the in-situ viscosity making the heavy oil flow through the porous media easier. Nonetheless, there are some adverse circumstances that restrict their use. Depth of the formation, thickness and surface weather conditions are some constrains that limit the applicability of the aforementioned techniques.

Non-thermal methods provide a notable alternative to recover heavy oil. Methods such as water flooding, polymer flooding and emulsion flooding improve the mobility ratio between the injected and displaced fluid, along with improving the sweep efficiency. Similarly, alkali-surfactant flooding increases the displacement efficiency by reducing the interfacial tension between the injected and displaced fluid. All these methods have been applied to heavy oil reservoirs with different levels of success, (Shah et al. 2010).

Poor conformance is the principal factor of unsuccessful heavy oil waterflooding projects. Emulsifying the injected water with crude oil is an innovative solution to increase the viscosity of the water and therefore improving the mobility ratio. An important aspect of the emulsions is to ensure their stabilization throughout the whole flooding. Surfactants and solid particles are the most common emulsions stabilizers.

However, solid particles seem to be the best option, because they may preserve the emulsion for longer periods of time. In addition, they are less expensive with respect to surfactants. Smaller particles, in the order of 1 to 100 nanometers, may stabilize and generate small enough emulsions able to flow through the pore throats and also keep the stabilization, no matter the tortuosity of the rock, (Zhang, T. et al. 2010).

Currently, emulsion flooding has been conceived as generating the emulsions at the surface and then injecting them into the reservoir. In this work, the ability of creating in-situ oil-in-water (o/w) emulsion with solid nanoparticles as stabilizers, that will maximize heavy oil recovery and reduce costs is proposed and evaluated.

**Status of the solid-stabilized emulsions for EOR processes**

Emulsions not only may be generated by using surfactants, but also using solid particles as emulsifiers. Natural clays, such as kaolinite, bentonite, and treated fumed silica have been found to be effective solids to stabilize the emulsions. There are two main concerns regarding solid stabilized emulsions, or pickering emulsions, for deployment in porous media; one of them involves the particles size because if it is very large it might plug the pore throat. The other concern involves emulsion stabilization because the stabilized emulsions must last during the whole duration of the injection project without breaking. The size problem can be addressed using a smaller particle size, such as nanoparticles. They are small enough to be able to flow through the pore throats of most conventional heavy oil reservoirs without almost any restriction.

Emulsion flooding can be seen as a technical and economical alternative to thermal methods. Emulsion flooding is able to improve the mobility ratio, and it can be applied to recover viscous oils up to 3000 cP, (Kaminsky et al. 2010). Furthermore, emulsions can be generated by mixing produced oil either in the surface or in-situ, which reduces costs, and increases the efficiency of the EOR project, (Bragg 1999).

Solids-stabilized emulsion is not a new concept. Pickering (1907) realized that a sufficiently smaller insoluble solid might act as an emulsifier between the oil and water increasing the emulsion stability. “Pickering emulsions” have been studied and used in different areas such as the cosmetic, food, paint and pharmaceutical industries, (Arditty et al. 2004); however, there are only a few projects related to EOR process.

Nanoparticles used as emulsion stabilizers have become more important in EOR processes, because their high adsorption energy allow the emulsions to last for long periods of time (Saigal et al. 2010). They are also able to flow through the porous media due to their small size, which is between 1 to 100 nanometers (Kaminsky et al. 2010; Zhang, T. et al. 2010).

**Research objectives**

The objective of this work is to evaluate the generation of nanoparticle-stabilized o/w emulsions in a heavy oil saturated sandstone core, as well as to determine the additional oil recovered by the emulsions. Hydrophilic nanoparticles of 5 nm in size are injected as water dispersion into the sandstone core to emulsify the heavy oil. The hydrophilic nature of the nanoparticle allows the water to trap the residual oil droplets transporting them out of the core.

**Methodology**

The methodology consisted in testing a number of aqueous dispersions with different nanoparticle concentrations. The dispersions were mixed with heavy oil utilizing a stirrer to provide enough energy to create the emulsions. Once the dispersions were tested, the one that emulsified the largest amount of heavy oil was selected as the injection fluid for the later core flooding experiments.

