IntechOpen

Chemical Enhanced Oil Recovery (cEOR)

a Practical Overview

Edited by Laura Romero-Zeron

CHEMICAL ENHANCED OIL RECOVERY (CEOR) - A PRACTICAL OVERVIEW

Edited by **Laura Romero-Zerón**

Chemical Enhanced Oil Recovery (cEOR) - a Practical Overview
http://dx.doi.org/10.5772/61394
Edited by Laura Romero-Zeron

Contributors

Aliya Yernazarova, Gulzhan Kaiyrmanova, Almagul Baubekova, Azhar Zhubanova, Antoine Thomas, Stefan Iglauer, Lezorgia Nekabari Nwidee, Ahmed Barifcani, Stephen Theophilus, Mohammad Sarmadivaleh, Rongjia Tao, Martin Fernø, Luis A. Alcazar-Vara, Luis S. Zamudio-Rivera, Eduardo Buenrostro-Gonzalez

© The Editor(s) and the Author(s) 2016
The moral rights of the and the author(s) have been asserted.
All rights to the book as a whole are reserved by INTECH. The book as a whole (compilation) cannot be reproduced, distributed or used for commercial or non-commercial purposes without INTECH’s written permission.
Enquiries concerning the use of the book should be directed to INTECH rights and permissions department (permissions@intechopen.com).
Violations are liable to prosecution under the governing Copyright Law.

Individual chapters of this publication are distributed under the terms of the Creative Commons Attribution 3.0 Unported License which permits commercial use, distribution and reproduction of the individual chapters, provided the original author(s) and source publication are appropriately acknowledged. If so indicated, certain images may not be included under the Creative Commons license. In such cases users will need to obtain permission from the license holder to reproduce the material. More details and guidelines concerning content reuse and adaptation can be foundat http://www.intechopen.com/copyright-policy.html.

Notice

Statements and opinions expressed in the chapters are these of the individual contributors and not necessarily those of the editors or publisher. No responsibility is accepted for the accuracy of information contained in the published chapters. The publisher assumes no responsibility for any damage or injury to persons or property arising out of the use of any materials, instructions, methods or ideas contained in the book.

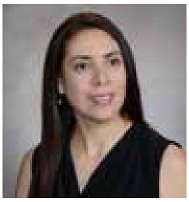
First published in Croatia, 2016 by INTECH d.o.o.
eBook (PDF) Published by IN TECH d.o.o.
Place and year of publication of eBook (PDF): Rijeka, 2019.
IntechOpen is the global imprint of IN TECH d.o.o.
Printed in Croatia

Legal deposit, Croatia: National and University Library in Zagreb

Additional hard and PDF copies can be obtained from orders@intechopen.com

Chemical Enhanced Oil Recovery (cEOR) - a Practical Overview
Edited by Laura Romero-Zeron
p. cm.
Print ISBN 978-953-51-2700-0
Online ISBN 978-953-51-2701-7
eBook (PDF) ISBN 978-953-51-4171-6

Meet the editor



Laura Romero-Zerón has been a chemical engineer and a professor in the Chemical Engineering Department at the University of New Brunswick since 2004. She holds a PhD degree in Chemical and Petroleum Engineering from the University of Calgary. Her research interests include optimization of EOR chemical (surfactant) flooding, development of surfactant carrier systems, polymer flooding, formulation of self-assembling polymeric systems, conformance-improvement treatments, heavy oil recovery, and bitumen upgrading among others. She has published numerous scientific papers, coauthored a book in the area of reservoir conformance improvement, authored three book chapters on EOR, and edited a book on EOR and bioremediation of oil-contaminated sites. Romero-Zerón is an SPE member and holds the US SPE Petroleum Engineering Certification.

Contents

Preface

The global industrial outlook indicates that the commercial application of chemical enhanced oil recovery (cEOR) processes will significantly grow worldwide over the next decade, driven by energy security requirements, increasing global oil demand, and technology development.

This release, which is divided into three sections for a total of six chapters, offers a straightforward presentation of practical concepts on cEOR. In the first section, Chapter 1 surveys the most commonly applied EOR processes, recent technological improvements, and opportunities for EOR field applications. The second section includes the next four chapters that are focused on cEOR processes such as polymer flooding, polymer gels and foams, surfactant flooding, and microbial enhanced oil recovery. The final section containing the sixth chapter describes the electrorheology (ER) technology as an effective approach for modifying the viscosity of crude oils. Each chapter offers wide-ranging information on the corresponding EOR processes, conceptual foundations of each EOR method, and process benefits and limitations and highlights on the performance of some field applications.

The practical-oriented style of this book is intended as a valuable source for a broad audience ranging from field operators, reservoir engineers, reservoir managers, EOR researchers, and other oil field professionals responsible for EOR screening, laboratory testing, managerial decisions, development and planning of strategies, and technical parameters for the customized field application of chemical EOR flooding. It does so by providing crucial knowledge about the basic principles and mechanisms of cEOR processes but also gives practical details to aid the proper process design for field applications. Thus, the level of presentation tends to be practical and realistically suited for readers looking to improve their knowledge and understanding of these processes in a concise manner.

Hallmark features of this book include the following:

- Straightforward definitions of the different EOR processes, including the mechanisms responsible for incremental oil recovery to guide the decision-making process and the optimum field applicability of these processes
- Evidence-based information on EOR polymers and polymer flooding that is necessary for its successful implementation in the field
- New insights into polymer gel and foam propagation in fractured reservoirs obtained through advanced in situ imaging techniques (i.e., CT and MRI) at laboratory scale
- Description of a simple experimental visualization technique for the evaluation of cEOR (i.e., foam) in fractured reservoir formations useful if advanced in situ imaging techniques are not available
- Demonstration of the efficiency of the electrorheology (ER) technology in reducing the viscosity of heavy crude oils through experimental work at laboratory bench scale and field tests.

Laura Romero-Zerón
Chemical Engineering Department,
University of New Brunswick, NB,
Canada

Section 1

Enhanced Oil Recovery (EOR) Processes

Chapter 1

EOR Processes, Opportunities and Technological Advancements

Lezorgia Nekabari Nwidee , Stephen Theophilus ,
Ahmed Barifcani , Mohammad Sarmadivaleh and
Stefan Iglauer

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/64828

Abstract

Enhanced oil recovery (EOR) processes are well known for their efficiency in incrementing oil production; however, the selection of the most suitable method to adopt for specific field applications is challenging. Hence, this chapter presents an overview of different EOR techniques currently applied in oil fields, the opportunities associated with these techniques, key technological advancements to guide the decision-making process for optimum applicability and productivity and a brief review of field applications.

Keywords: enhanced oil recovery (EOR), mobility ratio, interfacial tension (IFT), capillary number, viscosity

1. Introduction

1.1. Oil recovery processes

Oil reservoirs run through series of production stages classified as primary (natural drive mechanism), secondary and tertiary recovery techniques. These stages designate production from a reservoir in a sequential pattern [1] with different recovery efficiencies over time (**Figure 1**). Oil recovery is predominantly influenced by capillary number (N_c) at the microscopic scale and mobility ratio (M) at the macroscopic scale [2]. Capillary number denotes the ratio of viscous forces to interfacial tension (IFT) forces (Eq. (1)):

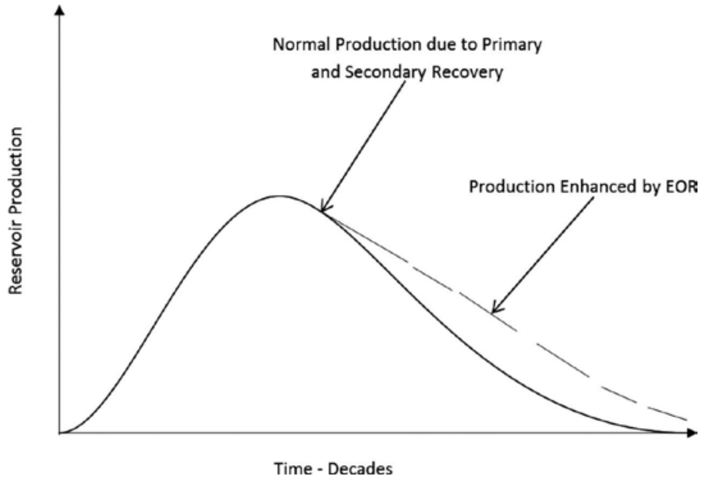


Figure 1. Reservoir production stages as a function of time [7].

$$N_c = V\mu / \sigma \tag{1}$$

where N_c represents capillary number; V is Darcy's velocity; μ is viscosity of displacing fluid; and σ is the interfacial tension (IFT) between the displaced and the displacing fluid [2–4]. It has been experimentally shown that an increase in capillary number (from a typical value around 10^{-7}) decreases residual oil saturation. This can be accomplished by an increase in the velocity of the injected fluid (i.e. Darcy's velocity, V) and/or viscosity of the displacing fluid (μ) and/or a reduction in IFT (σ) [5]. However, substantial increase in capillary number is required, thus, surfactant or alkaline flooding [6] is recommended as the most feasible option for micro-scale displacement. Mobility ratio (M) is the ratio of the mobility of the displacing fluid to the mobility of the displaced fluid Eq. (2)):

$$M = \lambda_{ing} / \lambda_{ed} \tag{2}$$

and

$$\lambda = k / \mu \tag{3}$$

where M is mobility ratio; λ_{ing} is displacing fluid mobility; λ_{ed} is displaced fluid mobility; k is effective permeability (m^2); and μ is fluid viscosity (Pa s) [2]. The stability of displacement, which is of key importance for macroscopic displacement efficiency, is ultimately determined by the mobility ratio (M) [2]. If M is less than or equal to 1 ($M \leq 1$), it is considered favourable, and displacement efficiency increases (**Figure 2**); however, if $M > 1$, the mobility ratio is seen as unfavourable [2] and residual oil will be inefficiently displaced.

