ENHANCED HEAVY OIL RECOVERY BY EMULSIFICATION WITH INJECTED NANOPARTICLES

A Thesis

by

ARTURO REY MARTINEZ CEDILLO

Submitted to the Office of Graduate and Professional Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Chair of Committee,	Robert H. Lane
Committee Members,	Maria A. Barrufet
	Yuefeng Sun
Head of Department,	Daniel Hill

December 2013

Major Subject: Petroleum Engineering

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. Furthermore, complex injection facilities are not required, which reduces operational costs.

In this research, 12 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 between heavy oil and nanoparticle dispersions, microscopy analysis to determine the amount of emulsion generated, and emulsion viscosity measurements. Results obtained from these experiments indicated that the nanoparticles lead to a reduction of the interfacial tension of the heavy oil and the dispersion. In addition, the presence of Sodium Chloride in the dispersion reduced still more of that interfacial tension, generating the largest amount of emulsions.

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 ranged from 20% to 64 % of OOIP were obtained. 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.

DEDICATION

This thesis is dedicated to my wife, Mirsha Blanco for all the love and support she has provided me since I met her.

ACKNOWLEDGEMENTS

I would like to thank my committee chair, Dr. Robert Lane for his teachings and supervision, and my committee members, Dr. Maria Barrufet and Dr. Yuefeng Sun for their guidance and support throughout the course of this research.

I would like to thank the Petroleum Engineering Department at Texas A&M University for giving me the opportunity to achieve this goal. Thanks also go to my colleagues, faculty and staff for making my time at Texas A&M University a great experience.

I would also like to thank my friends Raul Gonzales, Andres Del Busto, Francisco Tovar, Johannes Alvarez, Juan Lacayo, Gorgonio Fuentes and Jose Moreno for their valuable assistance and their useful advices.

Finally, thanks to my mother Isabel and my brother Guillermo for their encouragement, patience and love.

TABLE OF CONTENTS

Page

LIST OF FIGURES

Page

Page

LIST OF TABLES

I. 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. Moreover, they can be found in every continent, with Canada and Venezuela being the countries with the largest accumulation of them.

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 displace 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.

1.1 Significance of the non-thermal EOR process for the heavy oil reservoir exploitation

The EOR processes are commonly used techniques in the oil industry to extract remaining hydrocarbons in the reservoir after they have been exploited through primary recovery methods, that is, using only the reservoir's own energy or with any artificial lift system. EOR processes are classified in four main categories according to their action mechanism: waterflooding, chemical methods, miscible methods and thermal methods. Based on the reservoir's characteristics, i.e. type of hydrocarbons, depth and thickness, and reservoir's conditions, i.e. temperature, and pressure, EOR processes may be applied not only to maintain or restore the reservoir pressure but they also improve the volumetric sweep, and the oil displacement efficiency.

Unlike conventional reservoirs, some of the heavy oil reservoirs require EOR processes early in the development stages of the field because they have special features such as high viscosity/density, which makes them difficult and at times unviable for exploitation with primary recovery methods. Different sorts of EOR processes have been tested in heavy oil reservoirs; however, thermal methods have shown to outperform all the other methods since their main goal is to reduce the oil in-situ viscosity in order to improve oil displacement efficiency.

Unfortunately, there are some limitations in the application of thermal methods, i.e. the steam based methods such as steam flood, steam assisted gravity drainage (SAGD) and cyclic steam stimulation (CSS) are more effective in shallow and thick reservoirs to avoid heat loss in the wellbore and in adjacent formations respectively. Also, if the weather conditions are adverse, as in the North Slope or Alaska, it may reduce the heat efficiency. Moreover, steam generation requires great amounts of energy which increases the cost of the incremental barrel.

In response to thermal processes limitations, non-thermal processes have gained importance to recover heavy oil. Waterflooding projects have been carried out for more than 50 years in Canada(Miller 2005). Nevertheless, the results have not been favorable due to the difference in viscosities from the injected water and the formation's heavy oil. This yields unfavorable mobility-ratios, leading to low recovery factors (Mai and Kantzas 2009).

As technology, research and development advance, different solutions to improve poor mobility ratios have been tested. Increasing the viscosity of the water injected using polymers has shown positive results when it is applied in modest viscosity reservoirs, less than 100 cP (Fu et al. 2012). However, for more viscous oil, high concentration of polymer is required that makes difficult their injection and increases the costs of the process.

Alkali-Surfactant (AS) and Alkali-Surfactant-Polymer (ASP) flooding have also been tested in heavy oil reservoir. Surfactants reduce the interfacial tension between the injected fluid and the oil. Alkali is used to create in-situ surfactants when it reacts with acidic oil (Fu et al. 2012). Hence, if the interfacial tension is reduced, oil and water may be easily emulsified. Emulsions both water-in-oil (w/o) and oil-in-water (o/w) improve oil recovery because they modify the fluid's viscosity, and also improve the mobility ratio and plugging off high permeability channels (Mai et al. 2009).

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).

1.2 Status of the solid-stabilized emulsions for EOR processes

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.

1.2.1 Emulsions as a drive fluid for EOR processes

Application of o/w and w/o emulsion for EOR processes have not been extensively studied thus far; nonetheless, there are some projects related to emulsions flooding in order to both displace the oil in-situ, and reduce the water channeling in heterogeneous reservoirs.

McAuliffe (1973) described a field test where an emulsion injection was carried out to reduce water fingering in a waterflood project. The project consisted of injecting a "surface-prepared o/w emulsion" into the Midway-Sunset oil field. The emulsion was prepared using 70% of produce oil and 30% of fresh water with a minimum volume of sodium hydroxide as a stabilizer. Despite the fact that the emulsions were thermodynamically unstable due to the lack of a better stabilizer, the results showed that emulsions plugged high permeability zones increasing oil recovery and reducing water oil ratios.

The elaboration of o/w and w/o emulsions can also be made mixing used engine oil, and brine without any additional chemical emulsifiers as demonstrated by Fu and Mamora (2010). They stated this idea based on easy accessibility of the used engine oil, besides proposing a disposal alternative of it. They achieved the stabilization of the emulsion with the engine oil soot particles, surfactant additives already in the engine oil and by oil oxidation that created additional surfactants. The major constraint of this method is that the used engine oil will not always have a unique composition, which in turn makes each emulsion different. Therefore, it would be impossible to have a standard procedure to create the same emulsion each time. Additionally the emulsification process must be carried out at the surface, which greatly increases injection pressure of the drive fluid.

1.2.2 Solid stabilized emulsions flooding

The first attempt to apply solid-stabilized emulsions as an EOR method was developed by Bragg (1999). The emulsions were created mixing crude oil with brine and then they were stabilized with solid particles such as natural clays (kaolinite and bentonite) or treated fumed silica. The average particle size ranged from 1 to 2 microns. The emulsions were injected into a core saturated with heavy oil of 325 cP and a temperature of 140 °F. As a result, it was observed that after 1 pore volume of injected emulsions, the oil recovery was 2.1 to 3.8 times greater than the recovery reached by waterflooding. Furthermore, the emulsions were stable and showed a favorable mobility control. Although solid stabilized emulsions provided positives results, Bragg suggested that smaller particles would increase the emulsion stability.

1.2.3 Nanoparticle-stabilized emulsion flooding

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).

Zhang, T. et al. (2010) from The University of Texas at Austin tested the ability of applying w/o and o/w nanoparticle-stabilized emulsions in EOR processes. The emulsions were elaborated using decane, brine and two different types of silica nanoparticles, hydrophilic and hydrophobic. In order to create o/w emulsions, the hydrophobic nanoparticles were mixed with the decane and the brine. On the other hand, w/o emulsions were created with the hydrophobic nanoparticles. This study concluded that the nanoparticles provide high emulsion stabilization, up to several months, and they may be used to improve the mobility ratio in an emulsion flooding project.

In 2002 a pilot test was implemented by Exxon Mobil in the Celtic oil field in Canada where a nanoparticle-stabilized w/o emulsion was injected into a sandstone reservoir (Kaminsky et al. 2010). The emulsion was created at the on-site facilities mixing 60 vol% of formation water, 36 vol% of crude oil, 4 vol% of propane and less than 2 grams of oleophilic fumed silica nanoparticles per liter of emulsion. The injection layout was built with a central producing well, four injection wells and three observation wells. Three years into the project, it was concluded that the emulsion flooding was considerably stable and that it was able to flow through the porous media improving the heavy oil recovery.

1.2.4 Heavy o/w emulsion for pipeline transportation

Pipeline transportation of heavy oil is a significant issue that several authors have considered; the high density/viscosity and the high contents of asphaltene and paraffin leads to pipe obstruction and high pressure drops (Martínez-Palou et al. 2011)). Water external emulsions offer an optimistic solution because they have a lower viscosity, reducing pipe friction, and therefore needing less boost energy (Ashrafizadeh and

Kamran 2010). A successful example of transportation of o/w emulsions is the Orimulsion. It was a product conceived and patented by Bitumenes Orinoco S.A. (BITOR) in Venezuela in order to transport the bitumen produced in the Oricono Belt more efficiently. Additionally, it was used as a fuel for electric power plants substituting mineral coal (Gómez-Bueno et al. 1998). Unfortunately, the high level of pollutants generated by its combustion has made it unattractive to the industry (Oppelt 2001).

1.3 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.

1.4 Overview of methodology

The methodology followed in this research has the aim to investigate the potential of hydrophilic nanoparticles to generate heavy o/w emulsions in order to develop a new enhanced heavy oil recovery method.

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.

II. HEAVY OIL:

A VAST SOURCE OF ENERGY FOR THE FUTURE

2.1 Importance of heavy oil due to the natural depletion of conventional oil

Currently the rapid population growth demands for higher consumptions of energy, principally of hydrocarbons. This situation associated with the natural depletion of conventional oil production creates an unfavorable gap between oil produced and oil required for the future. Because of this, the oil industry needs to move beyond the development of conventional resources and produce hydrocarbons from unconventional ones. Because heavy oil represents more than two-thirds of the world total resources (Alboudwarej et al. 2006), this gap may be rapidly reduced by mastering heavy oil recovery processes.

2.1.1 Definition of heavy oil

Heavy oil is an unconventional resource that is mainly characterized by its high viscosity and high density when compared to conventional oil. High viscosity and high density arise from the loss of most of the lighter hydrocarbons, leaving behind high contents of asphaltenes, nitrogen, oxygen, sulphur and heavy metals (Attanasi and Meyer 2010).

2.1.2 Classification of heavy oil

Literature does not present a formal classification of heavy oil; however, there are some classifications accepted throughout the oil industry. The API classification is probably the most commonly used. API gravity is defined as the measurement of the relative density of oil when compared to water. API gravity is related to the specific gravity of the oil through the Eq. 1.

$$P \qquad \frac{\cdot}{\cdot \quad \cdot} - \quad . \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(1)}$$

According to the API gravity definition, heavy oil has less than 22.3° API gravity **(Table 2.1)**. Despite providing a fair distinction among all types of crude oils, the API gravity classification might not be optimal when used only to classify heavy oil. Its application is limited since it does not consider the viscosity, a property that affects the most heavy oil recovery and its transportation processes.

Table 2.1—Classification of crude oil according to API gravity.

Type of crude oil	**API gravity °API**
Light	> 31.1
Medium	22.3 - 31.1
Heavy	< 22.3

Another classification is given by the World Petroleum Congress where viscosity is the principal discriminator, and it serves to categorize heavy oil into heavy and extra-heavy or bitumen **(Table 2.2)**.

Table 2.2—Classification of crude oil according to the World Petroleum Congress

	API gravity °API	**Viscosity cP**
Heavy Oil	22 - 10	100 - 10,000
Extra heavy oil / Bitumen	< 10	> 10,000

2.1.3 Degradation of crude oil to origin heavy oil

Different explanations have been proposed about the origins of heavy oil. However, biodegradation seems to be the most widely accepted (Head et al. 2003). In order to have a biodegradation process, light and medium oil must have been generated and expelled from the source rock. Light and medium oil start a migration process away from the source rock. Some hydrocarbons may travel updip for long distances, in the order of the hundreds of miles, until they are trapped in shallow and cool reservoirs. These reservoirs may have contact with meteoric water creating conditions for biological activity (biodegradation). Biodegradation involves processes that oxidize the oil that directly affects the composition and the physical properties of oil. Biodegradation might decrease the density and increase the sulphur, acidity, viscosity and metal content (Head et al. 2003). Degradation of crude oil may also be caused by physical processes such as water washing or phase fractionation (Alboudwarej et al. 2006).

2.1.4 Estimation of global resources

Unlike conventional crude oil, heavy oil does not flow as easily, and it is necessary to use special equipment or sophisticated recovery methods to extract it. This increases both the production and refining costs and due to its high density and high viscosity its economic value is also depreciated. Nonetheless, despite these undesirable conditions, heavy oil has a great importance for the energy future because the estimated volumes are vast. The IEA estimates the amount of heavy oil to be between 9 and 13 Tbbl of oil in place worldwide. This represents more than two-thirds of the conventional resources (Alboudwarej et al. 2006) **(Fig. 2.1)**. The Western Canada Basin in Alberta with 2.5 Tbbl and the Orinoco Belt in Venezuela with 1.5 Tbbl are considered the largest deposits in the world. In addition, significant accumulations of heavy oil have been reported in other countries such as: the United States, Russia and Mexico.

Despite the fact that heavy oil resources are very vast, the current reserves are still lower than conventional oil reserves. Conventional oil reserves amount tos 2.25 Tbbl while heavy oil ones are estimated around 1.88 Tbbl (IEA-WEO-2012). This particular difference is because in-place hydrocarbon volumes can only be considered as reserves if they are technically and economically recoverable under current conditions. As the industry progresses in the improvement and development of new techniques for heavy oil recovery, it will be able to reduce cost and increase production volumes. Furthermore, if favorable oil prices are present, current heavy oil resources may be reclassified as reserves.

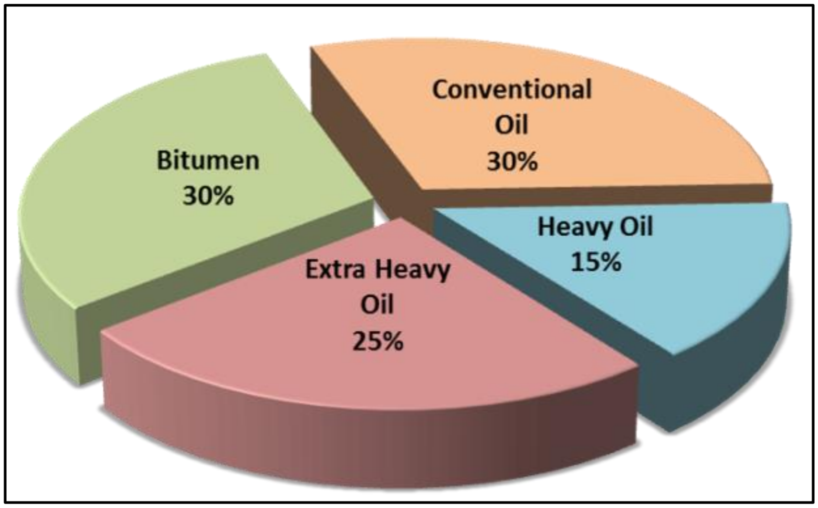

Fig. 2.1—Importance of the heavy oil lies in the great volume in-place since it represents 70% of the world total resources

2.2 Current status of the technologies of heavy oil recovery processes

Since the first discoveries of heavy oil reservoirs in the early twentieth century, the main challenge has been focused on finding the optimal techniques to exploit them at economically profitable rates that maximize their recovery factor. Throughout these years, different recovery techniques have been developed ranging from mining pits to more complex ones such as in-situ combustion. Normally, these types of deposits begin their exploitation through primary production methods up to reaching their economic limit. Thereafter, thermal methods are applied to reduce the oil viscosity and increase its mobility allowing, additional recovery that is often far above the initial one. An illustrative example is the Kern River oil field in Bakersfield, California. The Kern River oil field is a heavy oil field producing since 1899 with a primary recovery of 5-10%.

This field was subjected to a steam-flooding process in 1965 and it is estimated to achieve a final recovery of 80% (Nelder 2011).

Unfortunately, thermal methods cannot be applied to every reservoir; for example, steam flooding is more efficient if it is applied to shallow depth and thick reservoirs due to large heat losses (Falcone 2009). Other thermal methods, such as ISC, may be applied beyond these limitations but to the best of our knowledge they have not been sufficiently studied thus far.

Non-thermal EOR processes such as waterflooding, AS flooding, polymer flooding and emulsion flooding may provide an excellent alternative to overcome depth and thickness reservoirs issues. Moreover, these processes are less expensive than thermal methods, and if favorable reservoir conditions exist, (e.g. adequate porosity, permeability and a suitable oil viscosity) they may achieve high recovery factors.

Different technologies and EOR methods applicable to heavy oil have been classified in to three categories Primary, Thermal and Non-Thermal **(Fig. 2.2)**.