Core flooding tests were performed to prove the in situ emulsion generation by the injection of nanoparticle dispersion, and to verify that nanoparticle injection would lead to greater oil recovery. First, the heavy oil saturated cores were subjected to a secondary recovery process (waterflooding) until the water cut was 100%. Thereafter, the nanoparticles aqueous dispersion was injected as a tertiary recovery to evaluate the additional heavy oil recovery by the generation of a low viscosity o/w emulsion, and the reduction of the interfacial tension between the injected and displaced fluids.

## Experimental description and materials

**Modified silica hydrophilic nanoparticles**

Modified silica hydrophilic nanoparticles of 5 nm and 20 nm mean diameter were received from 3M Company as an aqueous suspension of 20 wt%. These nanoparticles were treated with alkyl ether to give them a hydrophilic nature. Because of this characteristic, the hydrophilic nanoparticles are able to stabilize o/w emulsions without the addition of surfactants.

## Heavy crude oil

Two different heavy oils samples were used in this study. **Table 1.1** shows the available properties of each sample.

#### Sandstone cores

Two different permeability sandstone cores were utilized in the flooding experiments. The effect of permeability on the emulsion generation and the final recovery was evaluated in these cores. The first type of core was Buff-Berea sandstone, with a permeability that ranged from 120 to 350 mD and a porosity of 22%. The second core was Bentheimer sandstone with a permeability of 2,000 to 2,540 mD and 24% of porosity.

#### Brine solution

A 5,000 ppm brine solution was prepared using deionized water and 5.0 wt% of sodium chloride (NaCl). This solution was made with the aim of measuring the core's porosity and permeability; in addition, it was used as displacement fluid in the waterflooding experiments and as a solvent of the nanoparticle dispersions.

#### Experimental procedures

To achieve the objectives of this research, the experiments were divided in two stages: first the mechanical emulsion generation, then the core flooding tests. Both stages were performed at ambient temperature. Procedures describing how these stages were conducted are detailed below.

#### Mechanical emulsion generation

To generate the emulsions, 25 ml of crude oil were placed in a 250 ml beaker in which a stirrer was run at 2,000 rpm. Then 25 ml of the nanoparticle dispersion was poured in small quantities. After 10 minutes in the stirrer, the emulsions were collected and stored in sample vials to be analyzed afterwards.

**Table 1.1.** Properties of the two heavy oils used in this research.

| Property | Heavy oil 1 | Heavy oil 2 |
|---|---|---|
| Density [$g/cm^3$] | 0.941 | 0.944 |
| API gravity [°] | 18.70 | 18.31 |
| Viscosity [cP] @ 72°F | 600 | 3,500 |

**Core flood experiment procedures**

In order to test the enhanced recovery potential by injecting hydrophilic nanoparticle dispersions, a series of core flooding tests was performed with two different types of heavy oil and two kinds of rocks with different permeabilities. The test procedure consists of two parts: (1) characterization of rock porosity and permeability; and (2) core flood measurements of secondary and tertiary recovery.

## Analysis of results

Emulsion generation experiments were carried out using a stirrer as the shear rate provider. Six different nanoparticle dispersions were tested to investigate the effect of the nanoparticle and NaCl concentrations in the generation of emulsions. Emulsions were created by mixing the nanoparticle dispersions with two types of heavy oil. Subsequently, a bench test analysis of each emulsion was performed in order to select the most appropriate dispersion, to be used as the injection fluid in the core flood experiments. Six core flood experiments were performed using the optimal dispersion, previously identified. The optimal dispersion yielded an incremental recovery, providing proof-of-concept that nanoparticle dispersion may be used as an injection fluid in an EOR process.

**Emulsion generation**

Six nanoparticle dispersions were created using nanoparticles concentrations of 0.5, 2.0, and 5.0 wt%. Three of them were made using deionized water, and the other three were made with a 0.5 wt% NaCl brine, with the aim to investigate the effects of nanoparticles and NaCl in the emulsification process.

The six dispersions were mixed with the two types of heavy oil, using a stirrer set at 2,000 RPM for ten minutes. Twelve samples were obtained as a result of this process. Additionally, four more tests were made using deionized water and brine without adding nanoparticles in order to establish the base cases of this experimentation process, **Table 1.2**.