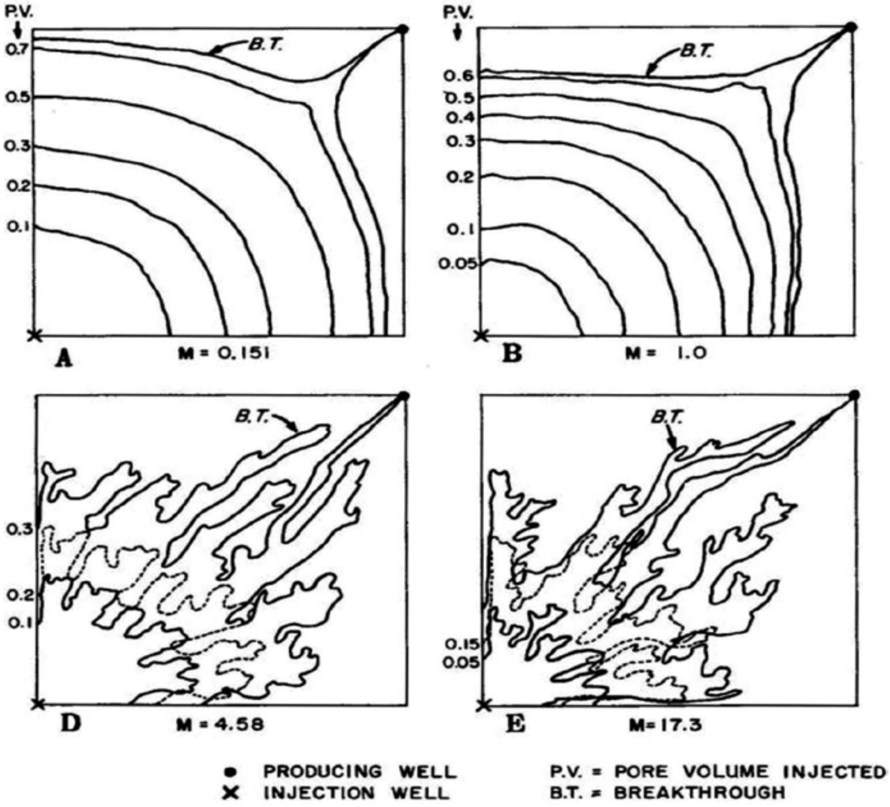


Figure 2. Displacement fronts during waterflooding for different mobility ratios and pore volumes injected until breakthrough [8].

Oil recovery efficiency is greatly dependent on the microscopic and macroscopic displacement efficiency. Generally, microscopic displacement efficiency measures the extent to which the displacing fluid mobilises the residual oil once in contact with the oil [1, 3, 9], and it is greatly controlled by factors such as rock wettability, relative permeability, IFT and capillary pressure [2]; note that a decrease in oil viscosity, IFT or capillary pressure of the displacing fluid can increase the microscopic efficiency [10].

Macroscopic displacement efficiency, otherwise known as volumetric sweep efficiency, measures the extent to which the displacing fluid is in contact with the oil-bearing parts of the reservoir (metre to hectometre scale, Eq. (4)) [1, 2, 9, 11], and it is influenced by the rock matrix heterogeneities and anisotropy, displacing and displaced fluid mobility ratio and injection and production well(s) positioning [1, 3]. The product of microscopic (E_d) and macroscopic (E_V) displacement efficiency yields the overall displacement efficiency (E) of any oil recovery displacement process [1].

$$E = E_d E_v \tag{4}$$

and

$$E_v = E_i E_a \tag{5}$$

where E_i is the vertical sweep efficiency [3] and E_a is the areal sweep efficiency.

Natural drive mechanisms recover oil during the initial or primary production stage of a reservoir by means of the natural energy present in the reservoir without the need of supplying any additional energy [12–15]. These natural mechanisms use the pressure difference between the reservoir and the producing well bottom [15–17]. The total recoverable oil using this method is considered inefficient, as recovery is usually less than 25% of the original oil-in-place (OOIP) [2].

Secondary recovery techniques are applied when the natural reservoir drive is depleted ineffectively and inadequately for augmenting production. This technique involves injection of either natural gas or water [3, 12] to stimulate oil wells and maintain reservoir pressure in the injection wells [2, 12]. The injected fluids act as an artificial drive to supplement the reservoir energy [9, 18]. Such fluids boost the flow of hydrocarbon towards the wellhead [19]. If the injected fluid is water, the process is usually termed waterflooding; if the injected fluid is gas, the process usually involves pressure maintenance operations [17, 20]. Gas-cap expansion into oil columns (wells) displaces oil immiscibly due to volumetric sweep-out [1]. Diverse methods are used for fluid injection into oil reservoirs to support the natural forces [17]. Recovery efficiencies in the secondary stage vary from 10 to 40% of the original oil-in-place [16, 17, 20]. Other gas processes, whose mechanisms entail oil swelling and viscosity reduction, or favourable phase behaviour [1], are enhanced oil recovery (EOR) processes. Tertiary recovery techniques otherwise called enhanced oil recovery (EOR) processes demonstrate enormous potential in recovering stranded oil trapped at the pore scale after primary and secondary recovery techniques by capillary pressure-driven snap-off [21], which leaves behind in the reservoir about one-third of OOIP [22]. The stranded oil is often located in regions considered inaccessible [23–25]. EOR methods can extract more than half of the total OOIP and significantly more than the primary and secondary recovery methods [26]. Notably, the impact of EOR on oil production is colossal as an increase in recovery factor by only 1% can yield 70 billion barrels of conventional oil reserves globally without the exploitation of unconventional resources [2]. In comparison to primary and secondary recovery methods, EOR undeniably is a better alternative as its contributions to global oil production entails a more economically feasible process.

2. Enhanced oil recovery (EOR)

Improved oil recovery (IOR) is often erroneously used in place of enhanced oil recovery (EOR). IOR and EOR are two different concepts: IOR is a wider concept that embroils ultimate recovery of oil by any means [2]. The EOR is mainly driven by the ability to recover more oil at an economically feasible production rate [27]. The EOR can be described as a subset of IOR

[28]. EOR uses several processes and technologies (**Figure 3**) to increase or uphold recovery from existing fields [29]. These processes often involve the injection of fluid(s) and most recently microbes into a reservoir. These fluids, in turn, supplement the reservoir natural energy for effective oil displacement into the producing well thus yielding an interaction between injected fluid and the reservoir rock/oil system that creates a favourable condition for oil recovery [1]. The key drive for EOR spins around its capability of turning residual cumulative oil into reserves with oil (million barrels) produced from existing fields [30–32], which is achieved by overcoming the physical forces confining hydrocarbons underground (**Table 1**) [1, 33].

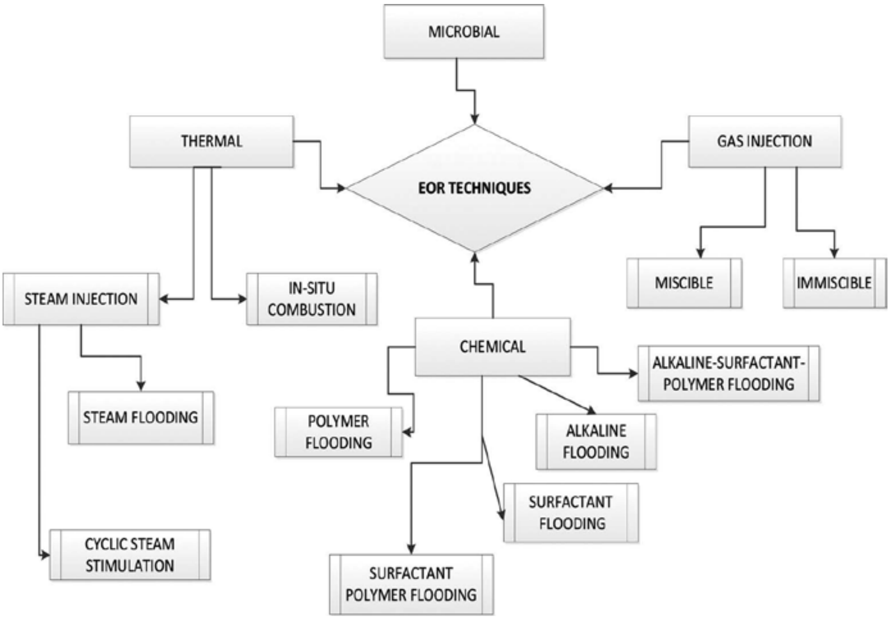


Figure 3. Classification of EOR techniques.

2.1. Thermal EOR (TEOR)

Oil recovery using thermal techniques involve the introduction of heat energy into oil reservoirs. Reservoir temperatures are substantially increased to achieve a significant decrease in oil viscosity [34], which yields a corresponding oil mobility effect. During the process, usually, a shift in rock wettability occurs, which enhances the chances for better oil recovery [29]. Current reports predict that only approximately 30% of the global oil reserves are light oil while the remaining 70% are heavy crude oils [34]. Increasing recovery of these heavier crudes can unlock approximately 300 billion bbl (Bbbl) of oil [35]; thus, TEOR is mainly applicable to heavy and viscous oil formations [34]. The TEOR is considered an effective technique for unlocking such heavy oil reservoirs. Several billion barrels of oil have been recovered using TEOR; for instance, more than 4 Bbbls of oil were produced in the USA through steam flooding

(SF) from 1980 to 2002 [36]. Despite its effectiveness in heavy oil formations, TEOR can also be deployed in light oil reservoirs [29]. TEOR is perhaps the best used EOR method for up surging production particularly steam flooding [37], although the environmental footprint is enormous when compared to conventional oil production [29].