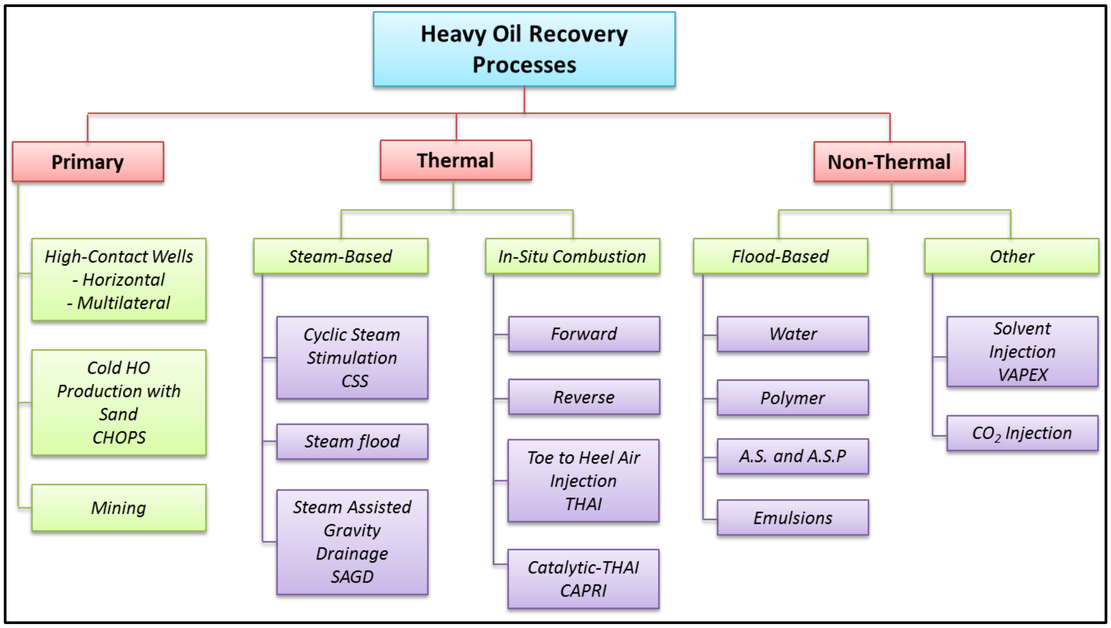

Fig. 2.2—Heavy oil recovery process may be divided in Primary, Non-Thermal and Thermal methods

2.2.1 Primary recovery methods

These methods are mainly used in very shallow (<300 ft) or surface oil accumulations such as the Canadian tar sands. These methods are also applied when heavy oil can flow by itself as in Orinoco Oil Belt in Venezuela. Primary recovery methods have low economic and technical risk and in most cases they are the first step along the oil field development project (Shah et al. 2010). They are subdivided as: open pit mining, high contact wells, and cold heavy oil production with sands (CHOPS).

Open pit mining

If the bitumen deposits are close to the surface, they can be recovered using surface mining operations. This process consists in removing all the soil over the bitumen and then excavating a pit in order to extract the hydrocarbons. Mining processes may recover up to 90% of the total bitumen in place (Clark et al. 2007). However, they are limited to maximum depths of 300 feet. Additionally, surface mining has a high environmental impact and companies are subjected to land reclamations. This process has only been used in Western Canada and Russia (Shah et al. 2010).

High contact wells: horizontal and multilateral

Horizontal and multilateral wells have been extensively used in the Orinoco heavy oil belt in Venezuela due to the oil in-situ viscosity which is sufficiently low that it can flow at reservoir temperatures. In addition, the horizontal sections and the multiple branches are drilled to maximize contact area with the reservoir, allowing the well to produce at economic rates (Fipke and Celli 2008). Progressive cavity pumping (PCP) or electric submergible pumps (ESP) are almost always utilized along with horizontal and multilateral wells to reduce the hydrostatic pressure in the wellbore and lifting the oil.

Cold heavy oil production with sand (CHOPS)

Dusseault (2002) defined CHOPS as the primary heavy oil recovery process that consists of the intentionally production of sand along with the oil from thin and shallow reservoirs. This method, combined with a progressive cavity pumping (PCP), has been widely applied in Canada and Venezuela, increasing oil production rates significantly. However, the application of CHOPS has to be carefully evaluated since the continuous sand production causes the creation of high permeability networks or wormholes that are unfavorable for future EOR operations. In addition, CHOPS has a recovery factor of 5 to

15% (Shokri and Babadagli 2012). Although, it is better than high contact wells, it is outperformed by steam-flood methods. There are also concerns associated with environmental problems due to sand disposal and possible subsidence effects that cannot be ignored.

2.2.2 Thermal enhanced heavy oil recovery methods

Thermal EOR methods have as main objective to increase the mobility of the viscous oil through the injection of heat into the reservoir, to raise the temperature, and to reduce the oil viscosity. It may be carried out by injecting either steam or air to combust the oil in-situ. The efficiency of these methods will depend on the heat losses in the wellbore and the reservoir, and the heat transfer to the oil (Shell 2012). They are subdivided as: Cyclic steam stimulation (CSS), steam flooding, steam assisted gravity drainage (SAGD), and in-situ combustion (ISC).

Cyclic steam stimulation (CSS)

Cyclic steam stimulation, also known as "huff and puff", is a single well technique that involves three stages starting by the injection of high pressure steam into the reservoir from 2 to 30 days. Then, the well is shut-in from 5 to 30 days to soak the near-wellbore reservoir allowing the heat transference from the steam to the heavy oil. Finally, the well is open to production, and the heated oil and the condensed water are produced until the oil rate becomes uneconomic. The production stage may last up to one year (Revana and Erdogan 2007). Once the cycle is completed, the process is repeated as many times as the geological features and fluid properties allow producing additional heavy oil. Recovery factors typically are in the range of 20% to 35% of OOIP (Clark et al. 2007; Shah et al. 2010).

Steam flooding (Steam drive)

Steam flooding is a multi-well pattern technique that consists in the continuous injection of steam into the reservoir to enhance recovery. The steam is used to heat up the oil to reduce its viscosity and improve its mobility. In contrast to the CSS method, this technique adds an energy drive mechanism by displacing the viscous oil towards the producing wells. Despite the heat losses from the surface facilities to the reservoir and the override effects caused by the density difference between the heavy oil and the steam, the recovery factors may be high (Matthews 1983). There are many successful projects, such as the Duri field in Indonesia and the Kern River field in California with recoveries of 70% of the OOIP.

Steam assisted gravity drainage (SAGD)

Steam assisted gravity drainage is a steam based recovery method first conceived by Dr. Roger M. Butler et al. (1981), which involves the drilling of two parallel horizontal wells separated vertically from 16 to 23 ft. from one to another with an horizontal displacement from 1,600 to 5,000 ft. long (Clark et al. 2007). The process starts with the injection of steam into the reservoir through both wells to heat and mobilize the oil between them, with the purpose of establishing communication (Butler

1994). Afterwards, steam is continuously injected by the injection well (upper). The injected steam travels upwards into the reservoir forming a steam chamber and transferring the steam's heat by convection to the heavy oil; thus, it reduces the oil's viscosity. The lesser viscous oil flows downward (gravity influence) along with the condensed water, where it is pumped out of the ground through the producer well (lower). Because of the characteristics of the process, it is suited for extra heavy oil and bitumen, as well as for high vertical permeability reservoirs. Expected recovery factors are in the order of 50% to 70% (Alboudwarej et al. 2006).

In situ combustion (ISC)

In-situ combustion (ISC), or fire flood, is a method that consists of the continuous injection of air into the reservoir to generate a combustion front where a small portion of oil is burned. The generated heat reduces the viscosity of the unburned heavy oil improving its mobility. Moreover, due to the high temperatures reached at the combustion front, a fraction of heavy oil is in-situ upgraded by cracking (Alboudwarej et al. 2006). As the combustion front moves forward to the production well, the forefront heated oil (oil bank) is driven principally by combustion-gas drive as well as water and steam drive (Sarathi 1999).

The process may be cataloged as forward in-situ combustion if the combustion front starts close to the injector well and the combustion front moves in the same direction of the injected air. If the combustion front starts close to the producer well and it moves in the opposite direction of the injected air, it is known as reverse in-situ combustion (Thomas 2008). In the reverse combustion, zones near the producer well are initially heated to lower their viscosity to facilitate the flow of the oil that is beyond this initially heated oil. However, this technique has only been tested successfully at laboratory scale (Shah et al. 2010). Forward combustion is considered as “dry” if only air is injected to maintain the combustion front, or “wet” if water is also injected along the air to better displace the oil. According to Sarathi (1999), in wet combustion less heavy oil is used as fuel. Moreover, it is more efficient since water provides better heat transport and drive mechanism.

ISC has several advantages over steam based methods, for example it does not require an energy source to generate the steam. In addition, it is not depth restrict and it can be applied either to heavy or light oil reservoirs (Sarathi 1999). Additionally, there is no heat loss from the surface to the reservoir and thermal efficiency within the reservoir is high due to the in-situ nature of the process. Recovery factors greater than 50% have been documented in the Suplacu de Barcau field, Romania and Bellevue field, Louisiana, US (Turta et al. 2007). Nevertheless, this process has not been widely implemented in the field because of the difficulty to control the combustion front, coupled with the generation of flue toxic gases and gravity segregation of the combustion front (Hincapie et al. 2011).

Toe to heel air injection (THAI) and catalytic upgrading process in situ (CAPRI)

Toe to heel air injection (THAI) is an ISC based technique. It was designed to address common problems in conventional ISC, such as control of the combustion front, gas override and air channeling. THAI is an innovative technology developed by Dr. Malcolm Greaves at the University of Bath in England and patented by PETROBANK in Canada. It combines a vertical air injector well, generally settled at the top of the reservoir, and a horizontal producer well in a line-drive close to the bottom of the reservoir (Greaves et al. 2001; Xia and Greaves 2006).

The process begins with a preheat stage where steam is injected in both the vertical well and the horizontal well ("toe") to establish communication between them. Thereafter, air is injected in a controlled manner into the formation by the vertical well to generate and propagate the combustion front throughout the horizontal well from the "toe" to the "heel" (Thomas 2008). Temperatures over 600 °C are reached in the combustion front reducing the oil viscosity and thermal oil cracking. Movable fluids flow in a stretch zone called "the mobile oil zone" (MOZ), where they are driven by gravity to the horizontal well (Xia et al. 2003).

Currently there are no commercial projects using THAI. However, laboratory studies using Canadian heavy crude oil have exhibited recovery factors greater than 80%. Furthermore, heavy oil samples have experienced increments in the order of eight API degrees with viscosity reductions from 100,000 cP to 50 cP during the ISC.

Taking advantage of the efficiency of THAI, a variation of it was developed in order to upgrade the cracked oil even more. CAPRI acts as a subsurface refinery. It consists in packing the horizontal section of the producer well with a catalyst to develop a catalytic cracking process. Results obtained in laboratory show that is possible to upgrade the produced oil from four up to six API degrees additional to the THAI process. Moreover, a considerable reduction in the amount of heavy metals and asphaltenes was observed. This process seems to be a good alternative as it enhances the benefits of THAI, while reducing refining cost as well as environmental impacts (Greaves and Xia 2001).

2.2.3 Non-thermal enhanced heavy oil recovery methods

According to the literature, non-thermal EOR methods have not been widely used to recover heavy oil, mainly because these processes do not improve the fluid flow characteristics of the oil as the thermal methods do. However, they should not be dismissed because they may be used in deep and thin formations, and they eliminate the energy requirement to generate heat, which leads to a reduction of capital costs and may lead to the economic success of a project.

Waterflooding

Waterflooding is not a common recovery technique in heavy oil reservoirs. The main problem associated to waterflooding in heavy oil is the significant difference between the heavy oil viscosity and the water-injected viscosity. Whereas heavy oil viscosity may be greater than 100 cP; injected water has a viscosity around 1 cP. This difference causes an unfavorable mobility ratio, which results in oil bypassing due to the viscous channeling through the reservoir.

Regardless of the adverse conditions to apply waterflooding in heavy oil reservoirs, some projects have been implemented in Canada (Adams 1982; Miller 2005) because waterflooding is a well understood technique and it is not as expensive as thermal methods (Mai and Kantzas 2009). Estimated ultimate recovery from 20% up to 45% can be obtained if the heavy oils have an oil gravity greater than 15° API, viscosity in the order of 100 cP and a well spacing less than 50 acres (Lu et al. 2010). However, increasing the viscosity of the injected-water is recommended to obtain a better sweep efficiency and improve recovery factors (Brook and Kantzas 1998).

Polymer flooding

Injecting water into heavy oil reservoirs may not deliver the recoveries because of the adverse mobility ratio. Nonetheless, if the water-injected viscosity is increased by adding a water-soluble polymer, (e.g. polyacrylamide or polysaccharide) mobility and sweep efficiency may be improved resulting in higher recoveries (Asghari and Nakutnyy 2008). According to Needham and Doe (1987), polymer flooding may be more effective than waterflooding due to the effects that the polymers have over fractional flow, as a result of the improvement in the mobility ratio as well as the polymer flow through unswept zones.

Polymer flooding has been more effective for medium oil than heavy oil reservoirs. However, some heavy oil reservoirs have been treated with this process with a relative level of success (Selby et al. 1989). Some limitations of this process are increased injection pressure due to the polymer solution's high viscosity as well as the degradation of the polymers in the rock with concomitant loss of viscosity/mobility of the drive fluid. Laboratory tests show high recoveries, up to 70% with a polymer concentration of 10,000 ppm in 1% of brine solution and a heavy oil of 1,000 cP (Asghari and Nakutnyy 2008).

Alkali-surfactant (AS) and alkali-surfactant-polymer (ASP) flooding

Alkali-surfactant flooding is a promising method to increase heavy oil recovery. It is based on the reduction of the interfacial tension (IFT) between heavy oil and injected water by injecting an alkali/surfactant solution into the reservoir. The reduction of the IFT allows the generation of emulsions responsible for the heavy oil recovery.

Laboratory studies have shown the in-situ creation of w/o and o/w emulsions. Since, w/o emulsions are more viscous than the original oil, the displacement front created during the flooding improves the sweep efficiency (Ali et al. 1979). Conversely, other researchers suggest that the external water phase emulsions can emulsify the heavy oil and produce it as an o/w emulsion (Bryan and Kantzas 2009). A third view involves the in-situ generation and the interaction of w/o and o/w emulsions into the reservoir. In this view, w/o emulsions provide the drive mechanism while the o/w emulsions plug off the high permeability channels reducing the viscous fingering and improving the sweep efficiency (Bryan and Kantzas 2008; Mai et al. 2009).

The ASP process adds a polymer to increase the viscosity of the AS solution to reduce the water channels and give a better mobility control (Arihara et al. 1999). Pilot tests have been performed in Daquing oil field in China. This test obtained recovery factors up to 20% of the OOIP (Shutang and Qiang 2010). This process improves the results given by alkali/surfactants; however, the high capital costs limit its commercial use.

Vapor extraction (VAPEX)

VAPEX takes the concept of SAGD but replaces the steam injection with vaporized hydrocarbon solvents (e.g. ethane, propane and butane). VAPEX reduces the heavy oil viscosity by diluting it with vaporized hydrocarbon solvents in order to increase mobility of the oil (Das 1998). As the solvent vapor is injected, it creates a vapor chamber over the horizontal injector and it is diffused and absorbed by the heavy oil. Consequently the heavy oil viscosity is reduced and upgraded by deasphalting (Upreti et al. 2007). The mobile oil drains to the horizontal producer by gravity. The process continues until it reaches the economic limit. Compared to SAGD, the VAPEX process is energy and economically efficient because it does not require a great amount of energy. This reduces a great deal of the capital and operational costs (Pourabdollah and Mokhtari 2013). The major constraint of this process is the slow diffusion of the solvent resulting in low production initial rates (Upreti et al. 2007).

Carbon Dioxide (CO_2) injection

CO_2 injection has been widely used in the U.S. as an EOR process in medium and light oil reservoirs. Due to its high miscibility with those types of oil at supercrital and liquid phase, the oil swells and its viscosity is reduced, improving the final recovery. Moreover, this process can also be seen as a potential alternative to store CO_2 produced by anthropogenic sources, such as the coal based power plants (Sohrabi et al. 2007).

Unlike medium and light oil, miscible CO_2 injection in heavy oils becomes more difficult since it requires high injection pressures to reach the minimum miscibility pressure. However, immiscible injection has been seen as a solution to this problem. CO_2 gas injection in heavy oil has been studied by several authors. They have stated that CO_2 in gas phase is highly soluble in heavy oil reducing considerably the viscosity (Emadi et al. 2011).