**Table 1.2.** Sixteen emulsion generation experiments were conducted, to identify the optimum nanoparticle concentration to generate the largest amount of emulsions.

| | Crude Oil (cp) | Nanoparticle concentration (wt%) | Salinity (wt% NaCL) |
|---|---|---|---|
| 1 | 600 | 0.0 | 0.0 |
| 2 | 600 | 0.5 | 0.0 |
| 3 | 600 | 2.0 | 0.0 |
| 4 | 600 | 5.0 | 0.0 |
| 5 | 600 | 0.0 | 0.5 |
| 6 | 600 | 0.5 | 0.5 |
| 7 | 600 | 2.0 | 0.5 |
| 8 | 600 | 5.0 | 0.5 |
| 9 | 3,500 | 0.0 | 0.0 |
| 10 | 3,500 | 0.5 | 0.0 |
| 11 | 3,500 | 2.0 | 0.0 |
| 12 | 3,500 | 5.0 | 0.0 |
| 13 | 3,500 | 0.0 | 0.5 |
| 14 | 3,500 | 0.5 | 0.5 |
| 15 | 3,500 | 2.0 | 0.5 |
| 16 | 3,500 | 5.0 | 0.5 |

The experiments using deionized water and the heavy oil 1 showed a rapid phase separation due to density differences; emulsion generation was not observed. However, when the nanoparticles were added and their concentration was increased, an emulsified heavy oil fraction formed and increased as a fraction of total fluid with increasing nanoparticle loading. Similar results were observed with the nanoparticle-plus-brine dispersions, but with a larger emulsified heavy oil fraction, **Figura 1.1**.

Heavy oil 2 base cases also showed phase separation without emulsion generation. Emulsions samples from the nanoparticle dispersion and this type of heavy oil have similar tendencies to those obtained with the first heavy oil. However, samples made with brine greatly increased the emulsified heavy oil fraction, **Figura 1.2**.

## Nanoparticle dispersions and heavy oil interfacial tension

Interfacial tension (IFT) is an important property for the emulsion generation. If the interfacial tension is significantly reduced, the emulsification process may be achieved easily. Experiments were conducted to prove the hypothesis that the hydrophilic nature of the nanoparticles, due to their alkyl ether surface, may cause a reduction in the ITF, since the alkyl ether works as a surface-active agent.

The pendant drop method was used to measure IFT. This method showed that the IFT between the heavy oil and the nanoparticle dispersion is reduced as the nanoparticle concentration increases. In addition, if the salinity also increases, the IFT reduction is even larger. IFT was reduced when the nanoparticle and brine concentration were incremented.

**Figure 1.1.** Samples of emulsions generated using deionized water and brine with heavy oil 1.

**Figure 1.2.** Sample of emulsions generated using deionized water and brine with heavy oil 2.

The different concentration of nanoparticles changed the shape of the oil drop from a rounded-like drop to and rope-like drop, **Figures 1.3** and **1.4**. Rounded-like shapes were observed for lower concentrations due to an increment in the IFT. The opposite was observed for rope-like shapes in which higher concentrations yielded a reduction in the IFT.

The IFT for sample 16 (5.0 wt% of nanoparticle concentration, 0.5 wt% of NaCl and heavy oil 2) was too low to be measured. The reduction in IFT did not allow an oil drop to be formed, but a "rope-like oil" was formed instead, indicating a very low IFT; in fact it is clear that the second heavy oil's IFT is much more sensitive to increasing nanoparticle and brine loading than is the heavy oil 1 at all additive loadings. In contrast, in deionized water the heavy oil 1 exhibited the higher IFT.

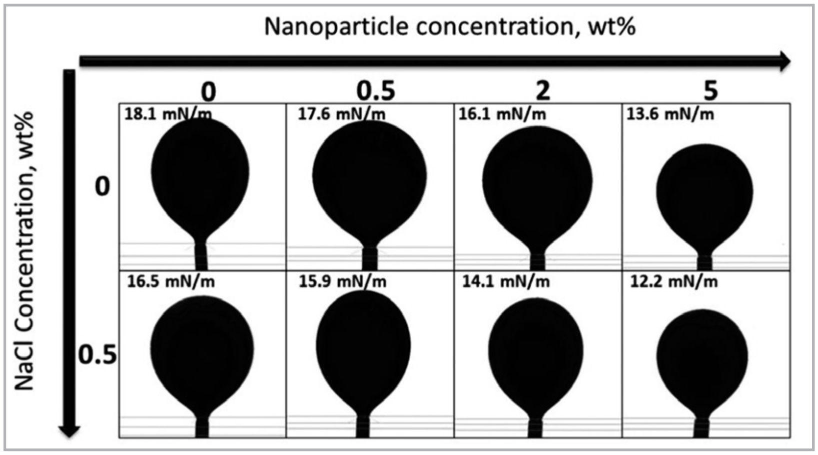


**Figure 1.3.** IFT between heavy oil 1 and the nanoparticle dispersions. A reduction in the IFT is observed according to the nanoparticle and NaCl concentration are increased.