EOR method	Mechanisms	Field applications	Technological development	Merits	Demerits	References
Thermal EOR (TEOR)						
In Situ combustion (ISC)	Air is injected into the reservoir as a dry process or with water (wet process) and oil ignition is performed alongside	India, Romania, Canada, U.S.	HPAI	• Suitable in both deeper and shallow reservoirs • Production is increased through a combination of mechanisms	• Eco-unfriendly (emissions from surface steam generation) • Mobility control issues • Expensive cost of operation	[1, 28, 29, 37, 41, 42, 54, 61, 63 – 66]
Steam injection						
• Cyclic steam stimulation • Steam flooding	Steam is injected into a well over a period Steam is injected into dedicated injection wells to displace oil towards a production well	Brazil, Venezuela, U.S., Indonesia, the former Soviet Union, Trinidad, Oman, China, Tobago, Canada,	THAI, Fast-SAGD, NCG-SAGD, OTSG, ST-EOR, GOGD, TAGOGD and TGD			
• Steam assisted gravity drainage (SAGD)	Oil is heated by circulating steam at a temperature that improves oil flow	Canada, Venezuela				
Chemical EOR (CEOR)						
Polymer flooding	Polymers are injected into the reservoir followed by water	Brazil, China, Oman, Canada, Suriname, Mexico, Argentina, Austria, U.S, India	PAM, HPAM, xanthan gum, HPAMAMPS, SAPc	• Inexpensive processes • Possibilities for incremental oil	• High tendency for chemical incompatibility • Issues with creating contact with the formation oil	[1, 25, 63], [68, 67, 86] [88, 109, 117–120]
Surfactant-polymer (SP) flooding	Separate surfactant slug and polymer slug are injected into the reservoir					
Surfactant flooding	Aqueous surfactants	Indonesia, Bahrain, U.S.				

EOR method	Mechanisms	Field applications	Technological development	Merits	Demerits	References
	solutions are injected into the reservoir					
Alkaline flooding	Aqueous solution of alkaline chemicals are injected into the reservoir	Hungary, India, U.S., Russia				
Alkaline-surfactant-polymer (ASP) flooding	Injections of blends of Alkali, Surfactants and Polymers in water into formation	China, U.S., India, Venezuela				
Gas EOR (GEOR)						
Miscible flooding	Injection of gas (CO_2, lean hydrocarbons) is performed to achieve miscibility with oil at pressures equal or higher than the minimum miscibility pressure (MMP)	CO_2–U.S., Canada, N_2 – U.S., Mexico Hydrocarbon gases – U.S., Venezuela, Libya, Canada	WAG, SWAG, PWAG, GAGD	• Production yields outweighs implementation expense • Significant amount of oil is recoverable especially with CO_2 flooding	• Presence of unfavourable mobility ratio • Limited gas sources and separation issues	[1, 25, 63, 68, 121, 132, 138, 140–142]
Immiscible flooding	Gas(N_2, CO_2, etc.) is injected below the MMP					
Microbial EOR (MEOR)						
Microbial	Microorganisms are injected into oil reservoirs for recovery purposes	Malaysia, India, Russia, Australia, Trinidad-Tobago, China, Former East Germany; Norway, Saudi Arabia; Poland; Canada, Oman, U.S., Romania, Hungary, Former Czechoslovakia	AMEC, Selective plugging, Indigenous microbiota stimulation, GEMEOR, EEOR	• Low operational costs • Eco-friendly	• Slow and low oil recovery capability • Requires multiple and often complex procedures	[14, 15, 19, 153, 162–165, 168, 169]

Table 1. Comprehensive breakdown of EOR processes.

2.1.1. Evolution of thermal EOR techniques

The early history of thermal recovery dates back to 1865 [34]; however, the first industrially significant TEOR project was conducted in 1931 close to Woodson, TX [38]. This was a steam injection test [34]. An advanced steam injection (cyclic steam injection) was later discovered upon release of accrued reservoir fluid pressure through a retrograde flow of injected steam; that coincidentally resulted in considerable oil production instead of the expected steam [34]. Subsequent large-scale TEOR projects were conducted in Tia Juana [39] and Mene Grande fields, both located in Venezuela. Upon discovery of the Venezuelan field (Mene Grande), steam flooding was selected as the optimal TEOR method, and a continuous steam injection over several weeks was deployed, with the wells shut in for short time intervals to support heat transfer within the reservoir [29].

2.1.2. Thermal EOR classification

The two key types of thermal EOR techniques are *in situ* combustion (ISC) and steam injection. Steam injection includes three basic categories [28]: namely, cyclic steam stimulation (CSS; huff-and-puff), steam flooding and steam-assisted gravity drainage (SAGD).

2.1.3. Mechanisms of TEOR techniques

2.1.3.1. In situ combustion

In *in situ* combustion, air is injected into viscous oil reservoirs to generate heat by burning a portion of the existing oil [28, 29, 40, 41]. The ISC can be a forward or reverse process, which is mainly dependent on the combustion front. The combustion fronts move in the direction of the injected air (forward combustion) or away from the air (reverse combustion). In practice, forward combustion process is generally adopted. Oil recovery is achieved using this process through the energy generated by the combustion reaction between the injected air and the oil:

- The oil is ignited and air is constantly injected to propagate the combustion front away from the well [10, 42].
- Reservoir fluids are displaced at the elevated temperatures (600–700°C) zone.
- The fluids advance towards the production wells [42] and the lighter ends are transported downstream which mixes with the crude oil.
- The heavy ends are burned resulting in the production of large amount of flue gases [10, 42].

Process benefits. ISC efficiently displaces oil in the regions contacted by the hot fluids in the advancing front, oil recovery rates are mostly high and this process is more cost effective than steam flooding as it uses air. There is a negligible effect of reservoir permeability on the ISC processes, which is effective for oil recovery in various formations as follows [10]:

- Deep reservoirs: depths up to 11,000 ft.
- Shallow reservoirs: <1500 ft.

- Light oils: >30° API.
- Heavy oils: 10–20° API.

Process limitations. Compressed air must be used and the operational variables are complex and difficult to control (i.e. controlling the advancing combustion front) [1]. The ISC process requires very high temperatures, in the order of 700°C and above. The high temperature of this process often damage production tubing and equipment (i.e. failure of pumps, valves, etc.) [43]. Furthermore, an adequate knowledge (i.e. rigorous laboratory evaluation) of the ISC dynamics is required for understanding the stability of the combustion front [44].

2.1.3.2. Steam injection

Steam injection entails the injection of steam into shallow, thick and permeable reservoirs containing high viscosity crude [32]. Steam injection processes include steam flooding, cyclic steam stimulation (CSS) and steam-assisted gravity drainage.

In steam flooding, steam is injected into dedicated injection wells, so that the reservoir fluids are driven towards a separate set of producers [45]. Oil recovery is achieved through:

- Constant injection of steam into the formation.
- The injected steam heats the chamber around the injection well.
- The chamber expands in the direction of the production well leading to oil viscosity reduction [46] and substantial oil displacement.

Process benefits. The introduction of steam into the reservoir efficiently displaces oil [47] by heating the oil to a temperature at which its viscosity is sufficiently decreased [48]. Steam flooding is the most applied EOR technique worldwide because it is very effective in rendering high oil recovery ratios. Higher sweep efficiency is achieved with steam flooding than with the application of cyclic steam stimulation or CCS.

Process limitations. Steam flooding is an expensive venture. Significant heat loss (i.e. heating of injection tubing, heating of overburden and under burden rock, etc.) occurs during the extensive steam injection periods [43]. Avoidance of sand plugging at the bottom hole [49], prevention of steam channelling [50] and improvement of steam sweep efficiency [51] are still key challenges of steam flooding operations, especially in super heavy oil formation. Early steam breakthrough at the producing wells decreases the rate of recoverable oil [49].

Cyclic steam stimulation is applied in three stages as follows [45, 52]:

- *Steam injection*. In this stage, adequate quantities of steam are injected during a pre-established period of time.
- *Soaking stage*. After the injection of the required volume of steam, the well is shut-in for several days or weeks to maximise heat transfer and heating of the oil that results in oil viscosity reduction [52, 53].
- *Production stage*. The well is open to production. Initially, a high oil flow rate is attained; however, it progressively decreases. Oil production might be supported by artificial lifting.

As the reservoir temperature declines, the oil flow rate drops significantly; at this point in time, another cycle of CSS is applied to re-attain the high oil production rates [52, 53]. CCS applied for several cycles, until commercial oil flow rates are obtained.

Process benefits. CSS is effective in reducing the viscosity of the oil due to the cyclic application of steam in the same well with potential for substantial oil recovery, especially in heavy oil reservoirs having thick pay zones (>15 m) [54]. However, the CSS oil recovery factor is low in comparison to steam flooding.

Process limitations. The CSS process is complex. Excessive heat loss occurs and the radius of the heated zone is insignificant [55]. Application of CSS in thin heavy oil (<6 m) reservoirs is uneconomical [54].