Despite heavy oil's viscosity reduction, CO2 injection in a gas phase by itself cannot produce commercial volumes of heavy oil. The great contrast in viscosity between fluids causes an adverse mobility ratio and therefore a poor conformance (Zhang et al. 2006). This process can be improved by alternating injection of CO_2 and a higher viscous fluid. Technologies such as water alternating gas (WAG) (Zheng and

Yang 2012), chemical alternating gas (CAG) (Zhang, Y. et al. 2010) and foam injection (Emadi et al. 2011) have shown favorable results, making these techniques potential alternatives for heavy oil recovery.

III. EXPERIMENTAL DESCRIPTION

3.1 Experimental materials

3.1.1 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.

3.1.2 Heavy crude oil

Two different heavy oils samples were used in this study. The first sample is from a Louisiana Oil field and the second is from the Kern River oil field in California. **Table 3.1** shows the available properties of each sample.

Table 3.1—Properties of the two heavy oils used in this research

Property	Louisiana Heavy Oil (LA HO)	Kern River Heavy Oil (KR HO)
Density [g/cm^3]	0.941	0.944
API Gravity [°]	18.70	18.31
Viscosity [cP] @ 72°F	600	3,500

3.1.3 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.

3.1.4 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.

3.2 Emulsion generation and properties bench test

3.2.1 Emulsification

An emulsion is generally defined as a mixture of two immiscible substances (e.g. oil and water) where one substance is dispersing in the other. The application of shear through mechanical means is usually necessary to generate an emulsion. In this study bulk emulsions were prepared to determine optimum loading of nanoparticles to minimize shear required for emulsion formation, using the following equipment and methodology.

Stirrer

A CAFRAMO model RZR50 stirrer was used to generate the emulsions. See **Fig. 3.1**. It operates by rotating a blade propeller at high speeds up to 2,000 rpm. The emulsification procedure consisted in a 150 ml beaker filled with 25 ml of nanoparticle dispersion and 25 ml of heavy oil with the stirrer's propeller fully immersed. The propeller was positioned off the center of the beaker to reduce the vortex formed by the centrifugal forces which appeared to inhibit emulsion generation. A shearing time of 10 minutes was established to generate the emulsions.

Fig. 3.1—CAFRAMO RZR50 stirrer

3.2.2 Properties measurement

Essential properties of generated emulsions such as viscosity and interfacial tension were measured. The viscosity of the emulsion is the most important property in this process since the o/w emulsions trap the viscous oil transporting it out of the rock as a lower viscosity fluid. The emulsion samples were prepared as is stated in section 3.2.1. Evaluating the reduction of the interfacial tension between heavy oil and nanoparticle dispersion is another important aspect of the emulsions generation that may impact ultimate oil recovery.

Viscosity measurements

A Brookfield DV-III Ultra Programmable Rheometer (**Fig. 3.2)** was used to measure the fluids' viscosity. Additionally, an enhanced UL adapter was attached to the rheometer to probe small amounts of fluid. The UL adapter consists of a sample chamber and a spindle. The rheometer calculates the shear stress at a given shear rate; these values are plotted in a Cartesian "xy" graph where the resulting slope is the viscosity.

Interfacial tension measurements

Interfacial tension (IFT) was measured by the pendant drop analysis using an Optical Contact Angle Measurement System OCA 15Pro (**Fig. 3.3)**. The OCA 15Pro software automatically calculates the IFT fitting the drop shape image to the Laplace-Young equation.

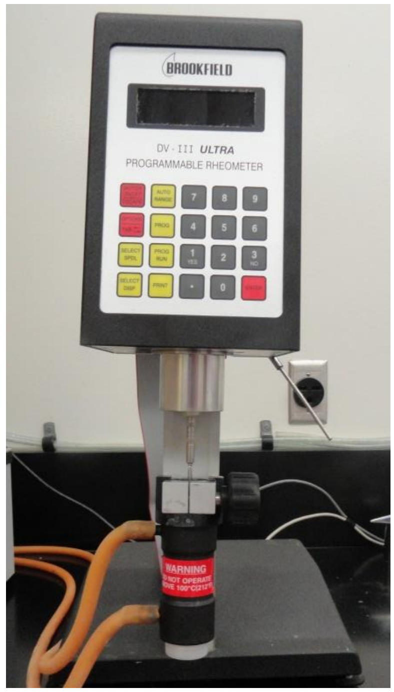

Fig. 3.2—Brookfield DV-III Ultra Programmable Rheometer

Fig. 3.3—Interfacial tension System OCA 15Pro

3.3 Core flooding system

Multiple core flooding experiments were carried out to evaluate the in-situ emulsion generation as well as prove that the nanoparticles can be used as an EOR method to recover heavy oil. The core flooding system is integrated with the following elements: a Teledyne ISCO syringe pump and a heavy oil accumulator, a core holder and a hydraulic pump to generate confinement pressure. These elements were interconnected with / 8” stainless steel tubing. See **Fig. 3.4**.

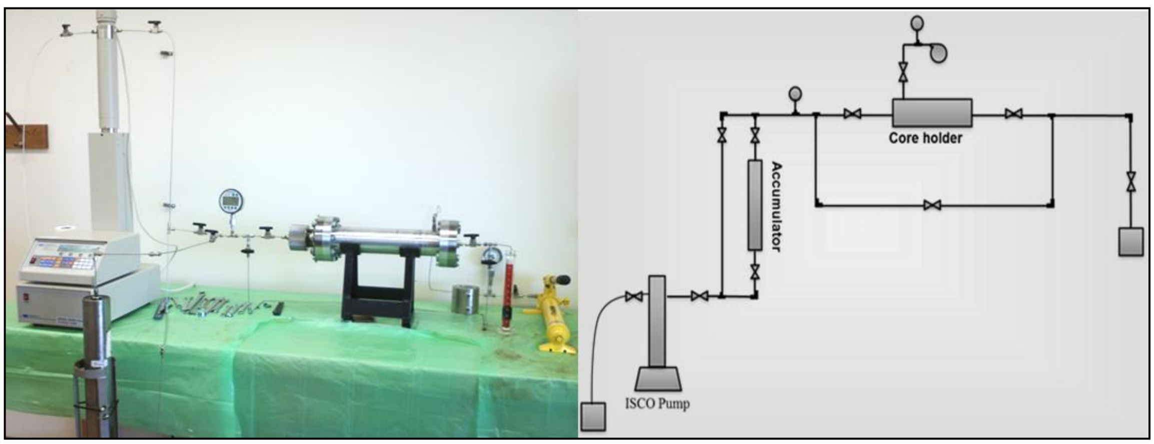

Fig. 3.4—Actual and schematic core flooding system

The Teledyne ISCO syringe pump along with the accumulator were used as the injection system. When brine or nanoparticle dispersion was injected directly into the core, the accumulator was isolated from the system through the valves. To saturate the core with heavy oil, valves were switched so that the syringe pump was connected to the accumulator inlet; the accumulator outlet fed the inlet to the core holder.

The core holder is fabricated in aluminum and it is able to support pressures up to 3,000 psi. It is designed to hold cores with a maximum length of 1 ft. and 1 in. of diameter. It is comprised of three sections: an inlet cap with an adjustable plunger, this plunger should be adjusted until it is in contact with the core, a main cell body where the core is placed, and an outlet cap with a fixed plunger. In this research, cores of 6 in. length were positioned in the core holder abutted by a series of three perforated aluminum plugs to span the core holder length. The cores and the plugs were placed in a rubber sleeve and secured at the ends by plungers. A hydraulic pump was used to fill the annulus between the rubber sleeve and the main cell body with hydraulic oil; additionally, it was also used to apply the overburden pressure over the rubber sleeve.

3.4 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.

3.4.1 Mechanical emulsion generation

To generate the emulsions, 25 ml of crude oil were placed in a 250 ml beaker in which the 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.

3.4.2 Core flood experiment procedures

In order to prove 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.

Porosity

Core porosity was calculated by measuring the bulk volume and the pore volume of the core. This was done following the steps shown below.

1. Bulk volume (V_b) was calculated assuming that the cores have cylindrical shapes and using Eq. 2. Given that core plugs are not uniform, averages of diameters and length were calculated. For the diameter, measures of ten different points were taken, and for the length five measures were taken both using an electronic Vernier Caliper.

$$V_b = \pi \, \bar{r}^2 \bar{l} \quad (2)$$

2. Pore volume (V_p) was calculated with the liquid saturation method represented in Eq. 3. Dry weight (m_{dry}) of the core plugs was measured after placing them in an oven for 24 hours to remove any liquids present in the pores. In order to obtain the

wet weight (m_{wet}) of the core plugs, they were saturated with brine and weighed. To guarantee 100% saturation, core plugs were placed in a desiccator full of brine and connected to a vacuum for 24 hours. Brine density was measured using a densimeter.

$$V_p = \frac{m_{wet} - m_{dry}}{\rho_b} \quad (3)$$

3. Finally, porosity was calculated as the bulk volume and pore volume ratio, as depicted in Eq. 4.

$$\phi = \frac{V_b}{V_p} = \frac{\frac{m_{wet} - m_{dry}}{\rho_b}}{\pi \, \bar{r}^2 \bar{l}} \quad (4)$$

Brine permeability

Permeability to various fluids (k) was calculated by applying Darcy's law, as described in Eq. 5.

$$q = \frac{kA}{\mu L} \Delta p \quad (5)$$

The permeability calculation procedure consists of the following steps:

1. Place the brine saturated core plug in the core holder, and apply a confining pressure of 1,800 psi with the manual pump.
2. Set up the syringe pump to the core holder and start the brine injection at a specific rate (q) until the steady state is reached. At this moment the pressure drop (Δp) value is registered. This step was done for several different injection rates.
3. Plot q vs Δp values and draw a trend line (**Fig. 3.5**).
4. The value of the trend line slope represents the value of the core plug permeability to brine.

Irreducible water saturation (Sw_{irr}) and initial oil saturation (So_i)

Before starting the secondary and tertiary recovery test; the core plugs must be prepared to the initial conditions of oil and irreducible water saturations. To obtain these values the next procedure was followed:

1. Once the core plug is 100% saturated with brine and installed in the core holder; the syringe pump is connected to the oil accumulator inlet, which is also connected to the core holder *via* its outlet.
2. Crude oil injection starts at a rate equivalent of a Darcy velocity of 1 ft/d.
3. Keep the injection rate until the water production ends.
4. Initial oil and irreducible water saturations are calculated with material balance.

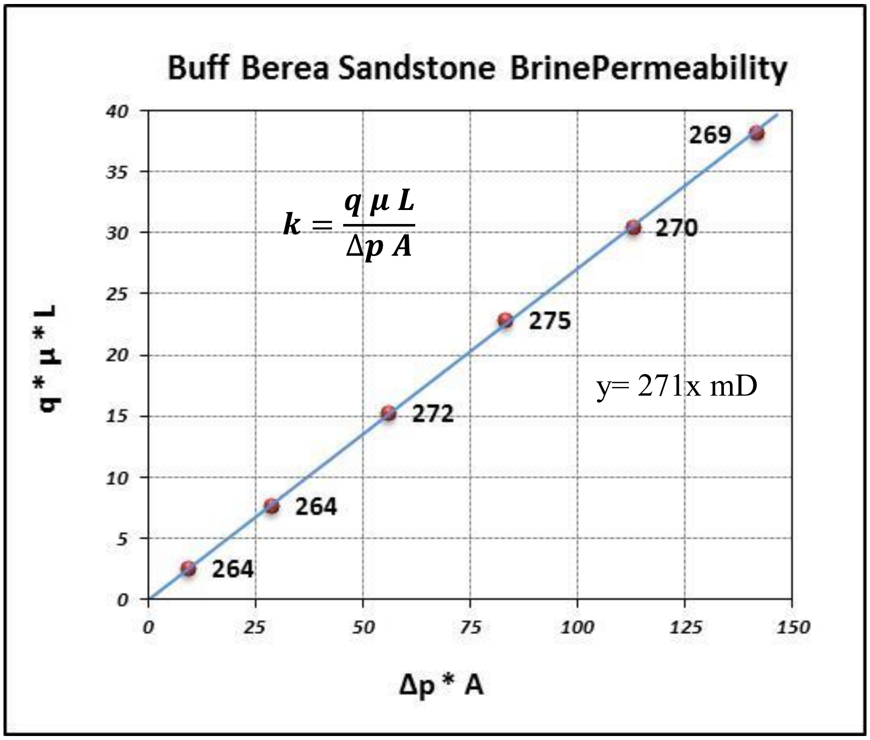

Fig. 3.5—Core permeability to brine was measure at different injection rates and its corresponding pressure drop.

Waterflooding (Secondary recovery)

Once the core plug has been saturated with heavy oil until the irreducible water saturation is reached the secondary recovery process is started. A brine of 5,000 ppm NaCl is used as the displacement fluid. The waterflooding process was completed following the next steps:

1. Place the brine directly in the syringe pump and connect it to the core holder.
2. Start the brine injection at a rate equivalent of a Darcy velocity of 1 ft/d.
3. The brine is injected until the water cut is 100%.
4. The heavy oil recovery is calculated using a material balance.

Nanoparticle dispersion flooding (EOR-Tertiary recovery)

In order to achieve the research objectives; an EOR process was performed after the waterflooding process. The EOR consists of the injection of a hydrophilic nanoparticles dispersion, which function is to emulsify the residual heavy oil and to facilitate its extraction from the core plug. The next steps describe the procedure followed in this stage:

1. Place the nanoparticle dispersion in the syringe pump and connect it to the core holder.
2. Start the nanoparticle injection with a low injection rate and increment it until a rate where emulsions generation is reached. Injection rates equivalent of a Darcy velocity from 1 to 500 ft/d were set.
3. The nanoparticle dispersion is injected until the heavy oil or emulsion production is zero.
4. Collect the produced fluids in a vial that has a tightly-closeable lid, and place them in an oven for 24 hours at a temperature of 85° C to break the emulsion and measure the oil volume.

IV. 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.

4.1 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 two types of heavy oil, described in the previous chapter, 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 4.1**). Base line samples containing no nanoparticles and no or 0.5% NaCl solution were also evaluated.

Table 4.1— 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 Louisiana heavy oil 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 (**Fig. 4.1**).

Kern River heavy oil 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 (**Fig. 4.2**).

Fig. 4.1—Samples of emulsions generated using deionized water and brine with Louisiana heavy oil

Fig. 4.2—Sample of emulsions generated using deionized water and brine with Kern River heavy oil

4.1.1 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. The pendant drop 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 (**Fig. 4.3**). IFT was reduced when the nanoparticle and brine concentration were incremented.

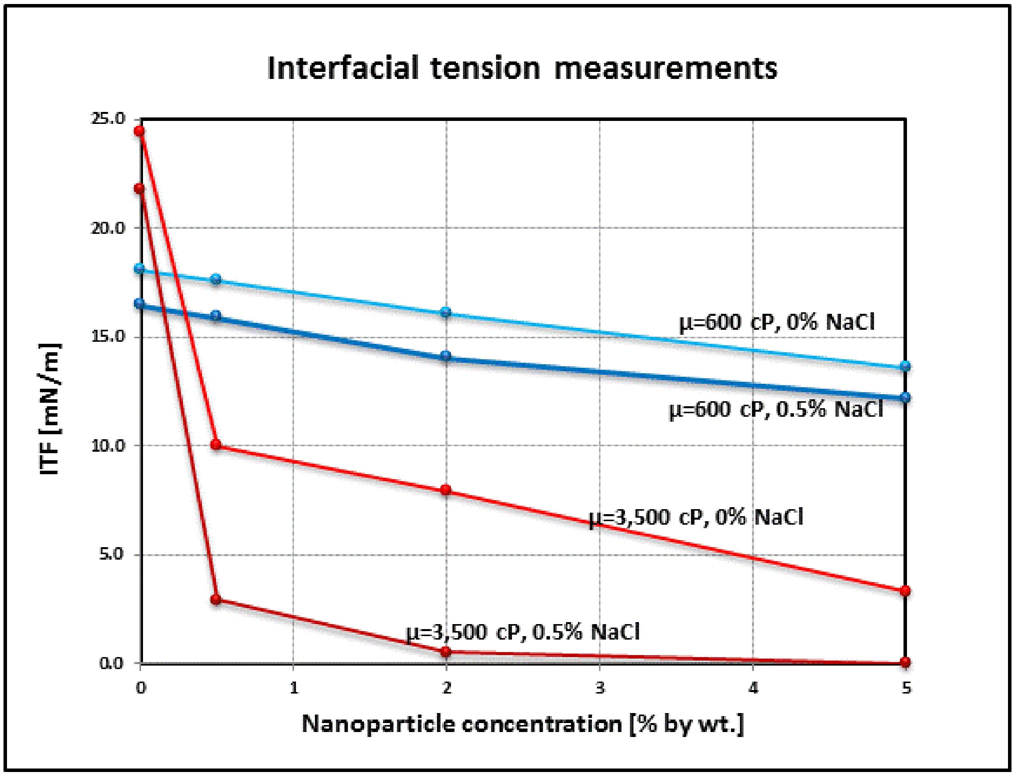

Fig. 4.3—IFT measurements show the reduction of IFT when the nanoparticle and salt concentration is increased

The different concentration of nanoparticles changed the shape of the oil drop from a rounded-like drop to and rope-like drop (**Fig. 4.4** and **Fig. 4.5**). 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 Kern River heavy oil) 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. n fact it is clear that the Kern River oil's FT is much more sensitive to increasing nanoparticle and brine loading than is the Louisiana oil at all additive loadings. In contrast, in deionized water the Kern River oil exhibited the higher IFT.