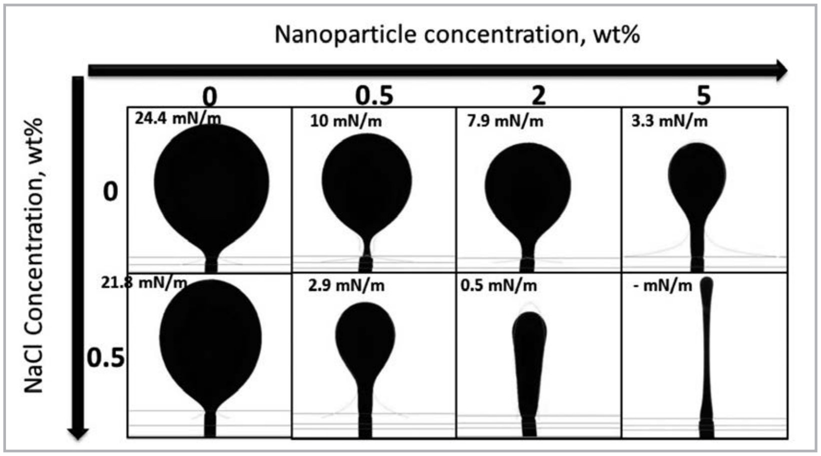


**Figure 1.4.** IFT between heavy oil 2 and the nanoparticle dispersions. IFT was not measured in the final experiment since the oil drop was not formed.

## Microscopic emulsion imaging

Microscopic images of the emulsions were taken to prove the generation of emulsions, as well as to see the effects of nanoparticles and brine concentration, **Figure 1.5** and **Figure 1.6**. A greater number of emulsions can be seen in samples 12 and 16 as a result of the high nanoparticle concentration. Hence, the maximum emulsion generation was observed with the higher nanoparticle concentration. The emulsions made with the heavy oil 1 did not form as many emulsion as the emulsions made with the heavy oil 2.

**Selection of the nanoparticle dispersion for further EOR experiments**

The pendant drop experiments showed an IFT reduction as the nanoparticle concentration increased. When NaCl was added this reduction was further increased. Microscope images confirmed that a larger number of emulsions were generated when the IFT was lower. Finally, rheology experiments showed that the nanoparticles emulsions behave as low viscous fluid.

The dispersion made with 5.0 wt% of nanoparticle and 0.5 wt% of NaCl concentrations was selected to perform the core flooding experiments, due to its emulsion generation capacity and ITF reduction. Additionally, the dispersion made with a 2.0 wt% of nanoparticle and 0.5 wt% of NaCl was also tested because if the results are favorable in terms of recoveries, the reduction in nanoparticle concentration would improve the project economics.