In steam-assisted gravity drainage (SAGD), steam is constantly injected using two horizontal wells—the upper steam injector well and the lower producer well (collects the heated oil and water). The injector and producer wells counterbalance the effect of high viscosity of the oil through prolonged steam (heat)—oil contact and provide the drive force for the movement of the oil towards the producer well [56]. SAGD is influenced by the gravity drainage of the heated oil and condensed water [57]. The process efficiency is predominantly controlled by fluid mobility. In SAGD, oil recovery is achieved when:

- The upper horizontal well injects steam into a chamber at a temperature that significantly reduces the viscosity of the heavy oil and/or bitumen, which improves oil flow.
- At the edge of the chamber, heat is released through condensation [57] and reduction in oil viscosity occurs.
- Then the heated oil drains by gravity through the steam chamber towards the production well (lower horizontal well) [58].
- The injection of steam and production of oil occurs concurrently and constantly [59]

and the oil production rate is controlled by the expansion of the steam chamber [56].

Process benefits. SAGD is very efficient in recovering bitumen and heavy oil. Oil production increases with the increase in oil pay thickness (>15 m) [60], thus production can be considered economical.

Process limitations. Possible loss of injected steam due to poor process control which can lead to low oil recovery rate. SAGD oil production is considered uneconomical in pay zones with thickness <15 m [61], due to the high steam-to-oil ratio (SOR) required.

This process is susceptible to low mobility control and rapid gravity segregation. The mobility control is considered a limitation as the steam viscosity is much lower than the viscosity of the oil and water. Similarly, the density of steam is much lower than the density of oil and water [1]. Thus, an upward migration of steam to the top of the reservoir often occurs and the steam overrides a larger part of the heavy oil zone. This issue can be partially controlled by heat conduction away from the steam contact [1]. Other limitations of the SAGD process are the significant production of CO_2 emissions during steam generation at surface facilities, heat losses and equipment problems due to the high temperature of the process [1].

2.1.4. TEOR field applications

TEOR, specifically steam injection, and *in situ* combustion have shown great potential worldwide. Steam injection projects have been reported in California, Indonesia, Oman, Alberta (Canada), Venezuela and the former Soviet Union [37]. Field trials of steam injection have been conducted in Brazil, China, Trinidad and Tobago [29]. CSS has been applied in California, Alberta and Venezuela. ISC projects have been reported in Romania, the USA, Canada and India [29]. SAGD is mainly carried out in Alberta, Canada for the recovery of bitumen. SAGD has also been tried in Venezuela, although it has not been very successful [29, 37].

2.1.5. Technological advancement in TEOR techniques

New areas of research have been considered to tackle fiscal and environmental issues related to TEOR processes (i.e. huge capital expenditures and significant generation of CO_2 emissions). These recent advances comprise the development or improvement of several TEOR process such as the Toe-to-Heel Air Injection (THAI) process [62], Fast-SAGD [60], Enclosed Trough Solar Once-Through Steam Generator (OTSG) EOR System [64], Solar Thermal Enhanced Oil Recovery (ST-EOR) [29], Gas-Oil Gravity Drainage (GOGD), Thermally Assisted Gas-Oil Gravity Drainage (TAGOGD), Tertiary Gravity Drainage (TGD) [65] and High-Pressure Air Injection (HPAI) [29, 63].

2.2. Chemical EOR techniques (CEOR)

In chemical EOR (CEOR) techniques, oil is recovered through the injection of chemicals [62, 66, 67]. CEOR is predominantly suitable for heavily depleted and flooded formations (i.e. mature reservoirs) [68]. Typical chemicals are polymers, surfactants, alkalis and formulated mixtures thereof [62, 33, 69]. The efficiency of such formulations is normally screened in laboratory studies [69– 71] and each chemical has different effects on oil production [72]. For example, the application of surfactants or alkali or its mixtures can substantially reduce the interfacial tension between brine and oil [69, 73–75]; significantly improving the microscopic sweep efficiency at the pore scale [76, 77]. Mobility ratios can be considerably improved by adding polymers to the injected water [62, 78]. The addition of polymer to the injection brine increases the viscosity of the aqueous phase, which leads to an improved macroscopic displacement, as water under-riding is lessened [79]. The addition of surfactants improves the microscopic displacement efficiency through: (a) the reduction of the oil-water interfacial tension [72, 80, 81] and (b) the production of oil-water emulsions [62], which mobilises residual oil. The addition of alkalis induces the *in situ* formation of natural surfactants by reacting with the acidic components contained in the crude oil (generally heavy oils). These natural surfactants function in the reservoir in the same fashion as synthetic surfactants [62, 82].

2.2.1. Evolution of chemical EOR

In the last few years, CEOR has been undergoing a rebirth. Since the 1960s, polymer flooding has been globally the most widely used of the three types of CEOR techniques [83]. CEOR has experienced significant chemical developments since its first applications in the 1960s and 1970s [83]. For example, micellar flooding in the 1970s and 1980s was very effective in light and medium oil reservoirs, where CEOR processes applied micellar floodings at surfactant concentrations ranging from 2 to 12% [83]. However, the concentrations of surfactant used have notably decreased to values ranging from 0.1 to 0.5% [84]; while at the same time, micellar floodings at these low surfactant concentrations have demonstrated significantly increased efficiency. In the face of the current oil price instability, interest in surfactant for CEOR processes, have maintained a constant growth trend [84]. However, at present, the high cost of surfactants makes very difficult the economic justification for field applications of surfactant flooding.

2.2.2. Chemical EOR classification

The most common CEOR techniques are polymer, surfactant, alkaline, surfactant-polymer (SP) and alkaline-surfactant-polymer (ASP) flooding.

2.2.3. CEOR techniques and oil recovery mechanisms

2.2.3.1. Polymer flooding

For several decades, hydrogel polymers have been used for mobility control. Likewise, polymers in combination with surfactants and alkalis have been applied over the years to improve both the microscopic and macroscopic sweep efficiency [85]. In recent times, several new polymers for EOR (**Table 2**) have been developed such as synthetic polymers (i.e. polyacrylamide or PAM) (**Figure 4**), hydrolysed polyacrylamide (HPAM), biopolymers (i.e. xanthan gum) and superabsorbent polymer composite (SAPC) [4, 66, 85].

Polymers	**Molecular weight**	**Polymer description**	**EOR application**	**References**
Hydrogel		• Non-newtonian or pseudo plastic fluids • The fluid viscosity is a function of shear rate	• Used mainly for mobility control • Used in combination with surfactants and alkali for improvement of sweep efficiency	[85]
Polyacrylamide (PAM)	>1 × 10^6 g/mol	• First synthetic polymer used for thickening aqueous solutions • The thickening potentials exist in its large molecular weight • >High adsorption capacity on mineral surfaces	• Increases the brine viscosity • Improves EOR performance	[4, 66, 85]

Polymers	Molecular weight	Polymer description	EOR application	References
Hydrolysed polyacrylamide (HPAM):	>20 million Da	• copolymers of PAM and polyacrylic acid (PAA) or acrylamide and acrylic acid • PAM is partially hydrolysed to form HPAM. This is achieved by reacting PAM with a base (sodium) to reduce the strong adsorbing behaviour of PAM • The degree of hydrolysis is usually in the range of 15–35%	• The most commonly used polymer for EOR • Oil recovery using HPAM is high owing to its viscoelasticity • Depending on the stability of the brine, HPAM can be used at a temperature up to 99 °C	[4, 66, 85]
Xanthan gum	$2\times50\times10^6$ g/mol	• A biopolymer produced by microbial (Xanthomonas campestris) action (through glucose or fructose fermentation) • Possess substantial hydrolytic degradation above 70 °C • Acts like a partially stiff rod with a fair resistivity to mechanical degradation • Xanthan gum for EOR is often in broth or concentrated form which makes it easy to dilute at suitable concentrations	• Effective for use in high salinity brine • Fairly compatibility with surfactants when used for EOR	[4, 85, 89]
Superabsorbent polymer composite (SAPC)		• Crosslinked hydrophilic polymers which have the potential to retain water in swollen form	• Effective for used as plugging agents in EOR processes	[85, 90]

Table 2. Effective polymers for EOR processes.

Among these polymers, HPAM (**Figure 4**) remains the most effective and commonly used polymer for enhanced oil recovery. According to Sheng [4], the effectiveness of HPAM relies in the following chemical features: (1) the lack of oxygen single bonds (-O-) in the polymer backbone (carbon chain) provides thermal stability; (2) the presence of non-ionic hydrophilic group (i.e. -$CONH_2$) promotes chemical stability and (3) the carboxyl group (-COO-) resulting from the hydrolysis of the amide groups reduces the adsorption tendency of HPAMs onto rock surfaces and increases its viscosity.

Other characteristics that makes HPAM very attractive for EOR includes: (1) fairly easy application with great potential for incremental oil at standard reservoir conditions (i.e. low temperatures and low salinity and hardness concentration); (2) availability of the polymer in various molecular range (>20 million Da); (3) the cost of the polymer is relatively low; and (4) its viscosifying and psychochemical characteristics [85].

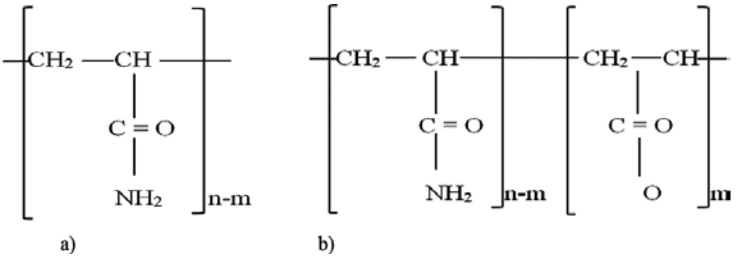


Figure 4. Structure of: (a) polyacrylamide (PAM), and (b) partially hydrolysed polyacrylamide (HPAM) (refer to **Table 2**).