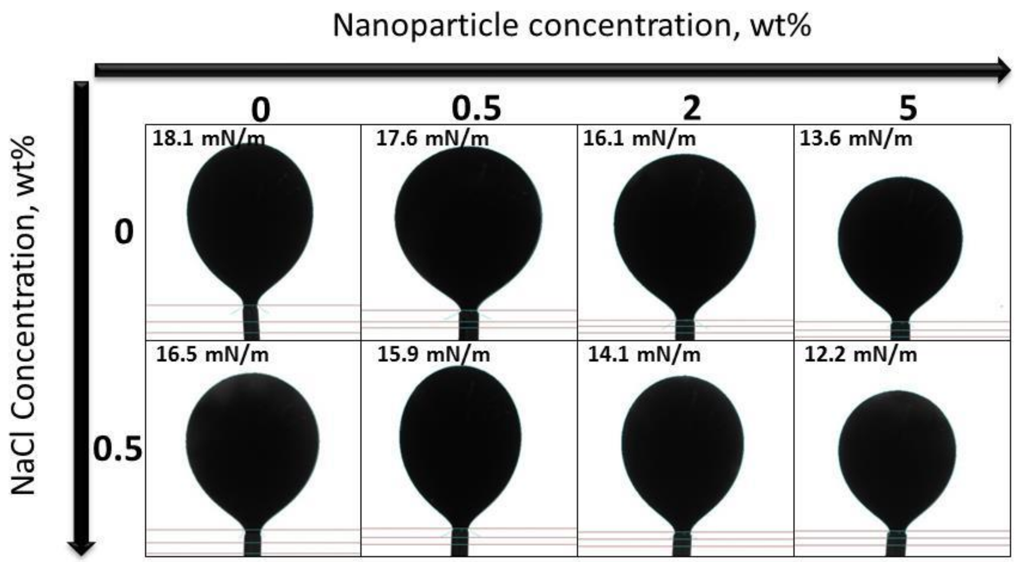

Fig. 4.4—IFT between Louisiana heavy oil and the nanoparticle dispersions. A reduction in the IFT is observed according to the nanoparticle and NaCl concentration are increased

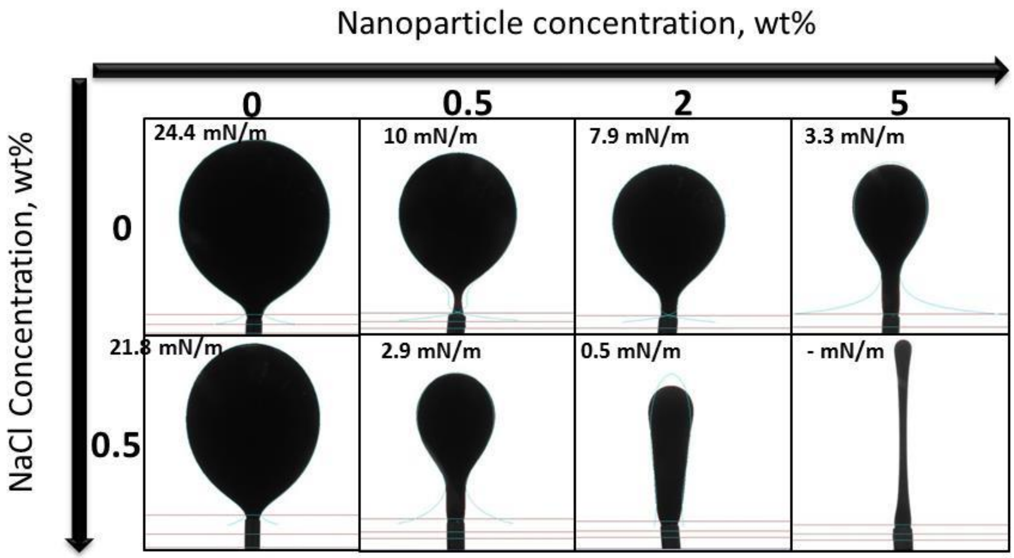

Fig. 4.5—IFT between Kern River heavy oil and the nanoparticle dispersions. IFT was not measured in the final experiment since the oil drop was not formed

4.1.2 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 (**Fig. 4.6** and **Fig. 4.7**).

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 Louisiana heavy oil did not form as many emulsion as the emulsions made with the Kern River heavy oil.

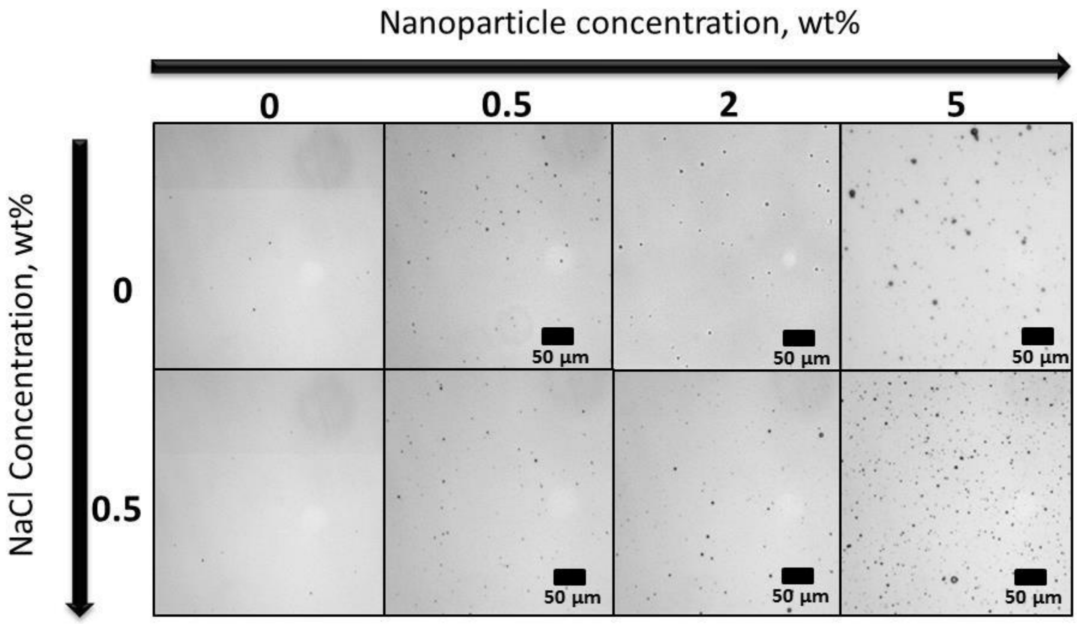

Fig. 4.6—Microscopic images of emulsions made with Louisiana heavy oil and the nanoparticle dispersions

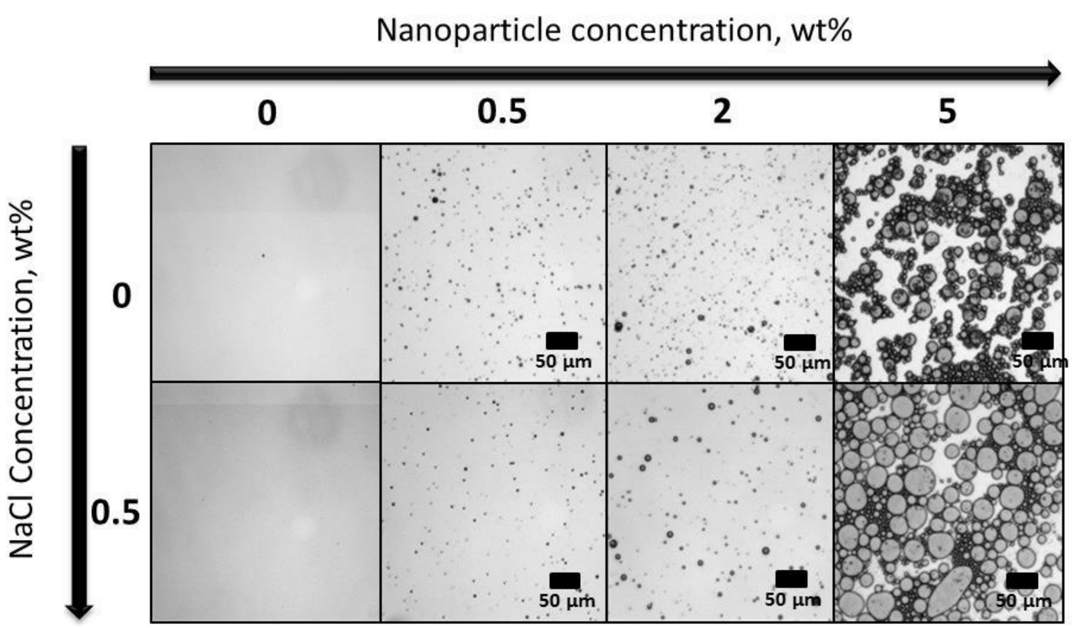

Fig. 4.7—Microscopic images of emulsions made with Kern River heavy oil and the nanoparticle dispersions

4.1.3 Emulsion rheology measurements

The rheology study of the emulsions plays an important role in this research. Since the o/w emulsions are characterized by their water external phase, emulsion viscosity should be close to that of water, at least for modest oil loadings in the emulsion. Measurements can be done to estimate the emulsion's viscosity and relate it to water's to assess the emulsions.

Results obtained from the rheometer show that, the emulsions created as it is described in section 3.2.1, have a shear-thickening (dilatant) behavior. This indicates that the apparent viscosity increases as the shear rate also increases. This behavior follows a power law model (Eq. 6).

$$\mu_a = K\,\dot{\gamma}^{n-1} \quad (4)$$

Where μ_a is the apparent viscosity of the fluid [SI unit Pa·s], K is the flow consistency index [SI unit Pa·s^n], $\dot{\gamma}$ is the shear rate [SI unit s^{-1}] and n is the dimensionless power law index.

All of the emulsion samples behaved as a low viscosity fluid. Emulsions made with 5.0 wt% of nanoparticles showed higher apparent viscosities at higher shear rates. In addition the more viscous heavy oil generated the more viscous emulsions at the same nanoparticle concentration. The effect of the NaCl in the apparent viscosity was more evident in the samples made with the Kern River oil and a concentration of 5.0 wt% of nanoparticles.

In **Fig. 4.8** illustrates the effect of the nanoparticle concentration in the emulsion viscosity. As more nanoparticles were added, the apparent viscosity tends to be higher.

On the other hand, **Fig. 4.9** shows the effect of the NaCl in the emulsion viscosities. Small increments in apparent viscosity were noticed in samples 7, 8, 15 compared with the samples without NaCl; however, sample 16 showed a larger increment.

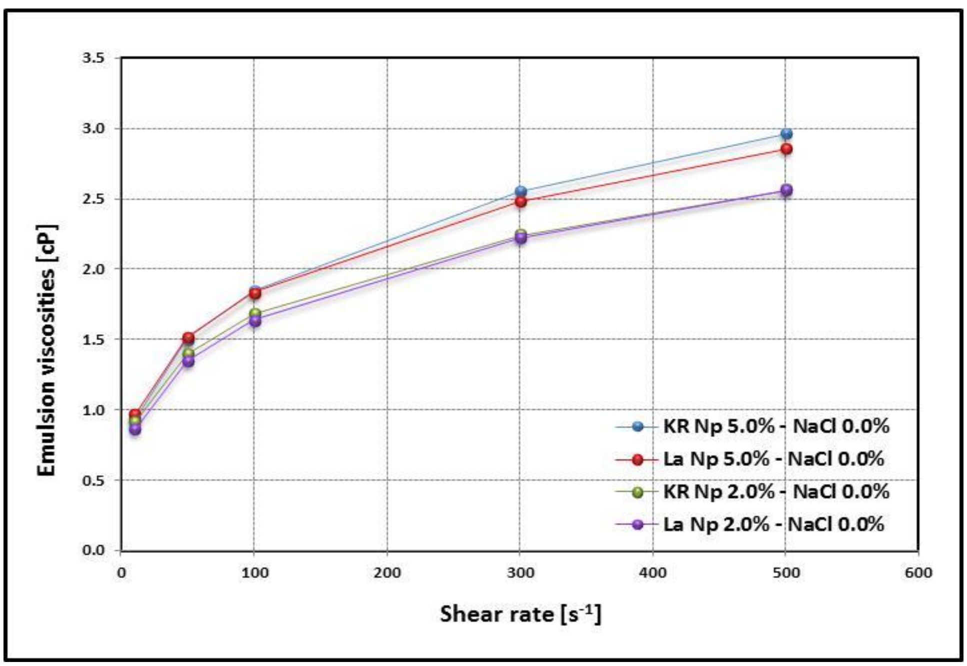

Fig. 4.8—Increments in nanoparticle concentration leads to an increment in the apparent viscosity; moreover, this viscosity is very low compared with the original heavy oil

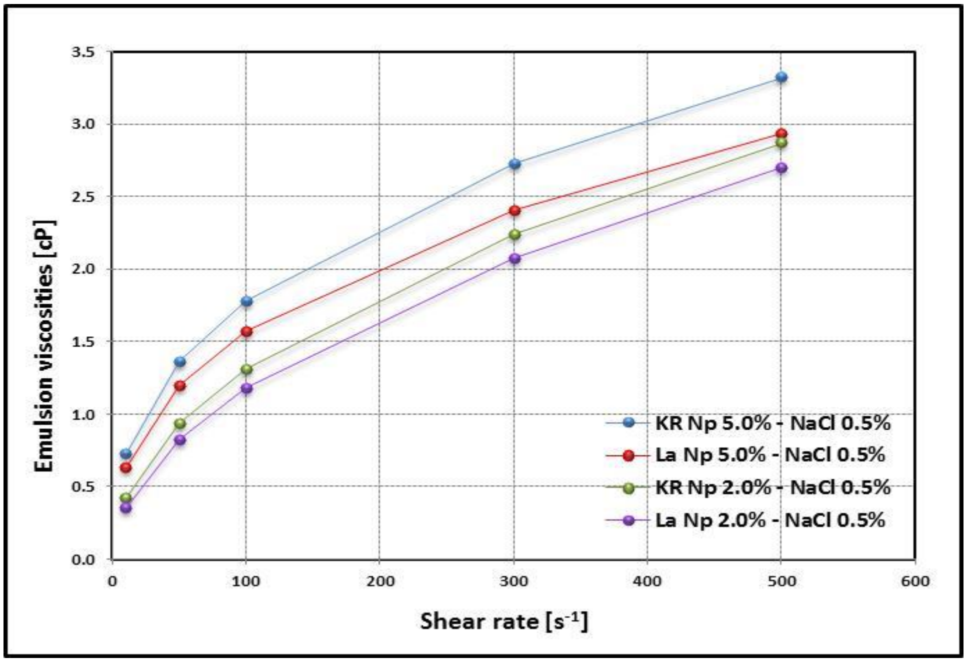

Fig. 4.9—Increments in apparent viscosity as a result of add NaCl were more noticeable in sample 16

4.1.4 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.

4.2 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 (**Fig. 4.10)**. The upper core is a Buff Berea sandstone and the lower 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.

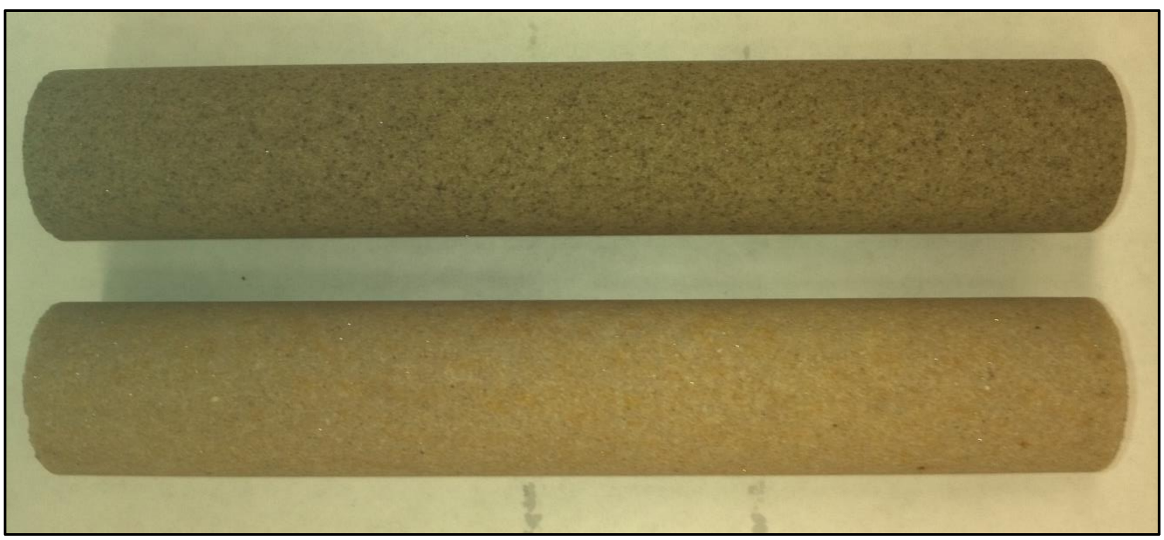

Fig. 4.10—Buff Berea and Bentheimer sandstone cores used in the flooding experiments

To set up the original saturation conditions, and also to calculate the rock-fluid properties for the previously described cores, the procedure outlined in section 3.4.1 was followed; results are depicted in the **Table 4.2**.