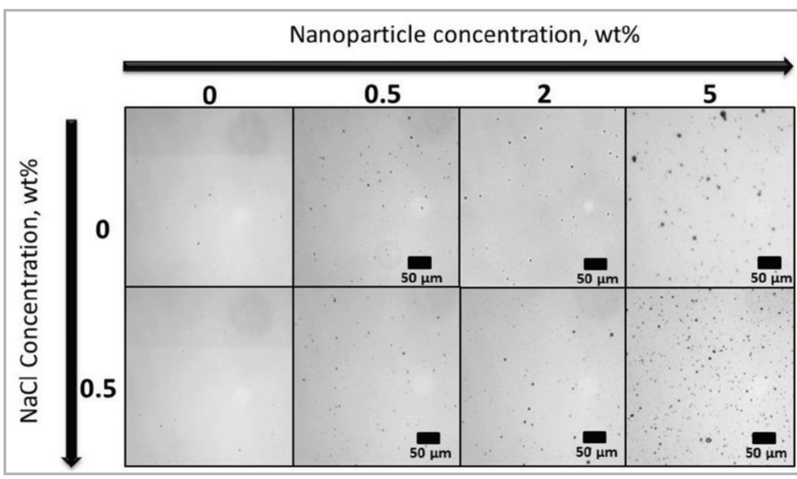


**Figure 1.5.** Microscopic images of emulsions made with heavy oil 1 and the nanoparticle dispersions.

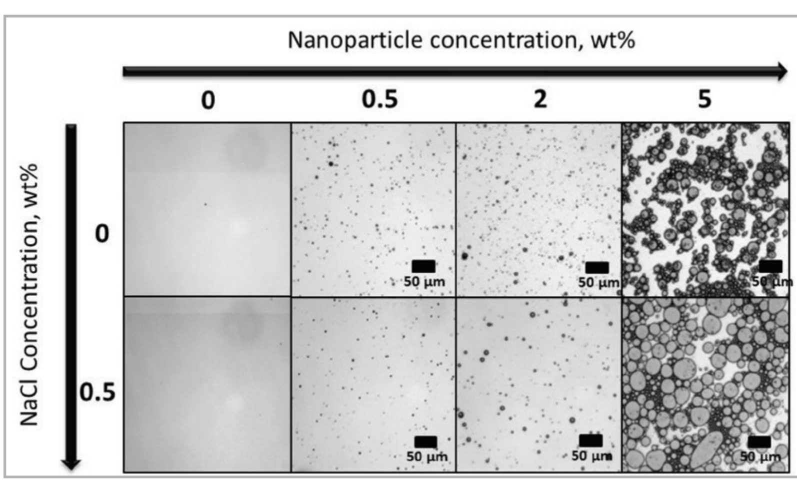


**Figure 1.6.** Microscopic images of emulsions made with heavy oil 2 and the nanoparticle dispersions.

## Core flooding experiments

Six core flooding (CF) experiments were carried out to validate the ability of the hydrophilic nanoparticles to generate o/w emulsions in the porous media as well as to assess the final recovery after the nanoparticle dispersion flooding.

Two different types of sandstone were used in these experiments to explore the effect of permeability in emulsion generation. The cores were cylindrical-shaped, 6 inches long with a radius of 1 inch. The first core is a buff berea sandstone and the second is a Bentheimer sandstone. The buff berea sandstone core has a permeability that ranges from 120 to 350 mD while the permeability of the Bentheimer sandstone core ranges from 2,000 to 2,400 mD. The original core saturation conditions and the rock-fluid properties for the previously described cores are depicted in the **Table 1.3**.

**Table 1.3.** Rock-fluid properties and original saturation conditions.

| Core flooding (CF) | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Sandstone type | **BB (I)** | **BT (I)** | **BB (II)** | **BT (II)** | **BB (III)** | **BT (III)** |
| Pore Volume [cm3] | 16.5 | 18.0 | 16.2 | 18.1 | 15.9 | 17.3 |
| Porosity [%] | 22.0 | 24.2 | 21.6 | 24.1 | 21.1 | 24.1 |
| Permeability [mD] | 137.0 | 2,340.0 | 152.0 | 2,015.0 | 271.0 | 2,027.2 |
| Soi[%] | 25.1 | 14.7 | 23.8 | 13.9 | 22.0 | 14.0 |
| Swirr[%] | 74.9 | 85.3 | 76.2 | 86.1 | 78.0 | 86.0 |
| OOIP [cm3] | 12.4 | 15.4 | 12.4 | 15.6 | 12.4 | 14.9 |

## Core flooding 1: heavy oil 1 - buff berea sandstone (I)

The core flooding 1 was carried out with a buff berea sandstone core saturated with heavy oil 1. Absolute permeability of this core was 137 md with a 22% porosity and an OOIP of 12.4 $cm^3$. During the waterflooding stage, brine was injected at 1 ft/d; this lasted until oil production was no longer observed; a total of 3 PV of brine was injected, resulting in a recovery of 32 % of the OOIP.

Nanoparticle Dispersion 1 (ND1) was injected after waterflooding at different injection rates, resulted in an additional 32.3% oil recovery; the total oil recovery at the end of the experiment was 64.3%. **Tables 1.4** and **1.5**, shows a summary of the obtained results.