Xanthan gum is a biopolymer also commonly used for EOR applications. The main limitation of this biopolymer is its vulnerability to microbial degradation. Salt compliant microbes (aerobic and anaerobic) have the potential to degrade the xanthan gum chains, which results in viscosity loss [86–88]. Therefore, biocides are injected alongside with xanthan gum to avert microbial degradation [85]. However, xanthan performs remarkably well in brines having high salinity concentrations [85]. Generally, high salinity brines (i.e. 10,000 ppm TDS) polyacrylamide co-polymers shows lower viscosities than biopolymers [4]. Nonetheless, HPAMs have better potential for reducing the water relative permeability than xanthan during flow through formation rocks.

In polymer flooding, polymers (dissolved in water) are injected into the reservoir, followed by a long-term waterflooding, which is performed to drive the slug and the oil bank in the direction of the production wells. The addition of polymer to the injected brine increases the viscosity of the aqueous phase and reduces the effective permeability to water due to polymer retention (adsorption and mechanical trapping) in the formation rock.

The main objective of polymer flooding is to lower the mobility ratio of the waterflooding process. It is well established that the lower the mobility ratio, the more stable the displacing fluid front, and the more efficient the macroscopic displacement process. Therefore, mobility ratio (M) should be controlled to values less than one ($M < 1$) to prevent the onset of viscous fingering of the water phase through the oil phase, which will result in unswept regions, where oil is left behind the displacement front [1, 77].

The overall mechanisms of oil recovery by polymer flooding are as follows:

- Increasing of the water viscosity.
- Decreasing of the effective permeability to water due to polymer retention.
- Decreasing of the water-oil mobility ratio that improves the macroscopic sweep efficiency.

Process benefits. Polymers are effective brine viscosifying agents [85] and successfully reduced the effective permeability to brine (i.e. polymer retention). Overall, polymer flooding is a cost-effective EOR process.

Process limitations. Some of the limitations of polymer flooding are their susceptibility of polymers to thermal (i.e. high temperature reservoirs), chemical (i.e. high salinity and hardness concentration in the injected and formation brine), mechanical and bacterial degradation. Some polymer systems are incompatible with the reservoir fluids and conditions (i.e. temperature). The application of polymer flooding in low permeability rocks may cause problems of injectivity and formation plugging [85].

2.2.3.2. Surfactant flooding

Surfactants are amphiphilic in nature (hydrophobic and hydrophilic) and are soluble in water and organic solvents. Surfactants effectively reduce the interfacial tension (IFT) between oil and water (i.e. brine). Four basic categories of surfactants (**Table 3**) exist: anionic, cationic, non-ionic and zwitterionic [91, 92].

Surfactants	Surface charge	Mechanism
Anionic	Negative	• Most globally used surfactant for EOR • Displays low adsorption on reservoir rock surfaces (e.g. Sandstone) • Effective wettability alteration agent • Effective IFT reduction agent • Low cost in comparison to Cationic
Cationic	Positive	• Effective for wettability alteration in carbonate rocks than in sandstone. • Considered relatively unsuitable for application in sandstone (negatively charged) reservoirs due to its strong adsorption behaviour onto the rock surface
Nonionic	No ionic charge	• Mainly function as a copolymer. • Effective for improving phase behaviour of a system • Tolerant to high salinity and hardness • Fairly effective IFT reduction agent
Zwitterionic	Positive and negative	• Effective for IFT reduction • The effect of electrolytes, pH and temperature changes on zwitterionic is negligible • Exhibits better temperature resistance and salt tolerance than other surfactant types

Table 3. Effective EOR surfactants [4, 194].

In surfactant flooding applications, a dilute aqueous surfactant solution [93] is injected into the reservoir. Mechanistically, the injected surfactant migrates to the oil-water interface reduces the interfacial tension (IFT) between oil and water and essentially increases the miscibility of these phases [3]. To put this into perspective, in a typical waterflooding process, IFT is approximately 30 mN/m; the addition of small concentrations of surfactant (in the range of 0.1–5.0 wt%) to the injected water [1–3, 33, 94, 95] can significantly reduce IFT to values of 0.01 mN/m or lower [33]. The critical micelle concentration (CMC), phase behaviour and oil solubilisation ratio [97] are key parameters for the characterisation of the efficiency of the surfactant formulation. For effective oil displacement:

- Dilute aqueous surfactant solutions are injected in slugs.
- The injected slugs must attain ultra-low IFT.
- This leads to the mobilisation of the residual oil and creation of oil banks, which allows the continuous phase flow of oil and water [96].

Process benefits. Effective reduction of the interfacial tension between brine and water that significantly enhances the microscopic sweep efficiency.

Process limitations. The achievement of ultra-low IFT for effective residual oil mobilisation is a complex process. Large amounts of surfactants are required to achieve substantial oil recovery. The viscosity of the surfactant formulation is often lower than that the viscosity of the oil, thus, to augment the viscosity of the surfactant slug, the addition of polymers to the surfactant formulation is required. The high cost of surfactants makes its deployment in the field highly dependent on oil price [97].

2.2.3.3. Alkaline flooding

Alkaline flooding involves the injection of an aqueous solution of alkaline chemical such as sodium hydroxide, sodium carbonate or sodium orthosilicate in a slug form [2, 98, 99] (**Table 4**); the most commonly used alkaline chemical is sodium hydroxide [3].

Alkaline	Characteristics
Sodium hydroxide NaOH	• Most commonly used alkaline for EOR • Used for IFT reduction • Corrosion and scale formation issues
Sodium orthosilicate Na_4O_4Si	• Reduces water hardness through formation of silicates which are less soluble than the hydroxides • Better IFT reduction potentials than sodium hydroxide in hard water • Precipitation or scale formation issues
Sodium carbonate Na_2CO_3	• Weaker alkali in comparison to sodium hydroxide and sodium orthosilicate • Corrosion and scale formation issues

Table 4. Effective alkaline chemicals for EOR [4].

During alkaline flooding, the alkaline solution and organic acids present in the crude oil react to form natural surfactants *in situ*, which cause the reduction of IFT between the brine and oil. Natural surfactants induce the formation of oil and water emulsions and wettability alteration of the reservoir rock [3, 93, 100]. All these physicochemical interactions occur at the oil-water rock interfaces, which invariably improves oil recovery.

Process benefits. Alkaline flooding shows potential for heavy oil recovery in thin formations [101]. This process promotes effective IFT reduction and crude oil emulsification. Overall, alkaline flooding is characterised for low operational costs.

Process limitations. Scale formation is a serious issue during alkaline flooding. Furthermore, the low viscosity of the alkaline solution is associated with the occurrence of unfavourable fingering and poor volumetric sweep efficiency [102].

2.2.3.4. Surfactant-polymer (SP) flooding

In surfactant-polymer flooding, separate surfactant and polymer slugs are injected into the reservoir. The alternate injections of surfactant and polymer slugs have the potential to sweep larger reservoir volumes and to increase oil displacement efficiency.

The mobility control is established during SP flooding by injecting the chemical slugs according to the following injection scheme: surfactant slug, polymer slug [103], polymer buffer (to protect the integrity of the polymer slug) and chase water [104].

Accurate formulation of the surfactant-polymer (SP) mixture can promote capillary number increase (due to the presence of surfactants through IFT reduction) and reduction in mobility ratio. However, an incompatible SP formulation can cause surfactant and polymer phase separation even when oil is not present [103]. Two essential factors for consideration during SP flooding are: (a) IFT reduction and (b) viscosity increase [13, 104, 105]. In addition, the effective permeability to water is reduced due to polymer retention in the formation rock [106]. Therefore, an overall improvement of mobility ratio and sweep efficiency [106, 107] is achieved rendering incremental oil recovery [108].

Process benefits. Accurate SP formulation can achieve ultra-low oil-brine IFT, which promotes effective displacement of residual oil saturation.

Process limitations. The main limitation of the SP flooding process is chemical incompatibility among the additives and brine (injection and formation brine).

2.2.3.5. Alkaline-surfactant-polymer (ASP) flooding

ASP flooding uses alkali-surfactant-polymer cocktails for further improvement of oil recovery efficiency [107, 109]. The key reasons for the combination of the three chemicals are IFT reduction and mobility ratio improvement [2]. Alkali decreases surfactant adsorption onto rock surface through an increase of the negative charge density at the rock surface yielding a more water-wet surface [95, 110]. Surfactant decreases the IFT [111] between oil and brine, which promotes oil mobilisation and oil bank formation, whereas polymer offers mobility control [106]. The amount of chemical consumed per unit volume of oil produced during ASP flooding is usually low when the three chemical slugs (alkaline, surfactant and polymer) are injected in sequence or as a single slug [2, 100].

Process benefits. ASP is a cost-effective process. The synergistic effects of the ASP mixture make this process attractive for EOR applications.

Process limitations. Some of the limitations of the ASP process are related to issues with chemical separation, emulsions instability and scale formation that could make the process complex.

2.2.4. Technological advancement in CEOR techniques

Research has led to recent advances in CEOR aiming to improve the economic feasibility of the field application of CEOR processes. Particularly, the development and improvement of effective polymers for EOR is noticeable. Some of these polymers include polyacrylamides (PAM) [66, 85], hydrolysed polyacrylamide (HPAM—the most commonly used polymer) [66, 85], biopolymers (i.e. xanthan gum) [4, 85] and superabsorbent polymer composite (SAPC) [86]. Other recent modified polymers are hydrolysed polyacrylamide-acrylamido methyl propane sulfonic acid (HPAM-AMPS) co-polymers, and sulphonated polyacrylamides, which are produced as powders and self-inverting emulsions that are suitable for high temperature applications ranging from 104 to 120°C [85].