Table 4.2—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 [cm^3]	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
S_{wirr} [%]	25.1	14.7	23.8	13.9	22.0	14.0
S_{oi} [%]	74.9	85.3	76.2	86.1	78.0	86.0
OOIP [cm^3]	12.4	15.4	12.4	15.6	12.4	14.9

Core flooding experiments were divided in two stages. The first stage was a waterflooding process, where brine (see chapter 3) was used as the injected fluid. The second stage was the nanoparticle dispersion flooding; in this stage the nanoparticle dispersions were injected at different injection rates of 1 ft/d, 10 ft/d, 100 ft/d, 200 ft/d and 300 ft/d. In this way the necessary shear rate to generate the emulsions was achieved. CF1, CF2, CF3 and CF4 were completed using a nanoparticle dispersion made with 5.0 wt% of nanoparticles and 0.5 wt% NaCl brine (ND1). CF5 and CF6 were accomplished with the nanoparticle dispersion made with 2.0 wt% of nanoparticles and 0.5 wt% NaCl brine (ND2).

4.2.1 Effects of the ND1 on the in-situ emulsion generation and oil recovery

In this section, the results obtained from the CF1, are presented and discussed next. The ability of ND1 to produce additional heavy oil, after waterflooding, as o/w emulsions have been tested at different scenarios of rock permeability and oil viscosity. Results are presented below.

Core flooding 1: Louisiana heavy oil – Buff Berea sandstone (I)

The Core flooding 1 was carried out with a Buff Berea sandstone core saturated with Louisiana heavy oil. 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.

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%. **Table 4.3** shows a summary of the obtained results.

Table 4.3—Core flooding 1 experiment results

Core flooding	**1**
Heavy Oil type	LA HO
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 NF [%]	***32.3***
Final RF [%]	**64.3**

Fig. 4.11 shows the oil recovery and pressure profiles from CF1. It is observed that after 2.5 PV of injected brine the oil recovery remains constant, meaning there is no additional oil production. Furthermore, a maximum pressure of 105 psi is first observed followed by a 35 psi pressure drop at the end of waterflooding.

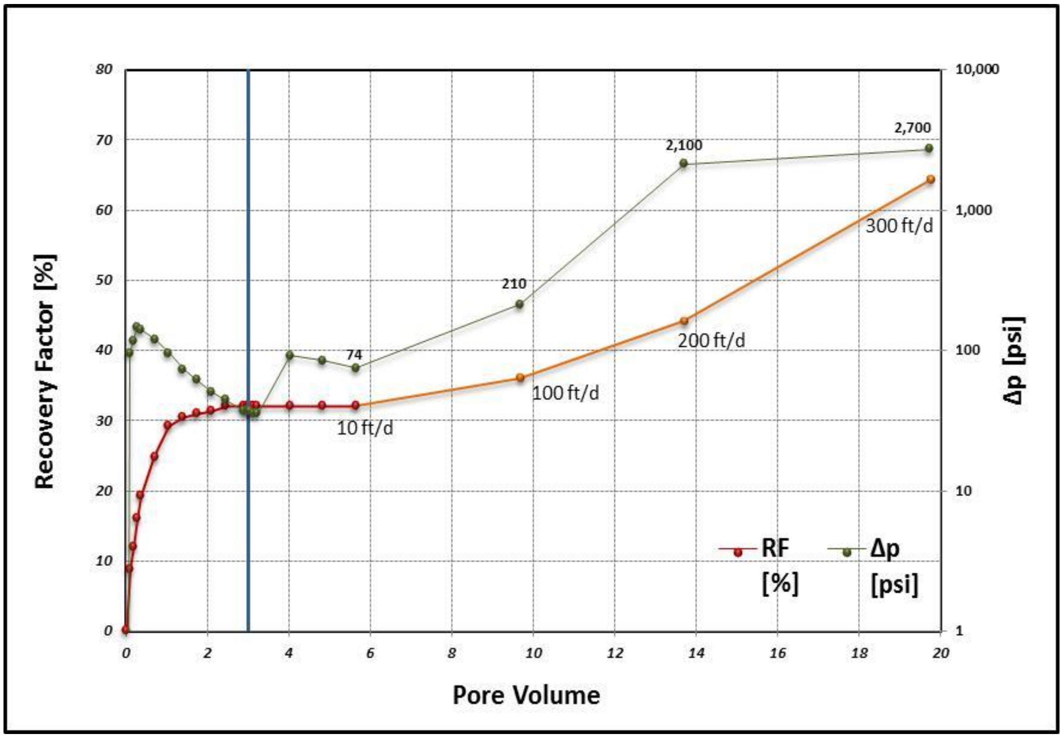

Fig. 4.11—Oil recovery and pressure profiles along the CF1

Thereafter, the ND1 was injected at 1, 10, 100, 200 and 300 ft/d for 0.25, 1.5, 4.0 and 6.0 PV respectively. Note that at lower injection rates no additional oil was produced. In addition at 100 ft/d, 200 ft/d and 300 ft/d crude oil was produced both as an emulsion and as a single phase. A substantial increment in pressure was observed at high rates because of the low rock permeability. Despite the significant oil recovered, a great volume of dispersion had to be injected due to the high injection rates needed to generate the emulsions. **Table 4.4** shows the results of the dispersion flooding. Effluents collected in this experiment are shown in **Fig. 4.12**. It was observed that ND1 was able to produce emulsions and crude oil.

Table 4.4—Recovery factors and injection pressures at each injection rate, 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**		

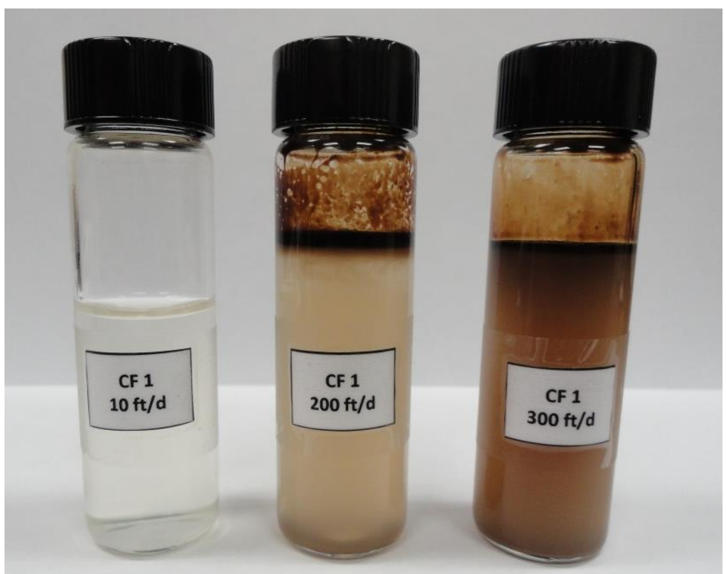

Fig. 4.12—Effluents collected from the CF1

Core flooding 2: Louisiana heavy oil – Bentheimer sandstone (I)

The Core flooding 2 was performed with a Bentheimer sandstone core saturated with Louisiana heavy oil. 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. **Table 4.5** summarizes the results of the CF2.

Table 4.5—Core flooding 2 experiment results

Core flooding	**2**
Heavy Oil type	**LA HO**
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 NF [%]	***39.0***
Final RF [%]	**63.1**

The results in **Fig. 4.13** show an important oil recovery at high injection rates without pronounced increments in pressure; however, due to the high permeability of this core enough shear rate values were not achieved to generate emulsions. Oil production in this experiment is related mainly to an IFT reduction.

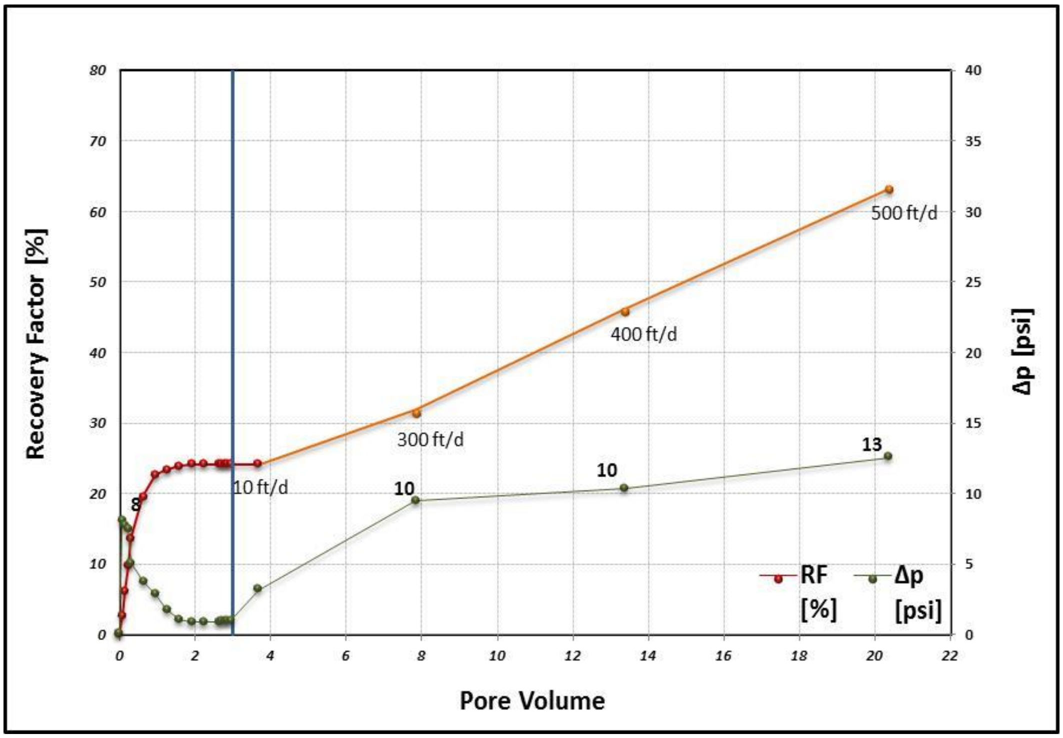

Fig. 4.13—Oil recovery and pressure profiles along the CF2

Table 4.6 presents the recovery factors of the nanoparticle flooding at each injection rate as well as its corresponding injection pressure. Injection rates of 1 ft/d and 10 ft/d did not produce additional oil. At 300 ft/d, 400 ft/d and 500 ft/d, crude oil was produced as a single phase and there was not emulsion generation (**Fig. 4.14**).

Table 4.6—Recovery factors and injection pressures at each injection rate, 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**		

Fig. 4.14—Effluents collected from the CF2.

Core flooding 3: Kern River heavy oil – Buff Berea sandstone (II)

The Core flooding 3 was carried out with a Buff Berea sandstone core saturated with Kern River heavy oil. 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 was 27.3% of the OOIP. **Table 4.7** summarizes the results of this experiment.

Table 4.7—Core flooding 3 experiment results

Core flooding	**3**
Heavy Oil type	**KR HO**
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 NF [%]	***20.2***
Final RF [%]	**47.5**

Fig. 4.15 clearly shows how the injection pressure was above 2,000 psi at all times. The arrangement of high permeability and high viscosity led to the generation of emulsion at low injection rates. However, it was not possible to continue the experiment for longer periods of time due to the pressure limitations of the core holder.

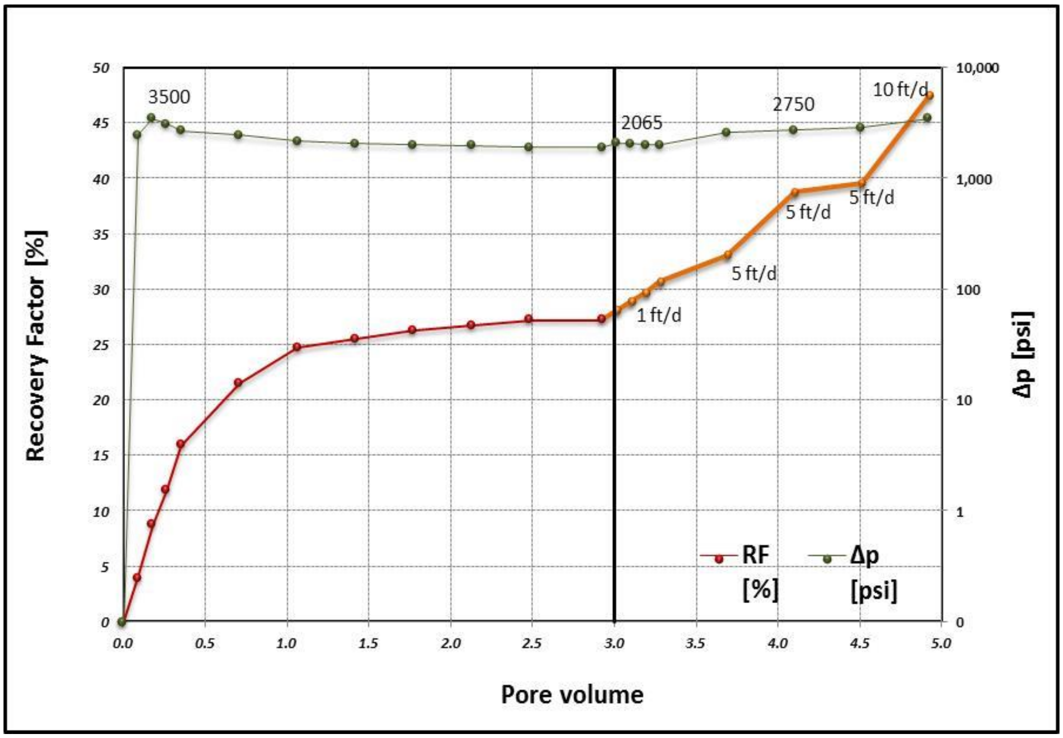

Fig. 4.15—Oil recovery and pressure profiles along the CF3

In this experiment, the nanoparticle dispersion was injected at 1 ft/d, 5 ft/d and 10 ft/d. Despite the low rates, there was oil production as emulsion and as a single phase due to a combination of high shear rates and an IFT reduction between heavy oil and the injected fluid (**Fig. 4.16**). **Table 4.8** details the results from this core flooding experiment.

Table 4.8—Recovery factors and injection pressures at each injection rate, CF3

Injection Rate (ft/d)	Recovery Factor (%)	PV Injected	Pressure (psi)	o/w Emulsions
1	2.6	0.27	2,065	yes
5	4.2	0.59	2,900	yes
10	9.1	0.9	3,500	yes
	15.8	**1.8**		

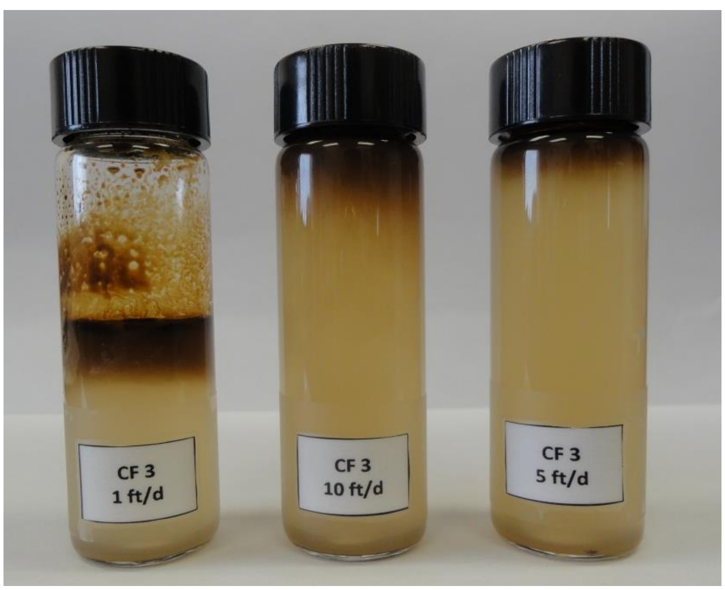

Fig. 4.16—Effluents collected from the CF3

Core flooding 4: Kern River heavy oil – Bentheimer (II)

Core flooding 4 was carried out with a Bentheimer sandstone core saturated with Kern River heavy oil. Brine permeability of this core was 2,015 mD with a 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. **Table 4.9** gives a summary of the results from CF4.