**Table 1.4.** Core flooding 1 experiment results.

| **Core flooding** | **1** |
|---|---|
| Heavy Oil type | HO 1 |
| Nanoparticles [wt%] | 5.0 |
| Sandstone type | BB (I) |
| Oil Recovered WF [ $cm^3$] | 3.9 |
| ***RF after WF [%]*** | ***32.0*** |
| Oil Recovered NF [ $cm^3$] | 4.0 |
| ***RF after NDF [%]*** | ***32.3*** |
| **Final RF [%]** | **64.3** |

**Table 1.5.** Recovery factors and injection pressures at each injection rate of NDF, CF1

| **Injection Rate (ft/d)** | **Recovery Factor (%)** | **PV Injected** | **Pressure (psi)** | **o/w Emulsions** |
|---|---|---|---|---|
| 1 | 0.0 | 0.25 | 37.0 | no |
| 10 | 0.0 | 1.5 | 91.0 | no |
| 100 | 4.0 | 4.0 | 210.0 | yes |
| 200 | 8.1 | 4.0 | 2,100.0 | yes |
| 300 | 20.2 | 6.0 | 2,700.0 | yes |
| | **32.3** | **15.8** | | |

## Core flooding 2: heavy oil 1 - bentheimer sandstone (I)

The core flooding 2 was performed with a Bentheimer sandstone core saturated with heavy oil 1. Absolute permeability of this core was 2,340 mD, porosity of 24.2% and an OOIP of 15.4 $cm^3$. After injecting 2.0 PV of brine the water cut was 100% and the recovery factor was 24.1 % of the OOIP.

During the nanoparticle flooding, there was not emulsion generation; however, additional single phase oil was produced. The additional recovered oil was 39% of the OOIP with a final recovery of 63% of the OOIP. **Tables 1.6** and **1.7** summarizes the results of the CF2.

**Table 1.6.** Core flooding 2 experiment results.

| **Core flooding** | **2** |
|---|---|
| Heavy oil type | **HO 1** |
| Nanoparticles [wt%] | 5.0 |
| Sandstone type | **BT (I)** |
| Oil Recovered WF [ $cm^3$] | 3.7 |
| ***RF after WF [%]*** | ***24.1*** |
| Oil Recovered NF [ $cm^3$] | 6.0 |
| ***RF after NDF [%]*** | ***39.0*** |
| **Final RF [%]** | **63.1** |

**Table 1.7.** Recovery factors and injection pressures at each injection rate of NDF, CF2.

| Injection Rate (ft/d) | Recovery Factor (%) | PV Injected | Pressure (psi) | o/w Emulsions |
|---|---|---|---|---|
| 1 | 0.0 | 0.25 | 1.0 | no |
| 10 | 0.0 | 0.75 | 3.2 | no |
| 300 | 7.8 | 4.2 | 9.5 | no |
| 400 | 14.3 | 5.5 | 10.4 | no |
| 500 | 16.9 | 7.0 | 12.6 | no |
| | **39.0** | **17.7** | | |

## Core flooding 3: heavy oil 2 - buff berea sandstone (II)

The core flooding 3 was carried out with a buff berea sandstone core saturated with heavy oil 2. The brine permeability of this core was 152 mD with a porosity of 21.6% and an OOIP of 12.4 $cm^3$. This experiment was the most difficult to complete since high permeability and high viscosity complicate the oil saturation and flooding processes. Throughout the waterflooding stage, the injection pressure was in the range of 2,000 psi range, reaching peaks of 3,500 psi, which is over the pressure limit of the core holder. Waterflooding was performed at an injection rate of 1 ft/d; oil production was not observed after 2.5 PV of injected brine. The recovery factor after waterflooding and ND flooding was 47.5% of the OOIP. **Tables 1.8** and **1.9** summarize the results of this experiment.