2.2.5 CEOR field applications

CEOR projects implemented in the United States in the 1980s did not show technical and/or economic success. However, in the last decade CEOR successes, specifically polymer flooding, which is the most applied CEOR method worldwide [112], has been reported in China [28, 113], along with ASP flooding successfully implemented at pilot and commercial scale in the Daqing, Xinjiang and Shengli oil fields in China [114].

Polymer flooding has also been reported in Canada (East Bodo field), Oman (Marmul field), Suriname (Tambaredjo field) and Mexico (Vacuum field) [115]. Other countries that have reported successful applications of ASP flooding are India (Viraj field), Venezuela (Lagomar LVA field) and in the United States (Cambridge Minnelusa field, the West Kiehl and Tanner fields in Wyoming, and Lawrence field in Illinois) [115, 116]. Surfactant flooding has been reported in Indonesia (Baturaja formation in the Semoga field), Bahrain (Mauddud field), Texas (Yates field and the Cretaceous Upper Edwards reservoir) and Wyoming (Cottonwood Creek field). Surfactant-polymer flooding has been reported in China (Gudong field) [115]. Alkali flooding has been reported in Hungary (H field), India (North Gujarat field), Russia (W field) and the United States (Whittier field in California) [115].

2.3. Gas injection EOR (GEOR) technique

In EOR gas injection (**Figure 5**), oil is displaced towards the production wells by injecting gas. Two predominant factors determine the success of this process: (a) the displacement efficiency and (b) the sweep efficiency. The displacement efficiency is the percentage of oil displaced by the injected fluid, whereas sweep efficiency accounts for the reservoir volume contacted (swept by) the injected fluids [12]. Gases commonly used for GEOR are carbon dioxide, hydrocarbon gases and nitrogen [62]. Among these gases, CO_2 is the most frequently applied and it accounts for over 50% of the GEOR production [67, 117]. For instance, in 2009, Ferguson et al. [118] reported that 101 GEOR projects in the US produced approximately 250,000 barrels of oil per day. In the United States, CO_2-EOR has been considered the best GEOR method to produce incremental EOR [119]. Nevertheless, GEOR processes are often associated with viscous and density fingering [1, 120].

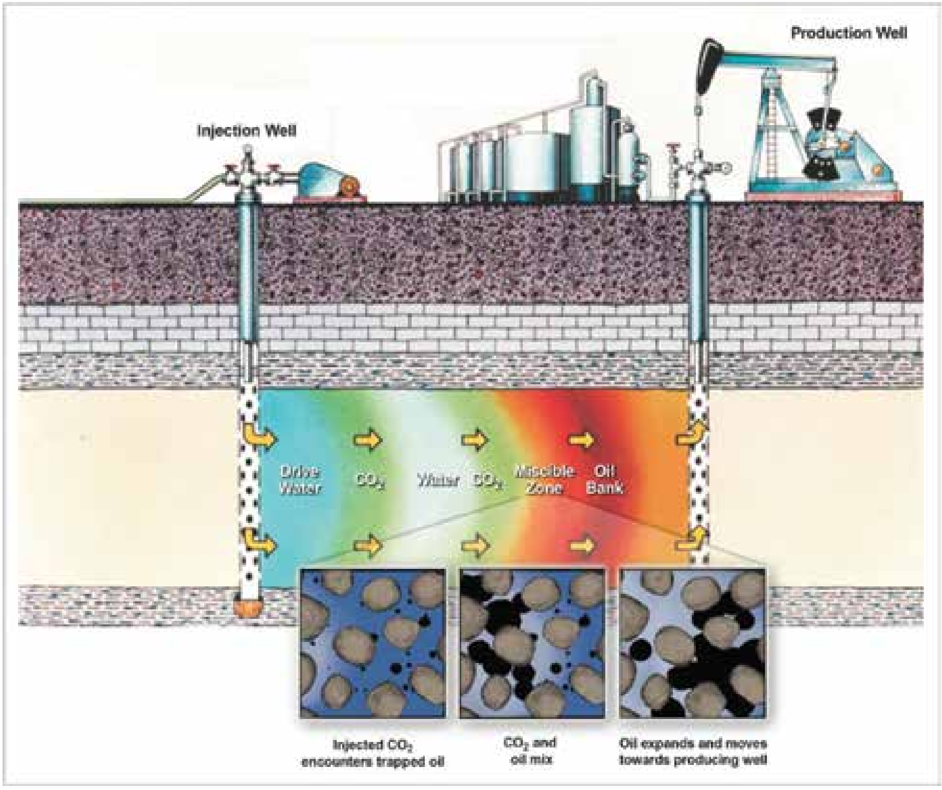


Figure 5. CO_2 gas injection EOR [121].

2.3.1. *Evolution of gas injection EOR*

Gas injection was first developed in the United States, where it is still largely applied. Gas injection is one of the oldest fluid injection processes implemented for pressure maintenance. The first gas injection project was a pressure maintenance job initiated in 1864, after drilling the Drake well in Titusville, Pennsylvania. The project was aimed at boosting fast oil production [12]. In 1930, the earliest gas drive project was successfully performed in West Texas [122]. In the 1970s, another gas injection trial was performed at the Surry County, Texas [119]. In the past two decades, gas injection has gained significant interest and recent projects are focused in combining hydrocarbon recovery with CO_2 geo-storage [123]. Geological storage of CO_2 (CO_2-EOR) is one of the most promising technologies for promoting ultimate oil recovery, while it simultaneously alleviates the problem of greenhouse gas accumulation in the atmosphere [124, 125]. CO_2-EOR has been extensively deployed since the mid-1980s in the Permian Basin of West Texas with high profit margins achieved over the past three decades [126].

2.3.2. *Types of gas injection*

The two main gas injection processes involve miscible and immiscible gas flooding.

2.3.3. Mechanisms of gas injection for EOR

2.3.3.1. Miscible flooding

In miscible gas flooding, gas completely mixes with the crude oil through single or multiple contacts between the gas phase and the crude oil phase. The gas injected reaches miscibility with the crude oil at or above the minimum miscibility pressure (MMP) [127]. MMP is the minimum pressure at which crude oil becomes miscible with the injected gas at the reservoir temperature [121]. MMP is a determining factor during miscible gas (e.g. CO_2) flooding, as displacement efficiency is highly dependent on it [128]. CO_2 achieves miscibility with crude oil through multiple contacts between the oil phase and the CO_2 phase. In this mechanism of multiple contact miscibility, light hydrocarbons (lighter-low carbon, low density) from the crude oil are transferred (vaporised) into the CO_2 phase. Progressively, the gas phase becomes richer in the vaporised light hydrocarbons, which continuously change the composition of the gas phase that eventually becomes heavier and denser. This heavier gas phase condenses into the crude oil zone ahead of the displacement front (i.e. miscible zone) causing the reduction in crude oil viscosity and density [121]. As miscibility occurs between the residual oil and the injected CO_2, the IFT between the gas and the oil phase becomes zero, thus this mixture is displaced as a single phase from the pores of the rock towards the producing well [121]. Very low residual oil saturation is achieved as the interfacial tension (IFT) in the miscible zone reduces to zero, thus there is no interface between oil and gas anymore [62, 129].

Process benefits. Miscible gas injection increases the overall displacement efficiency, minimises residual oil saturation, promotes ultra-low (near zero) IFT and increases oil production significantly. Based on operational costs, miscible gas flooding is usually more cost effective [115] in comparison to TEOR flooding methods.

Process limitations. Miscible gas injection requires higher (expensive) operational costs (i.e. high gas compression costs). The changes in the crude oil density during the miscibility process can alter the flow path of the oil during the period when the lighter hydrocarbons vaporise into the CO_2 gas phase or when the rich gas phase (CO_2 plus light hydrocarbons) dissolves (condenses) into the oil phase [130]. Failure in miscibility may occur if pressure is not at or above the MMP leading to an unsuccessful miscible displacement process.

2.3.3.2. Immiscible flooding

Immiscible gas flooding entails the injection of gas below the MMP. Below the MMP, there is no miscibility between CO_2 and oil [174]. Technically, immiscible flooding produces about half of the recovery of miscible gas flooding [131]. During immiscible flooding, incremental oil recovery is mainly achieved through oil swelling, which improves the macroscopic displacement efficiency [127]. At microscopic level, three-phase (oil-gas-water) flow is observed with a complex interplay of the different phases [63, 132, 133]. Although these microscopic processes are still poorly understood, there is clearly significant potential to further improve oil recovery at the pore level. Notably, constant immiscible gas flooding with gases such as CO_2 is more favourable to light oil than heavy oil reservoirs [134]. To improve recovery in heavy oil formations using CO_2, co-injection or the injection of water alternate gas, known as the WAG process, is performed to somehow control viscous fingering, gas channelling and early gas breakthrough. Upon injection of water and gas into the reservoir, a portion of the injected gas (CO_2) usually dissolves in the oil that leads to oil viscosity reduction [134]. A recent advancement in immiscible flooding is polymer water alternate gas (PWAG) for overcoming viscous fingering and improvement of sweep efficiency [134].

Process benefits. Immiscible gas injection improves oil displacement efficiency. The oil recovery potential from the application of this process is higher from light oil formations [134].

Process limitations. Viscosity ratios of the injected gas (i.e. CO_2) to oil (light or heavy oil) are unfavourable [134] triggering the occurrence of gravity override and viscous fingering through permeable zones [134], early gas breakthrough and poor sweep efficiency [135]. This process renders poor oil recovery potentials in heavy crude oil formations in comparison to thermal EOR.