Table 4.9—Core flooding 4 experiment results

Core flooding	**4**
Heavy Oil type	**KR HO**
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 NF [%]	***64.1***
Final RF [%]	**87.4**

The recovery factor and pressure profile of this experiment are shown in **Fig. 4.17**. High permeability of this sandstone core did not present a flow restriction; hence, there apparently was not enough shear to generate emulsion—at least there were no emulsions observed at the core outlet sample collector. Despite this fact, there was additional oil production in single phase; the recovery factor obtained by the nanoparticle dispersion flooding was the highest of the six experiments. The IFT reduction, observed in the pendant drop experiments, caused the oil production in this experiment.

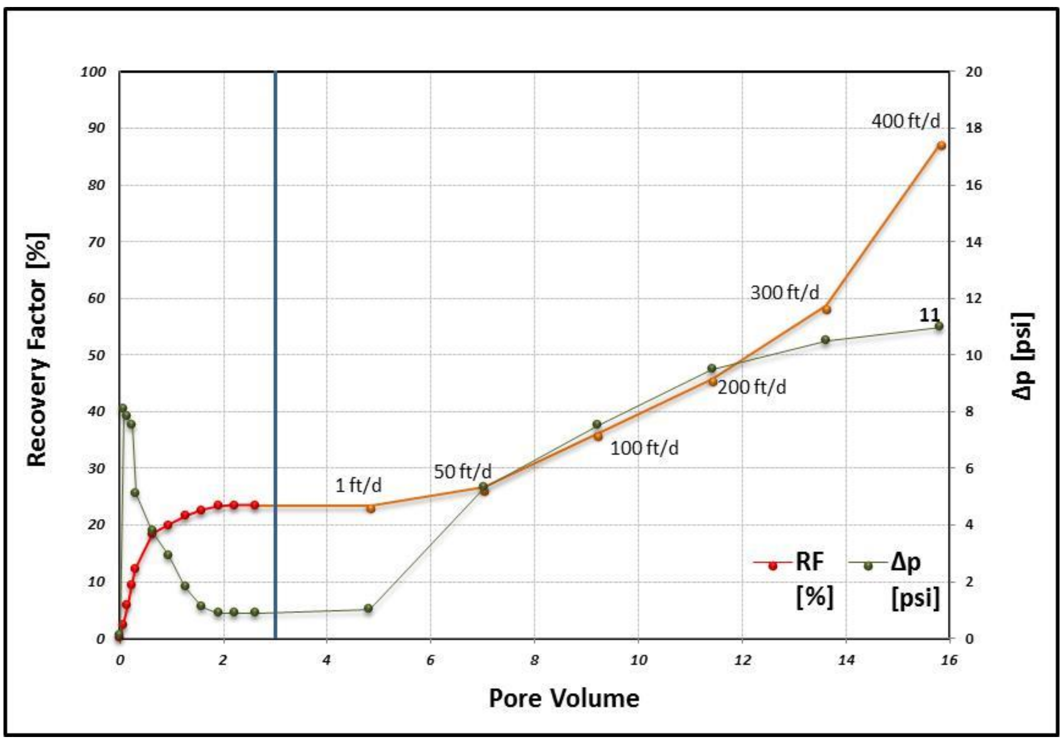

Fig. 4.17—Oil recovery and pressures profile along the CF4

Results shown in the **Table 4.10** indicate that at higher injection rates, the amount of produced oil was also higher. The injection pressure did not increase significantly when the injection rates were incremented. In this experiment not only the oil production was the largest, but the injected fluid volume was the smallest; no emulsions were observed (**Fig. 4.18**).

Table 4.10— Recovery factors and injection pressures at each injection rate, 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
	35.2	**11.0**		

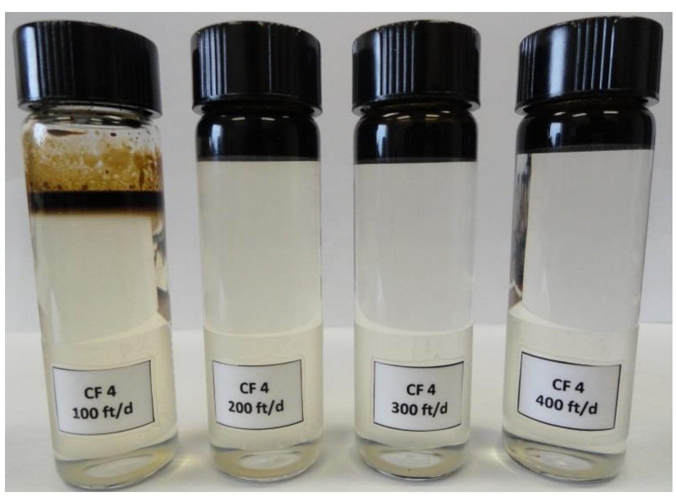

Fig. 4.18—Effluents collected from the CF2

Effect of permeability on the final oil recovery

The effect of permeability in any EOR process is fundamental for the success of the project. In addition, permeability of the rock is essential to select the optimum recovery process. The effect of permeability was investigated in this research to determine how it affects the heavy oil recovery during the nanoparticle dispersion flooding.

Effect of permeability on the lower viscosity heavy oil

Fig.4.19 shows a comparison of the recovery factor obtained from BB (I) and BT (I) sandstone cores. Brine permeabilities were 137 mD and 2,340 mD respectively. These cores were saturated with Louisiana heavy oil of 600 cP. Recovery factor after waterflooding was larger in the BB (I) sandstone because the lower permeability reduced the water channeling, improving the sweep efficiency. During the nanoparticle flooding, emulsions were not generated in the higher permeability core due to the lack of shear developed in the rock during flooding; it is believed that oil production from this rock is only due to a reduction in the ITF. However, final recoveries were similar in both experiments. The effect of permeability is also observed in **Fig. 4.20** where the pressure profiles of the experiments are compared. BT (I) sandstone did not offer any restriction to generate shear rate and obtain emulsions.

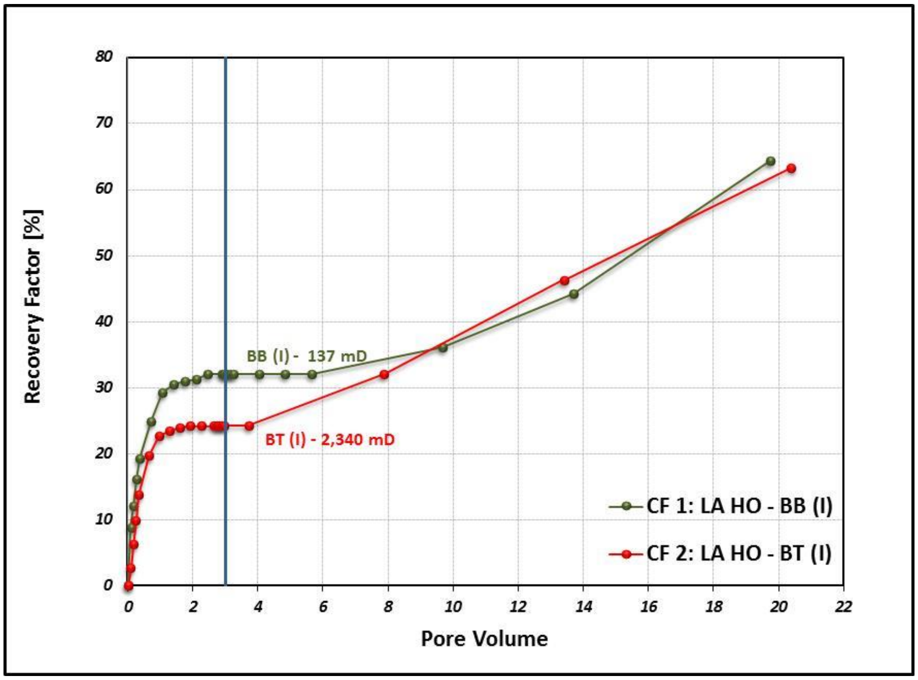

Fig.4.19—Recovery production profile from CF1 and CF2

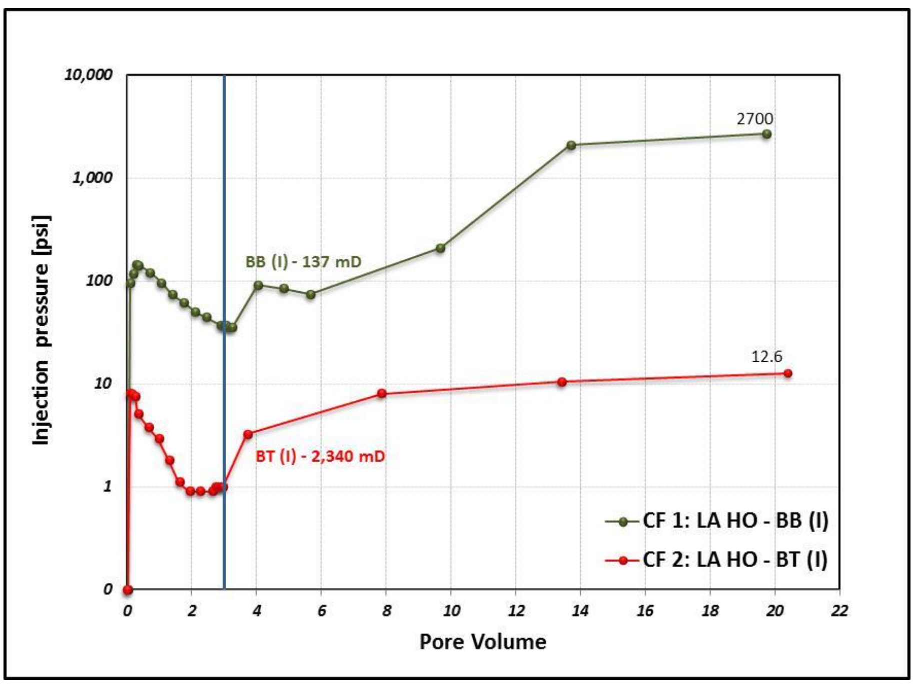

Fig. 4.20—Pressure profile from CF1 and CF2

Effect of permeability on the higher viscosity heavy oil

Oil recovery factors of the CF3 and CF4 are compared in **Fig. 4.21** in order to show the effect of permeability on the final recovery. The cores were saturated with Kern River heavy oil of 3,500 cP. CF3 was performed with the BB (II) core sandstone while CF4 was completed with the BT (II). Permeabilities of these cores are 152 mD and 2,015 mD respectively.

Emulsions were generated in CF3 at low injection rates, but due to high pressures the experiment was terminated early. **Fig. 4.22** shows that the permeability of the rock plays a significant role in the emulsion generation. Low permeability restricts fluid flow and increases shear rate which is favorable to emulsion generation. Despite the high oil recoveries in CF4, emulsions were not generated.

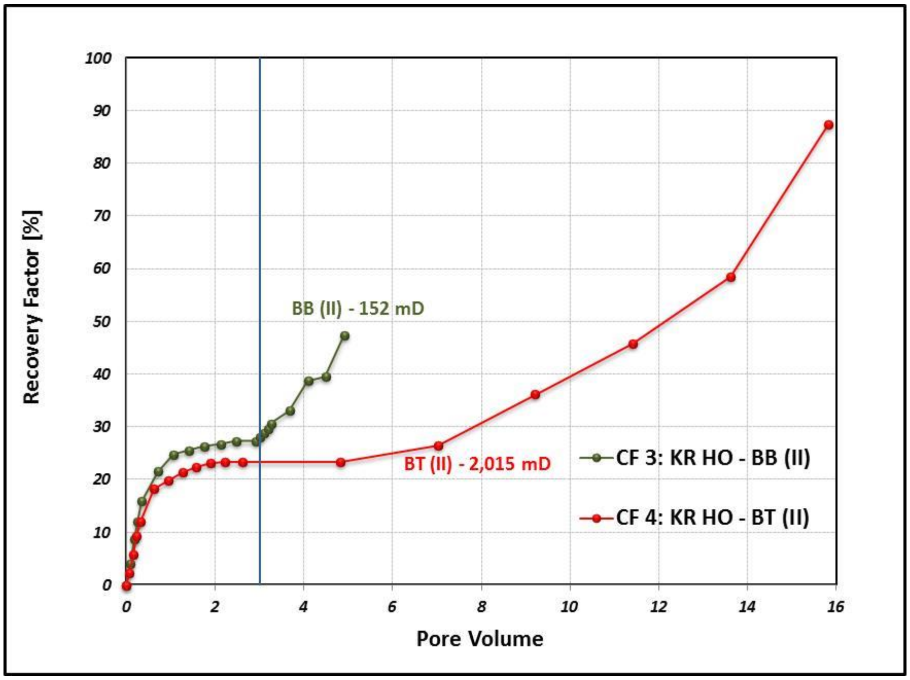

Fig. 4.21—Recovery production profiles of CF3 and CF4

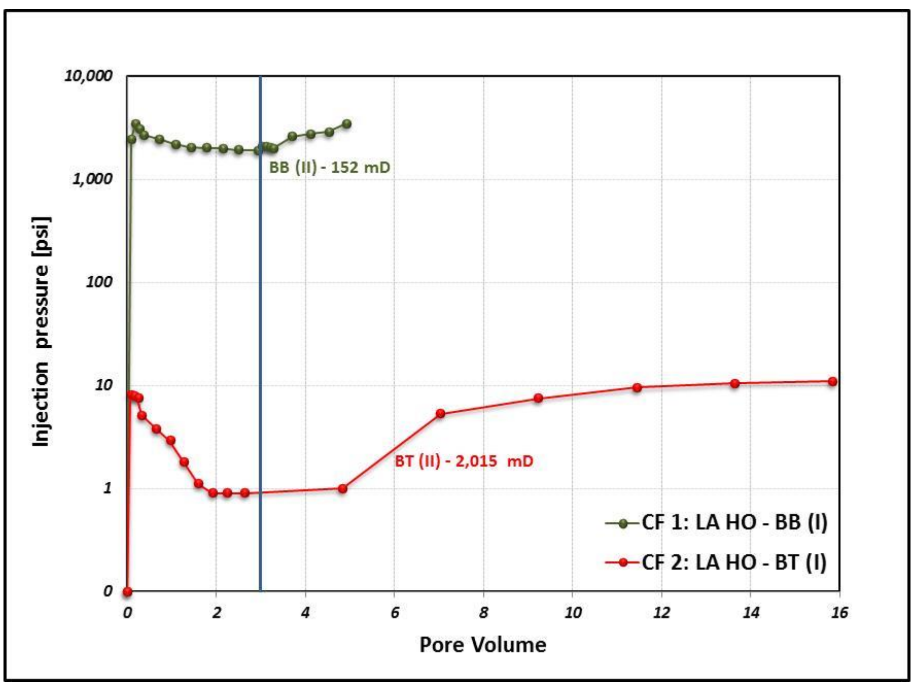

Fig. 4.22—Pressure profiles of CF3 and CF4

Effect of heavy oil viscosity on the final oil recovery

The effect of viscosity plays an important role on final recovery and therefore should be carefully evaluated. Difference in viscosities between the low-viscosity injected fluid and in-situ heavy oil may lead to by-pass of the heavy oil (viscous fingering of drive fluid), reducing the final recoveries. Mai and Kantzas (2009) concluded in their work that oil recovery decreases when oil viscosity increases.

Nanoparticle dispersion flooding; however, showed that the obtained oil recoveries were mainly due to an IFT reduction as well as to the generation of emulsions in those rocks with low permeability. These results are shown in the **Fig. 4.23** and **Fig. 4.24**.