**Table 1.8.** Core flooding 3 experiment results.

| **Core flooding** | **3** |
|---|---|
| Heavy oil type | **HO2** |
| Nanoparticles [wt%] | 5.0 |
| NaCl [wt%] | 0.5 |
| Sandstone type | **BB (II)** |
| Oil Recovered WF [ $cm^3$] | 3.4 |
| ***RF after WF [%]*** | ***27.3*** |
| Oil Recovered NF [ $cm^3$] | 2.5 |
| ***RF after NDF [%]*** | ***20.2*** |
| **Final RF [%]** | **47.5** |

**Table 1.9.** Recovery factors and injection pressures at each injection rate of ND, CF3.

| Injection Rate (ft/d) | Recovery Factor (%) | PV Injected | Pressure (psi) | o/w Emulsions |
|---|---|---|---|---|
| 1 | 3.4 | 0.27 | 2,065 | yes |
| 5 | 5.6 | 0.59 | 2,900 | yes |
| 10 | 11.2 | 0.9 | 3,500 | yes |
| | **20.2** | **1.8** | | |

## Core flooding 4: heavy oil 2 - bentheimer sandstone (II)

Core flooding 4 was carried out with a Bentheimer sandstone core saturated with heavy oil 2. Absolute permeability of this core was 2,015 mD with 24.1% porosity and an OOIP of 15.6 cm3. The waterflooding stage was completed with a brine injection rate of 1 ft/d obtaining a recovery factor of 23% of the OOIP. **Tables 1.10** and **1.11** give a summary of the results from CF4.

**Table 1.10.** Core flooding 4 experiment results.

| Core flooding | 4 |
|---|---|
| Heavy oil type | **HO 2** |
| Nanoparticles [wt%] | 5.0 |
| NaCl [wt%] | 0.5 |
| Sandstone type | **BT (II)** |
| Oil Recovered WF [ $cm^3$] | 4 |
| ***RF after WF [%]*** | ***23*** |
| Oil Recovered NF [ $cm^3$] | 10 |
| ***RF after NDF [%]*** | ***64.1*** |
| **Final RF [%]** | **87.4** |

**Table 1.11.** Recovery factors and injection pressures at each injection rate of ND, CF4.

| Injection rate (ft/d) | Recovery factor (%) | PV injected | Pressure (psi) | o/w Emulsions |
|---|---|---|---|---|
| 1 | 0.0 | 2.2 | 1.0 | no |
| 50 | 3.2 | 2.2 | 5.3 | no |
| 100 | 9.6 | 2.2 | 7.5 | no |
| 200 | 9.6 | 2.2 | 9.5 | no |
| 300 | 12.8 | 2.2 | 10.5 | no |
| 400 | 28.8 | 2.2 | 11.0 | no |
| | **64.1** | **13.2** | | |

## Core flooding 5: heavy oil 1 - buff berea (III)

The core flooding 5 was carried out with a buff berea sandstone core saturated with heavy oil 2. Absolute permeability of this core was 271 mD, with 21.1% porosity and an OOIP of 12.4 cm3. During the waterflooding stage, brine was injected at 1 ft/d. Oil recovery after waterflooding was 31.7% of the OOIP. **Tables 1.12** and **1.13** summarize the results of this experiment.

**Table 1.12.** Core flooding 5 experiment results.

| Core flooding | 5 |
|---|---|
| Heavy oil type | **HO 1** |
| Nanoparticles [wt%] | 2.0 |
| NaCl [wt%] | 0.5 |
| Sandstone type | **BB (III)** |
| Oil Recovered WF [ $cm^3$] | 3.9 |
| ***RF after WF [%]*** | ***31.7*** |
| Oil Recovered NF [ $cm^3$] | 2.0 |
| ***RF after NDF [%]*** | ***16.2*** |
| **Final RF [%]** | **47.9** |

**Table 1.13.** Recovery factors and injection pressures at each injection rate, CF5

| Injection Rate (ft/d) | Recovery Factor (%) | PV Injected | Pressure (psi) | o/w Emulsions |
|---|---|---|---|---|
| 1 | 0.0 | 0.3 | 34 | no |
| 10 | 0.0 | 1.7 | 72 | no |
| 100 | 4.0 | 4.2 | 185 | yes |
| 200 | 4.0 | 4.2 | 1,908 | yes |
| 300 | 8.1 | 6.3 | 2,455 | yes |
| | **16.2** | **16.6** | | |

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## Core flooding 6: heavy oil 1 - bentheimer (III)

Core flooding 6 was carried out using a bentheimer sandstone core saturated with heavy oil 1. Absolute permeability of this core was 2,027 md with 24.1% porosity and an OOIP of 14.9 cm3. During the waterflooding stage, 25.2% of the OOIP was recovered. Results of the CF6 are shown in the **Tables 1.14** and **1.15**.