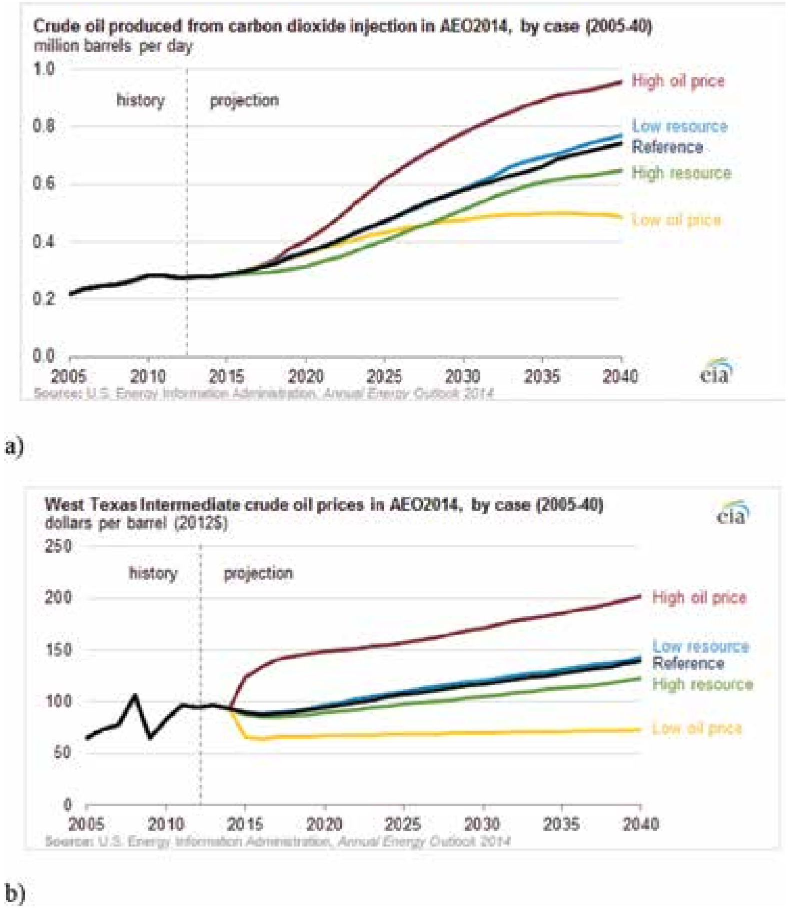
2.3.4. Technological advancement in GEOR techniques

Advances in gas injection EOR include water alternate gas (WAG) injection; the simultaneous water alternate gas injection (SWAG) [136], polymer water alternate gas (PWAG) injection [134], the development of CO_2 gas membrane separation technology and field applications of immiscible gas-assisted gravity drainage (GAGD) [137, 138].

2.3.5. GEOR field applications

As previously mentioned, CO_2, N_2 and hydrocarbon gases are used in GEOR. Technically, the injection of carbon dioxide (CO_2) and hydrocarbon gases achieve higher oil recovery efficiencies. However, natural gas is expensive and there is growing concern about its impact as greenhouse gas; thus, CO_2 is considered the most appropriate gas for injection, although oil recovery using CO_2 is also a costly venture. Certain costs are often associated with its deployment such as: (a) cost of the CO_2 itself which can add about $20–30 per barrel of oil produced [139]; (b) cost of surface facilities for separation of the CO_2 from the production streams and compressing it back into the oil reservoir; and (c) financial costs for the time delay associated with the re-pressurising of old reservoirs [139]. According to the US Energy Information Administration, Annual Energy Outlook (AEO) 2014 report (**Figure 6**), the application of CO_2 for EOR purposes appears to be dependent on oil prices. Hence, an economic feasibility study is recommended to ascertain whether or not a specific CO_2-EOR project is viable. For instance, an analysis between crude oil produced from CO_2 injection and the cost of injection using a case study was conducted for current, and forecasted (**Figure 6a** and **b**) projects to examine how oil prices would affect the feasibility of field implementation of CO_2-EOR. **Figure 6(a)** shows oil production in million barrels per day using CO_2-EOR and **Figure 6(b)** shows the West Texas Intermediate (WTI) crude oil prices (past and future projections) for different cases: a reference case that accounts for 10% of total US crude oil production, low and high oil prices and high and low oil and gas resources. **Figure 6(a)** clearly shows the effect of crude oil price and hydrocarbon resources on crude oil production. At low oil prices, the WTI crude oil is expected to reach $73 per barrel by 2040 (**Figure 6b**) with CO_2-EOR production expected to reach 480,000 barrels per day by 2040, which is less than 35% of the reference case. Therefore, this scenery will not favour the field application of CO_2-EOR [139]. While in the high oil price case ($202 per barrel that is 45% higher than in the reference case), expectations are that oil production will be 960,000 barrels per day by 2040 (30% higher than in the reference case of 740,000 barrels per day), which favours the profitable application of CO_2-EOR in old oil fields [139]. At the reference case, 10% of total US crude oil production is achieved using CO_2-EOR against the low oil price case (8%) and high oil price case (12%) [139]. **Figure 6(b)** also indicates that the low oil and gas resource case projects are more profitable than the high oil and gas resource case projects [139].

Despite the high production costs associated with CO_2-EOR processes, CO_2 injection into oil reservoirs at high pressure reduces the oil viscosity and causes oil to swell, which in turn yields an increase in cumulative volume of produced oil and in the percentage of recoverable oil [139]. In the United States, large oil production has been achieved through miscible CO_2



Source: U.S. Energy Information Administration, Annual Energy Outlook 2014

Source: U.S. Energy Information Administration, Annual Energy Outlook 2014

Figure 6. CO_2-EOR projected dependence on oil price. (a) CO_2-EOR as a function of time, oil price and hydrocarbon resources. (b) West Texas Intermediate (WTI) crude oil price as a function of time, number of fields that can profitable produced oil using CO_2-EOR technology and hydrocarbon resources [139].

flooding, specifically from West Texas, Wyoming and Mississippi oil fields, where natural sources of CO_2 are readily available at affordable price [131]. In North America, the majority of miscible CO_2 flooding projects are currently taking place in carbonates reservoirs in the Permian Basin of West Texas and in Saskatchewan, Canada (Weyburn-Midale oil field) [28]. CO_2-EOR successes in the United States are due to the readily available CO_2 sources located adjacent to oil fields, whereas in Canada, the CO_2 sources are located in North Dakota [28]. Prospective candidate oil fields for CO_2-EOR have been determined in Louisiana, Texas, the Gulf Coast, Mississippi, Alabama and in onshore areas of Florida [131]. Nevertheless, these fields are located away from existing natural CO_2 sources [131]. The incremental CO_2-EOR oil production from different regions in the United States (see **Table 5**) was 282,000 bpd in 2012; while in 2014 a constant oil production rate of 280,000 bpd was attained in 2014. A production rate growth to 615,000 bpd is expected by 2020 [140].

Year	Region / CO_2-EOR oil production in thousands barrels per day (MBPD)				
	Rockies	Gulf coast	Mid-continent	Permian basin	Total production
2012	36	43	17	186	282
2015	55	73	37	241	405
2020	103	153	58	301	615

Table 5. USA regional CO_2-EOR oil production projection [140].

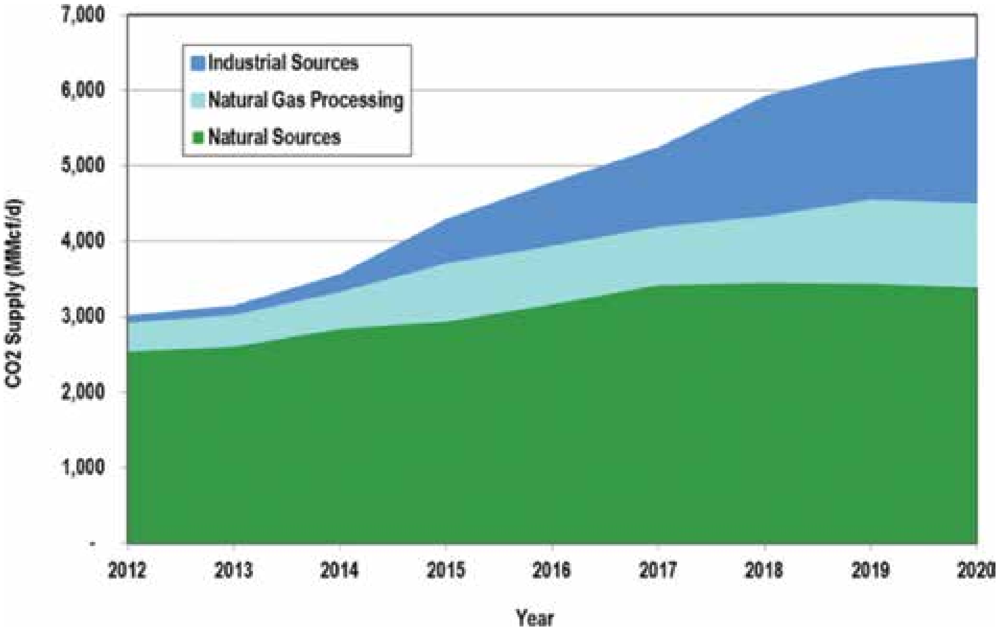
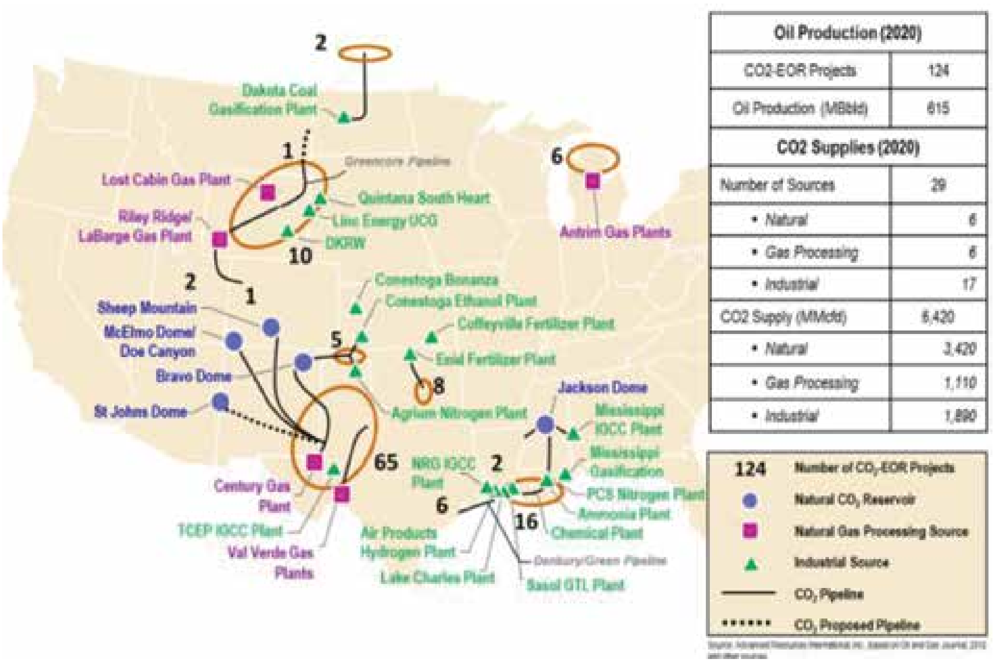