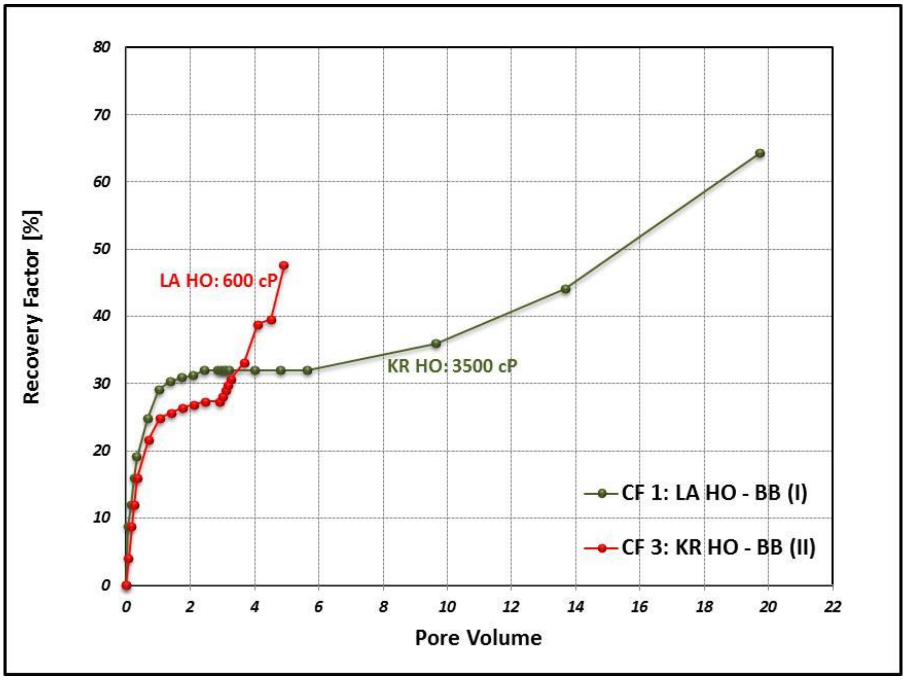

Fig. 4.23—Effect of oil viscosity in the CF1 and CF3

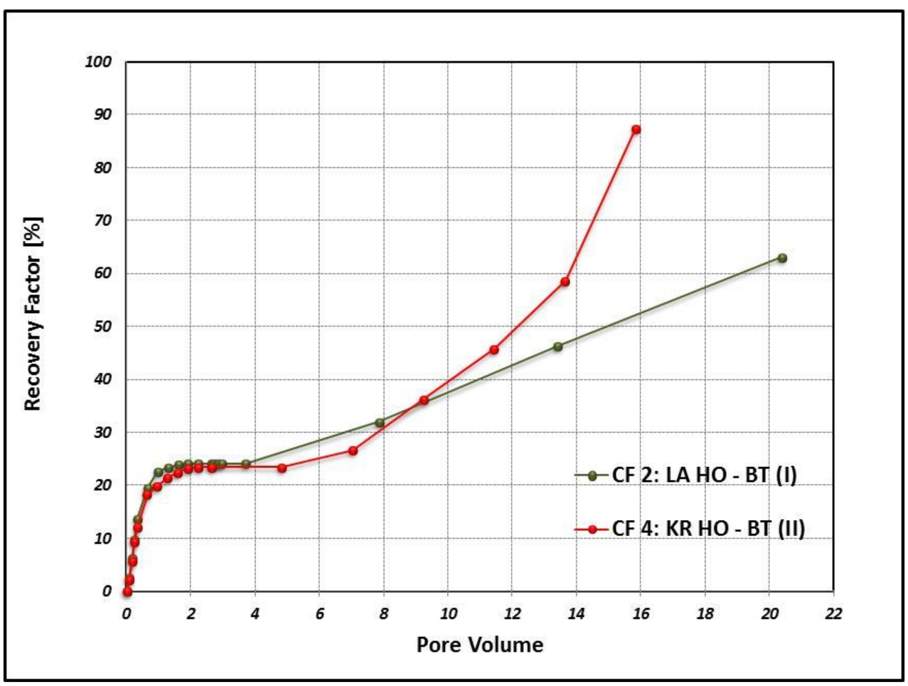

Fig. 4.24—Effect of oil viscosity in the CF2 and CF4

4.2.2 Effects of the ND2 on the in-situ emulsion generation and oil recovery

CF5 and CF6 were performed to investigate the effect of the ND2 in the oil recovery. A reduction in the nanoparticle concentration would imply a reduction of the elaboration cost of the dispersion. In addition, if the oil recovery is increased, the economic results of the projects can be improved.

Core flooding 5: Louisiana heavy oil – Buff Berea (III)

The Core flooding 5 was carried out with a Buff Berea sandstone core saturated with Louisiana heavy oil. Brine permeability of this core was 271 mD, with a 21.1% porosity and an OOIP of 12.4 cm^3. During the waterflooding stage, brine was injected at 1 ft/d. Oil recovery after waterflooding was 31.7% of the OOIP. **Table 4.11** shows a summary of the results of this experiment.

Table 4.11—Core flooding 5 experiment results

Core flooding	**5**
Heavy Oil type	**La HO**
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 NF [%]	***16.2***
Final RF [%]	**47.9**

ND2 was injected at different injection rates. Injection rates of 1 ft/d and 10 ft/d did not produced additional oil. Emulsion and crude oil was produced with injection rates higher than 100 ft/d. The oil recovery after ND2 flooding was 16.2 % of the OOIP. **Fig. 4.25** shows the oil recovery and injection profiles that resulted from this experiment.

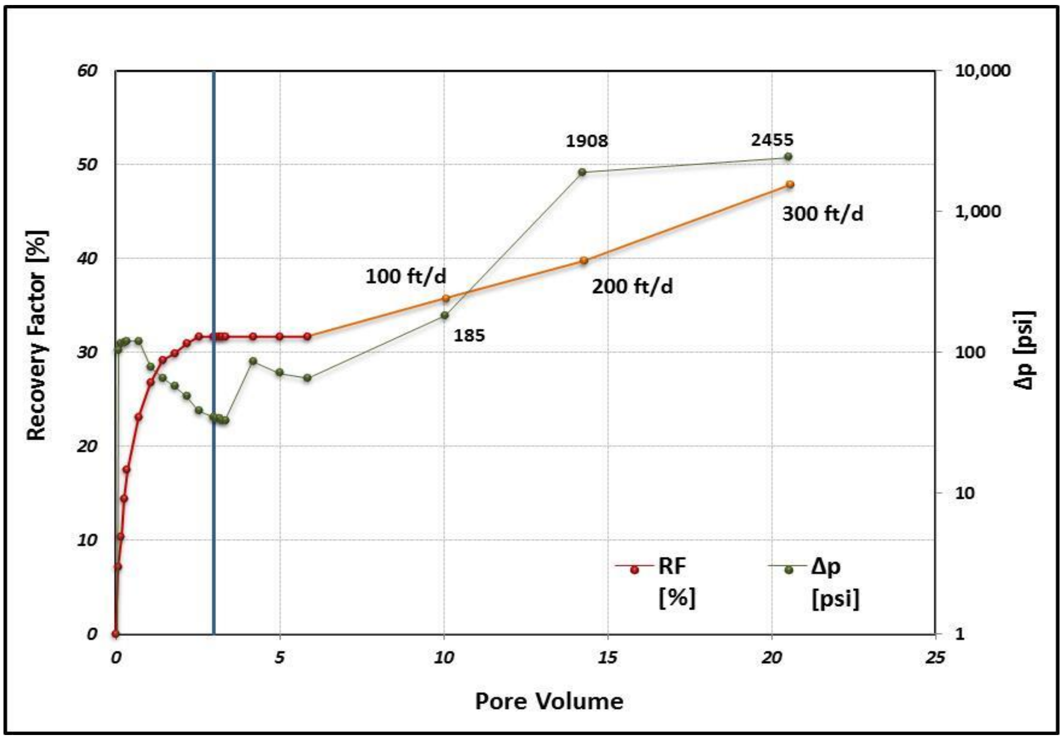

Fig. 4.25—Oil recovery and pressure profiles along the core flooding 5

Detailed results of the ND2 flooding are presented in the **Table 4.12**. It is important to highlight that there was additional oil recovery due to the emulsion generation at high injection rates (**Fig. 4.26**).

Table 4.12—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**		

Fig. 4.26—Effluents collected from the CF5

Core flooding 6: Louisiana heavy oil – Bentheimer (III)

Core flooding 6 was carried out using a Bentheimer sandstone core saturated with Louisiana heavy oil. Brine permeability of this core was 2,027 mD with a 24.1% porosity and an OOIP of 14.9 cm^3. During the waterflooding stage, 25.2% of the OOIP was recovered. Results of the CF6 are shown in the **Table 4.13**.

Table 4.13—Core flooding 6 experiment results

Core flooding	**6**
Heavy Oil type	**La HO**
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 NF [%]	***23.5***
Final RF [%]	**48.7**

Fig. 4.27 shows the oil recovery and pressure profiles of the CF 6. The Oil recovery profile exhibits an increment when the ND2 was injected at 100 ft/d, 200 ft/d and 300 ft/d. However, effluents show that there was not stable emulsion generation; the oil was produced primarily due to the IFT reduction and high flow rates (**Fig. 4.28**).

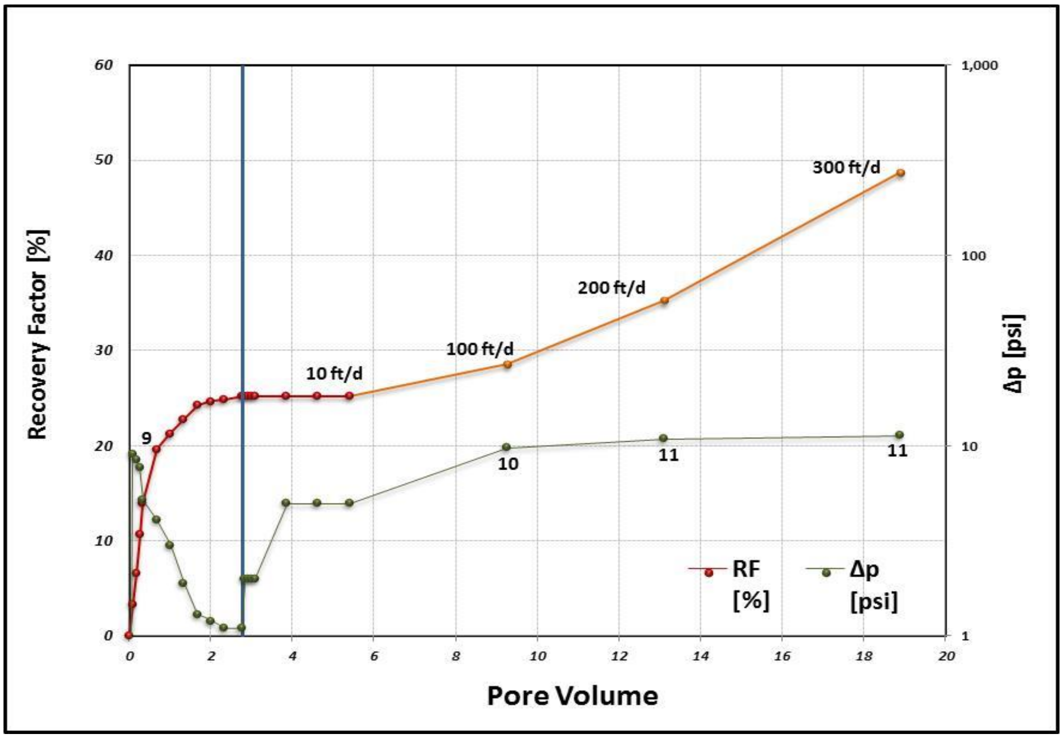

Fig. 4.27—Oil recovery and pressure profiles along the CF6. Due to the high rock permeability, the pressure drop remains low when it is compared with the lower rock permeability

Table 4.14 summarizes the results obtained after the ND2 was injected. Despite the high rates, the injection pressure did not significantly increase. It means that the injected fluid passed through the rock without any restriction hence it is believe that the additional oil recovery was due only to the IFT reduction (**Fig. 4.28**).

Table 4.14—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**		

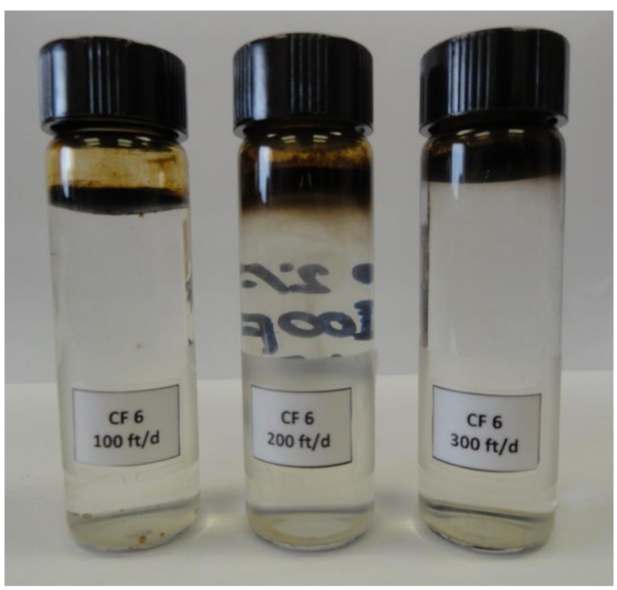

Fig. 4.28—Effluents collected from the CF6

Effect of the nanoparticle concentration on the emulsion generation and oil recovery

Fig. 4.29 and **Fig. 4.30** intent to compare the effects on the oil recovery when ND1 and ND2 are injected in two cores with the same permeability and saturated with the same type of heavy oil.

Fig. 4.29 compared the oil recovery profiles from the CF1 and CF5; these experiments were made with the Buff Berea sandstone core saturated with Louisiana heavy oil. The ND1 was used in CF1 and ND2 in CF5. Additional oil was produced in both core flooding as emulsions and crude oil; however, CF1 showed better recoveries. Final recovery factor in CF1 was 64.3% while in CF5 was 48.7%.

Fig. 4.30 shows oil recovery profiles from CF2 and CF6. This set of experiments was performed with the Bentheimer sandstone core saturated with Louisiana heavy oil. CF2 was completed with the ND1 and CF6 with ND2. Oil was produced with the nanoparticle dispersion flooding as crude oil. Emulsions were not observed in these experiments. Final oil recoveries in CF2 and CF6 were 63.1% and 48.7 % respectively.

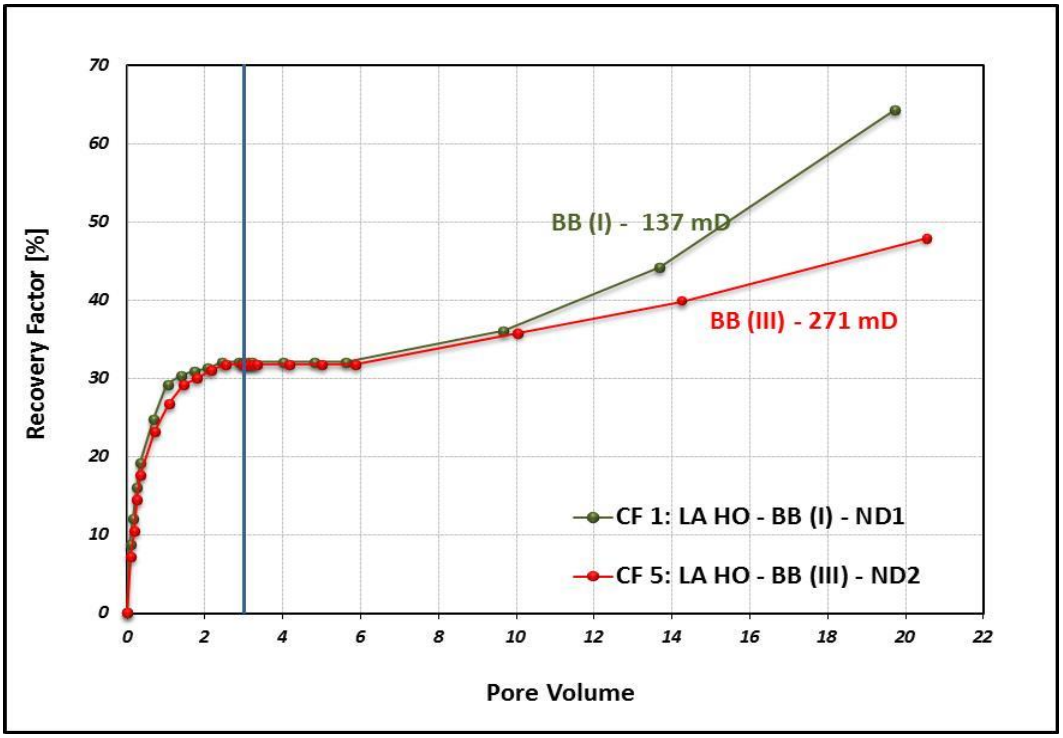

Fig. 4.29—Comparison of the ND1 and ND2 in Buff Berea sandstone

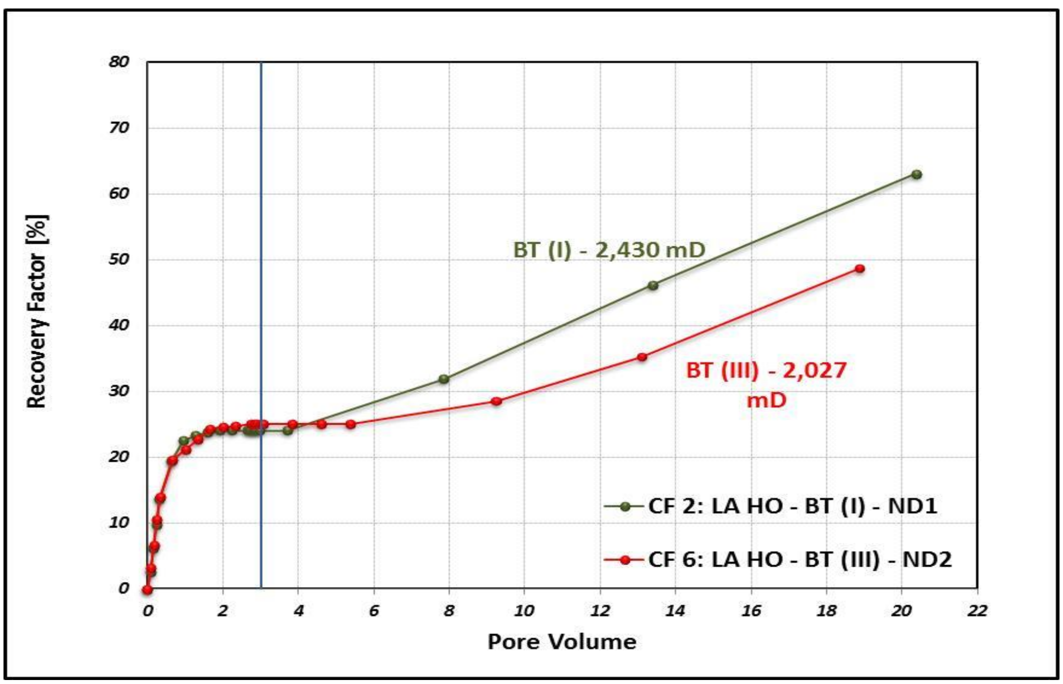

Fig. 4.30—Comparison of the ND1 and ND2 in Bentheimer sandstone

V. CONCLUSIONS AND RECOMMENDATIONS

5.1 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.