**Table 1.14.** Core flooding 6 experiment results.

| Core flooding | 6 |
|---|---|
| Heavy oil type | **HO 1** |
| Nanoparticles [wt%] | 2.0 |
| NaCl [wt%] | 0.5 |
| Sandstone type | **BT (III)** |
| Oil Recovered WF [ $cm^3$] | 3.8 |
| ***RF after WF [%]*** | ***25.2*** |
| Oil Recovered NF [ $cm^3$] | 3.5 |
| ***RF after NDF [%]*** | ***23.5*** |
| **Final RF [%]** | **48.7** |

**Table 1.15.** Recovery factors and injection pressures at each injection rate, CF6.

| Injection Rate (ft/d) | Recovery Factor (%) | PV Injected | Pressure (psi) | o/w Emulsions |
|---|---|---|---|---|
| 1 | 0.0 | 0.2 | 2.0 | no |
| 10 | 0.0 | 1.5 | 5.0 | no |
| 100 | 3.4 | 3.9 | 9.8 | no |
| 200 | 6.7 | 3.9 | 10.9 | no |
| 300 | 13.4 | 5.8 | 11.4 | no |
| | **23.5** | **15.3** | | |

## Conclusions

Based on results from bulk emulsion generation and core flooding experiments, the following is concluded:

- Stable heavy-oil-in-water emulsions can be created by mixing a silica nanoparticle dispersion and heavy oil applying adequate shear rate through mechanical means. Microscopic images and observed volumes in a graduated cylinder indicated relative amount of emulsion present.
- Emulsion generation was directly affected by nanoparticle concentration, NaCl concentration, and the type of heavy oil.
- Dispersion of 5.0 wt% nanoparticles generated the largest amount of emulsions. The amount of emulsions was proportional to the nanoparticle concentration over the attempted range of 0.5 – 5.0% wt% nanoparticle.
- Adding sodium chloride to the nanoparticle dispersions had a positive effect in the emulsion generations.
- Pendant drop experiments demonstrated a reduction in IFT as the nanoparticle and NaCl concentrations increased. We conclude that reduction of IFT assisted with the creation of emulsions.
- Core flooding experiments (5.0 wt% nanoparticles /0.5 wt% NaCl) carried out with the buff berea sandstone core, produced additional oil, both as o/w emulsions and free crude oil. However, high injection pressures were observed as a result of the low rock permeability; additionally, high injection rates were required for incremental oil production. CF1, CF3 and CF4, recovered 32.3%, 20.2% and 24.2% respectively of the OOIP, additionally to waterflooding (using the nanoparticle solution).
- Core flooding experiments conducted with the b bentheimer sandstone core, produced additional oil; however, there was no observable (produced) emulsion in these corefloods. It is possible that unstable emulsions were formed but broke before exiting the core. Or incremental oil production was due to IFT reduction without the necessity for emulsion formation. Nanoparticle dispersion flooding recovered 39%, 64.1% and 30.2% of the OOIP in the experiments CF 2, CF 4 and CF 6 respectively.

- The rock permeability was the most important parameter in stable in situ emulsion generation. Effluents showed that emulsions were generated in the lower permeability cores as a result of higher shear rates.

- Although emulsions were not generated in high permeability cores, the nanoparticle dispersion reduced the IFT, mobilizing the crude oil out of the core.

## Future work and recommendations

- Optimize emulsification of heavy oil by nanoparticles at lower shear than was attained in this work in order to provide a system suitable for a field pilot.

  ❖ Investigate effects of heavy oil composition (saturates, aromatics, resins, asphaltenes and total acid number) on emulsification using these types of nanoparticles.

  ❖ Investigate changes in nanoparticle surface properties (vary degree of hydrophilic modification) on emulsification of heavy oils of various compositions.

  ❖ Conduct more core flooding experiments with different types of rock and permeabilities in order to determine the limits where the emulsions may be generated.

- Due to the great amount of water necessary to obtain additional oil, analysis of the effluent dispersions are required to evaluate that their properties remain constant. If the properties do not change the dispersions may be recycled.

- Emulsion breakers must be tested in order to find the one(s) which optimizes breaking of produced emulsions.

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