- The viscosity of the emulsion presented a shear-thickening behavior. Viscosity values of emulsions were significantly reduced compared with the original heavy oil viscosity.

- 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 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.

5.2 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 rock 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.

REFERENCES

Adams, D.M. 1982. Experiences with Waterflooding Lloydminster Heavy-Oil Reservoirs. *Journal of Petroleum Technology* **34** (8): 1643-1650. DOI: 10.2118/10196-pa

Alboudwarej, H., Felix, J., Taylor, S. et al. 2006. Highlighting Heavy Oil. *Oilfield Review* **18** (2): 34-53.

Ali, S.M.F., Figueroa, J.M., Azuaje, E.A. et al. 1979. Recovery of Lloydminster and Morichal Crudes by Caustic, Acid and Emulsion Floods. *Journal of Canadian Petroleum Technology* **18** (1). DOI: 10.2118/79-01-02

Arditty, S., Schmitt, V., Giermanska-Kahn, J. et al. 2004. Materials Based on Solid-Stabilized Emulsions. *Journal of Colloid and Interface Science* **275** (2): 659-664. DOI: http://dx.doi.org/10.1016/j.jcis.2004.03.001

Arihara, N., Yoneyama, T., Akita, Y. et al. 1999. Oil Recovery Mechanisms of Alkali-Surfactant-Polymer Flooding. Paper presented at the SPE Asia Pacific Oil and Gas Conference and Exhibition, Jakarta, Indonesia. Society of Petroleum Engineers 00054330. DOI: 10.2118/54330-ms.

Asghari, K. and Nakutnyy, P. 2008. Experimental Results of Polymer Flooding of Heavy Oil Reservoirs. Paper presented at the Canadian International Petroleum Conference, Calgary, Alberta. Petroleum Society of Canada PETSOC-2008-189. DOI: 10.2118/2008-189.

Ashrafizadeh, S.N. and Kamran, M. 2010. Emulsification of Heavy Crude Oil in Water for Pipeline Transportation. *Journal of Petroleum Science and Engineering* **71** (3–4): 205-211. DOI: http://dx.doi.org/10.1016/j.petrol.2010.02.005

Attanasi, E.D. and Meyer, R.F. 2010. Natural Bitumen and Extra-Heavy Oil. *2010 Survey of Energy Resources*: 123-150.

Bragg, J.R. 1999. *Oil Recovery Method Using an Emulsion.* Patent: US 5855243. Exxon Production Research Company Houston, Tx. United States.

Brook, G. and Kantzas, A. 1998. Evaluation of Non-Thermal Eor Techniques for Heavy Oil Production. Paper presented at the Annual Technical Meeting, Calgary, Alberta. Petroleum Society of Canada PETSOC-98-45. DOI: 10.2118/98-45.

Bryan, J. and Kantzas, A. 2009. Potential for Alkali-Surfactant Flooding in Heavy Oil Reservoirs through Oil-in-Water Emulsification. *Journal of Canadian Petroleum Technology* **48** (2): 37-46. DOI: 10.2118/09-02-37

Bryan, J.L. and Kantzas, A. 2008. Improved Recovery Potential in Mature Heavy Oil Fields by Alkali-Surfactant Flooding. Paper presented at the International Thermal Operations and Heavy Oil Symposium, Calgary, Alberta, Canada. 2008, SPE/PS/CHOA International Thermal Operations and Heavy Oil Symposium SPE-117649-MS. DOI: 10.2118/117649-ms.

Butler, R.M. 1994. Steam-Assisted Gravity Drainage: Concept, Development, Performance and Future. *Journal of Canadian Petroleum Technology* **33** (2). DOI: 10.2118/94-02-05

Butler, R.M., McNab, G.S., and Lo, H.Y. 1981. Theoretical Studies on the Gravity Drainage of Heavy Oil During in-Situ Steam Heating. *The Canadian Journal of Chemical Engineering* **59** (4): 455-460. DOI: 10.1002/cjce.5450590407

Clark, B., Graves, W.G., Lopez-de-Cardenas, J.E. et al. 2007. Topic Paper #22 Heavy Oil. *National Petroleum Council*.

Das, S.K. 1998. Vapex: An Efficient Process for the Recovery of Heavy Oil and Bitumen. *SPE Journal* **3** (3): 232-237. DOI: 10.2118/50941-pa

Dusseault, M. 2002. *Cold Heavy Oil Production with Sand in the Canadian Heavy Oil Industry*. Alberta Department of Energy.

Dusseault, M. and Baoci, X. 2011. Chops: Canadian Technology Finds Lucrative Application Abroad. *Energy Bridge: Canada's Oil & Gas Magazine*.

Emadi, A., Sohrabi, M., Jamiolahmady, M. et al. 2011. Mechanistic Study of Improved Heavy Oil Recovery by Co2-Foam Injection. Paper presented at the SPE Enhanced Oil Recovery Conference, Kuala Lumpur, Malaysia. Society of Petroleum Engineers SPE-143013-MS. DOI: 10.2118/143013-ms.

Falcone, G. 2009. Chapter 7 Heavy Oil Metering Applications. In *Developments in Petroleum Science*, ed. Gioia Falcone, G.F.H. and Claudio, A.: Elsevier. Volume 54.

Fipke, S.R. and Celli, A.O. 2008. The Use of Multilateral Well Designs for Improved Recovery in Heavy-Oil Reservoirs. Paper presented at the IADC/SPE Drilling Conference, Orlando, Florida, USA. 2008, IADC/SPE Drilling Conference SPE-112638-MS. DOI: 10.2118/112638-ms.

Fu, X., Lane, R.H., and Mamora, D.D. 2012. Water-in-Oil Emulsions: Flow in Porous Media and Eor Potential. Paper presented at the SPE Canadian Unconventional Resources Conference, Calgary, Alberta, Canada. Society of Petroleum Engineers SPE-162633-MS. DOI: 10.2118/162633-ms.

Fu, X. and Mamora, D.D. 2010. Enhanced Oil Recovery of Viscous Oil by Injection of Water-in-Oil Emulsions Made with Used Engine Oil. Paper presented at the SPE Improved Oil Recovery Symposium, Tulsa, Oklahoma, USA. Society of Petroleum Engineers SPE-129902-MS. DOI: 10.2118/129902-ms.

Gómez-Bueno, C.O., Marcano, N., and Sanchez, A.C. 1998. Orimulsion® a Fuel from Heavy Oil, Engineered for Performance.

Greaves, M., Saghr, A., T. X. Xia, T. et al. 2001. Thai-New Air Injection Technology for Heavy Oil Recovery and in Situ Upgrading. *Journal of Canadian Petroleum Technology* **40** (3). DOI: 10.2118/01-03-03

Greaves, M. and Xia, T. 2001. Capri-Downhole Catalytic Process for Upgrading Heavy Oil: Produced Oil Properties and Composition. In *Canadian International Petroleum Conference*.

Head, I.M., Jones, D.M., and Larter, S.R. 2003. Biological Activity in the Deep Subsurface and the Origin of Heavy Oil. *Nature* **426** (6964): 344-352.

Hincapie, R., Tovar, F.D., and Alvarez, C.E. 2011. Feasibility for the Application of in Situ Combustion in Faja Petrolifera Del Orinoco (Fpo) Based in a Novel Screening Criteria for the Technology. Paper presented at the SPE Enhanced Oil Recovery Conference, Kuala Lumpur, Malaysia. Society of Petroleum Engineers SPE-144027-MS. DOI: 10.2118/144027-ms.

Kaminsky, R.D., Wattenbarger, R.C., Lederhos, J. et al. 2010. Viscous Oil Recovery Using Solids-Stabilized Emulsions. Paper presented at the SPE Annual Technical Conference and Exhibition, Florence, Italy. Society of Petroleum Engineers SPE-135284-MS. DOI: 10.2118/135284-ms.

Lu, X., Sun, S., and Xu, J. 2010. Application of Thermal Recovery and Waterflood to Heavy and Extra-Heavy Oil Reservoirs: Analog Knowledge from More Than 120 Clastic Reservoirs. Paper presented at the International Oil and Gas Conference and Exhibition in China, Beijing, China. Society of Petroleum Engineers SPE-130758-MS. DOI: 10.2118/130758-ms.

Mai, A., Bryan, J., Goodarzi, N. et al. 2009. Insights into Non-Thermal Recovery of Heavy Oil. *Journal of Canadian Petroleum Technology* **48** (3): 27-35. DOI: 10.2118/09-03-27

Mai, A. and Kantzas, A. 2009. Heavy Oil Waterflooding: Effects of Flow Rate and Oil Viscosity. *Journal of Canadian Petroleum Technology* **48** (3): 42-51. DOI: 10.2118/09-03-42

Martínez-Palou, R., Mosqueira, M.d.L., Zapata-Rendón, B. et al. 2011. Transportation of Heavy and Extra-Heavy Crude Oil by Pipeline: A Review. *Journal of Petroleum Science and Engineering* **75** (3–4): 274-282. DOI: http://dx.doi.org/10.1016/j.petrol.2010.11.020

Matthews, C.S. 1983. Steamflooding. *Journal of Petroleum Technology* **35** (3): 465-471. DOI: 10.2118/9993-pa

McAuliffe, C.D. 1973. Crude-Oil-Water Emulsions to Improve Fluid Flow in an Oil Reservoir. *Journal of Petroleum Technology* **25** (6): 721-726. DOI: 10.2118/4370-pa

Miller, K.A. 2005. State of the Art of Western Canadian Heavy Oil Water Flood Technology. Paper presented at the Canadian International Petroleum Conference, Calgary, Alberta. Petroleum Society of Canada PETSOC-2005-251. DOI: 10.2118/2005-251.

Needham, R.B. and Doe, P.H. 1987. Polymer Flooding Review. *Journal of Petroleum Technology* **39** (12): 1503-1507. DOI: 10.2118/17140-pa

Nelder, C. 2011. Heavy Oil of the Kern River Oil Field.

Oppelt, E.T. 2001. *Environmental Impacts of the Use of Orimulsion*. National Risk Managment Research Laboratory.

Pickering, S.U. 1907. Emulsions. *Journal of the Chemical Society 91*: 2001-2021.

Pourabdollah, K. and Mokhtari, B. 2013. The Vapex Process, from Beginning up to Date. *Fuel* **107** (0): 1-33. DOI: http://dx.doi.org/10.1016/j.fuel.2012.12.003

Revana, k. and Erdogan, M.H. 2007. Optimization of Cyclic Steam Stimulation under Uncertainty. Paper presented at the Hydrocarbon Economics and Evaluation Symposium, Dallas, Texas, U.S.A. Society of Petroleum Engineers SPE-107949-MS. DOI: 10.2118/107949-ms.

Saigal, T., Dong, H., Matyjaszewski, K. et al. 2010. Pickering Emulsions Stabilized by Nanoparticles with Thermally Responsive Grafted Polymer Brushes. *Langmuir* **26** (19): 15200-15209. DOI: 10.1021/la1027898

Sarathi, P.S. 1999. *In-Situ Combustion Handbook -- Principles and Practices*.

Selby, R., Alikhan, A.A., and Ali, S.M.F. 1989. Potential of Non-Thermal Methods for Heavy Oil Recovery. *Journal of Canadian Petroleum Technology* **28** (4). DOI: 10.2118/89-04-02

Shah, A., Fishwick, R., Wood, J. et al. 2010. A Review of Novel Techniques for Heavy Oil and Bitumen Extraction and Upgrading. *Energy & Environmental Science* **3** (6): 700-714.

Shell. 2012. Enhanced Oil Recovery. In *http://www-static.shell.com/content/dam/shell/static/future-energy/downloads/eor/eor-brochure-2012.pdf*, ed. Production, S.I.E.a. http://www-static.shell.com/content/dam/shell/static/future-energy/downloads/eor/eor-brochure-2012.pdf.

Shokri, A.R. and Babadagli, T. 2012. An Approach to Model Chops (Cold Heavy Oil Production with Sand) and Post-Chops Applications. Paper presented at the SPE Annual Technical Conference and Exhibition, San Antonio, Texas, USA. Society of Petroleum Engineers SPE-159437-MS. DOI: 10.2118/159437-ms.

Shutang, G. and Qiang, G. 2010. Recent Progress and Evaluation of Asp Flooding for Eor in Daqing Oil Field. Paper presented at the SPE EOR Conference at Oil & Gas West Asia, Muscat, Oman. Society of Petroleum Engineers SPE-127714-MS. DOI: 10.2118/127714-ms.

Sohrabi, M., Jamiolahmady, M., and Quraini, A.A. 2007. Heavy Oil Recovery by Liquid Co2/Water Injection. Paper presented at the EUROPEC/EAGE Conference and Exhibition, London, U.K. Society of Petroleum Engineers SPE-107163-MS. DOI: 10.2118/107163-ms.

Thomas, S. 2008. Récupération Assistée Du Pétrole : Panorama. *Oil & Gas Science and Technology - Rev. IFP* **63** (1): 9-19.

Turta, A.T., Chattopadhyay, S.K., Bhattacharya, R.N. et al. 2007. Current Status of Commercial in Situ Combustion Projects Worldwide. *Journal of Canadian Petroleum Technology* **46** (11). DOI: 10.2118/07-11-ge

Upreti, S.R., Lohi, A., Kapadia, R.A. et al. 2007. Vapor Extraction of Heavy Oil and Bitumen: Review. *Energy & Fuels* **21** (3): 1562-1574. DOI: 10.1021/ef060341j

Xia, T.X. and Greaves, M. 2006. In Situ Upgrading of Athabasca Tar Sand Bitumen Using Thai. *Chemical Engineering Research and Design* **84** (9): 856-864. DOI: http://dx.doi.org/10.1205/cherd.04192

Xia, T.X., Greaves, M., Turta, A.T. et al. 2003. Thai—a ' hort -Distance Displacement' in Situ Combustion Process for the Recovery and Upgrading of Heavy Oil. *Chemical Engineering Research and Design* **81** (3): 295-304. DOI: http://dx.doi.org/10.1205/02638760360596847

Zhang, T., Davidson, D., Bryant, S.L. et al. 2010. Nanoparticle-Stabilized Emulsions for Applications in Enhanced Oil Recovery. Paper presented at the SPE Improved Oil Recovery Symposium, Tulsa, Oklahoma, USA. Society of Petroleum Engineers SPE-129885-MS. DOI: 10.2118/129885-ms.

Zhang, Y., Luo, P., and Huang, S.-S.S. 2010. Improved Heavy Oil Recovery by Co2 Injection Augmented with Chemicals. Paper presented at the International Oil and Gas Conference and Exhibition in China, Beijing, China. Society of Petroleum Engineers SPE-131368-MS. DOI: 10.2118/131368-ms.

Zhang, Y.P., Sayegh, S., and Huang, S. 2006. Enhanced Heavy Oil Recovery by Immiscible Wag Injection. Paper presented at the Canadian International Petroleum Conference, Calgary, Alberta. Petroleum Society of Canada PETSOC-2006-014. DOI: 10.2118/2006-014.

Zheng, S. and Yang, D.T. 2012. Pressure Maintenance and Improving Oil Recovery Via Water-Alternating-Co2 Process in Thin Heavy Oil Reservoirs. Paper presented at the SPE Heavy Oil Conference Canada, Calgary, Alberta, Canada. Society of Petroleum Engineers SPE-157719-MS. DOI: 10.2118/157719-ms.