Figure 7. U.S. EOR supply and storage of CO_2 for EOR [140].

In the United States, the utilisation of CO_2 from natural gas processing and other industrial CO_2 sources for EOR amounted to 0.4 MMcf/d in 2012 [139]. It is predicted that by 2020, the volume of CO_2 will reach approximately 6.4 MMcf/d (**Figure 7**) and the key CO_2 sources will be obtained from industrial plants along the Gulf Coast and natural CO_2 sources. **Figure 8** displays the projected sources of CO_2 for EOR operations by 2020.



Oil Production (2020)	
CO2-EOR Projects	124
Oil Production (MBbl/d)	615
CO2 Supplies (2020)	
Number of Sources	29
• *Natural*	6
• *Gas Processing*	6
• *Industrial*	17
CO2 Supply (MMcfd)	6,420
• *Natural*	3,420
• *Gas Processing*	1,110
• *Industrial*	1,890

Figure 8. Projected CO_2-EOR operations and CO_2 sources by 2020 [140].

However, in the absence of a local CO_2 market, hydrocarbon gases, which are also excellent solvents for light oil reservoirs, can be used for oil production augmentation. For instance, hydrocarbon gases have been applied in Libya, Alaska, Canada and Venezuela [28]. Other gases aside CO_2 and hydrocarbon gases have been moderately applied. In the 1950s, N_2 gas was used for well completion and well workover processes [141]; N_2 has also been extensively used in oil field operations such as reservoir pressure maintenance, gas lift and gas cycling [111]. Most recently, N_2 has been used as a substitute for CO_2 due to its inert and noncorrosive nature. N_2 is most suitable for deep light to medium oil reservoirs [2, 111, 113] with a proven high recovery rate of about 45–90% of the original oil-in-place (OOIP) [111]. N_2 is considered economically viable for oil recovery by miscible gas displacement in high-pressure reservoirs where the high cost and poor accessibility to CO_2 and natural gas are an issue (**Figure 9**) [111, 142].

Miscible displacement conditions can be achieved using N_2 at high pressure, alongside with the reduction in oil viscosity [143]. N_2 gas injection has been reported for the Hawkins Field (Texas), Cantarell Field (Mexico) and Elk Hills (California) [144].

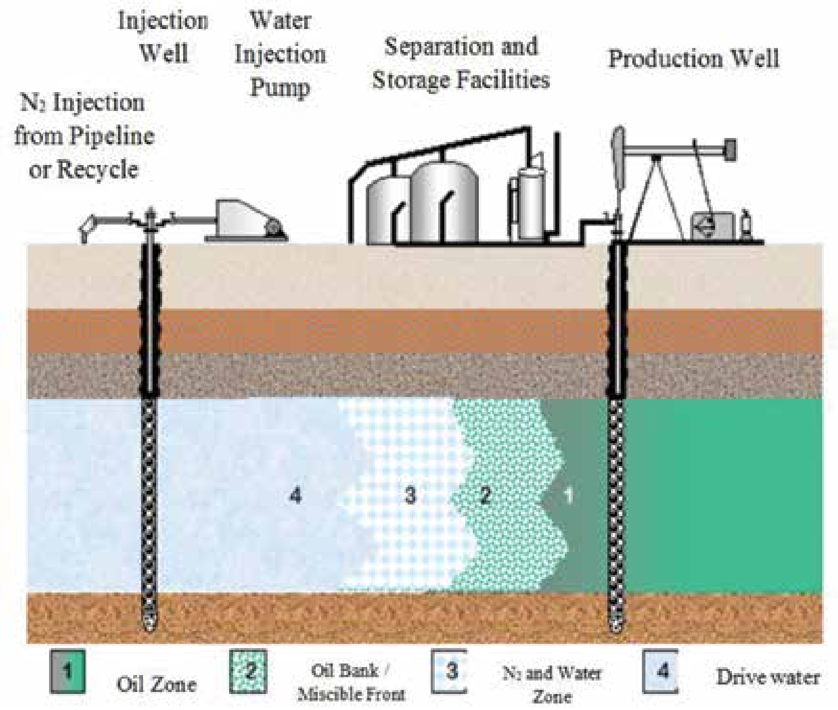


Figure 9. Nitrogen gas displacement EOR [111].

2.4. Microbial EOR

2.4.1. Microbial EOR techniques (MEOR)

In MEOR, indigenous or exogenous bacteria can be activated or injected into the reservoir to generate metabolic chemicals that interact with the crude oil and increase oil production [19]. For these applications, bacteria should be small, spherical and less than 20% of the size of the pore throats in the formation [145]. Small cell size (between 0.5 and 5.0 μm) penetrates easily through the reservoir porous medium [146]. Typically, mixed microbial populations are used in combination with metabolic products such as solvents, acids or gases to increase recovery and prolong the life span of the oil wells [14, 15, 19]. These metabolic products are produced by different bacteria (microbes) and exhibit different functionalities in MEOR processes Solvents such as acetone, butanol and propan-2-diol (produced by *Clostridium, Zymomonas* and *Klebsiella*) reduce oil viscosity and thus improve oil mobility [147, 148]. *Clostridium, Enterobacter and Methanobacterium* produce methane and hydrogen, which reduce IFT, oil viscosity [149] and increase oil mobilisation. Among several microbes used for MEOR processes. *Clostridium* microbes are the most applicable owing to their resistant endospores that enable survival at unfavourable conditions [150]. *Bacillus* strains are also effective MEOR agents [19, 20].

2.4.2. Evolution of microbial EOR (MEOR)

The MEOR process was first proposed by Beckmann in 1926, though it was brought to recognition in the 1940s through the work by ZoBell [151]. The first MEOR implementation happened in 1954 in the Lisbon fields in Union County, Louisiana, USA [14, 55]. The acceptance of MEOR as an oil recovery technique found worldwide resistance for decades. One of the reasons was that microbiology was less than 100 years old at the time this EOR technique was proposed. Therefore, the effectiveness of the MEOR process was viewed as a mere curiosity [19]. Prior to the 1940s university laboratories conducted MEOR research [145]. These research efforts continued and eventually led to MEOR growth from extended laboratory work in the 1980s to field level in the 1990s [19].

2.4.3. Mechanism of MEOR

MEOR involves the application of bacteria in oil reservoir for recovery purposes. The bacteria are mostly naturally occurring bacteria in reservoir rocks, hydrocarbon utilising or non-pathogenic [16]. These bacteria produce desired EOR chemicals *in situ* through metabolic reactions [19], that results from multiple biochemical process steps to generate the EOR chemicals [14, 15]. Nutrients (e.g. fermentable carbohydrates) are injected to provide favourable conditions for microbial metabolism [15], which results in the production of biosurfactants, biopolymers and gases (**Table 6**) [19].

MEOR agents (Microbes)	**Functionality**
Biosurfactants (i.e. Bacillus, Arthrobacter)	• IFT reduction between oil and water • Promotes oil emulsification owing to reduced IFT • Improvement of residual oil displacement • Effective for wettability alteration
Biopolymers (i.e. Bacillus, Xanthomonas)	• Water viscosity can be greatly improved which promotes mobility control • Effective for selective plugging • Used for modifying viscosity of the formation water and injectivity profile
Bacterial consortia (**Biogases:** Clostridium, Enterobacter; **BioSolvents:** Clostridium, Zymomonas; **Bioacids**: Clostridium, Enterobacter)	• Produces gases such as N_2, CH_4, CO_2, and H_2 that are effective in promoting oil viscosity reduction, IFT reduction, and oil swelling • Produces solvents such as alcohols and ketones which dissolves in oil and promotes IFT reduction and oil emulsification • Produces acids that promotes dissolution of clays increasing porosity and permeability
Biomass (i.e. Bacillus, Xanthomonas)	• Effective for selective plugging within the porous media • Effective for altering rock wettability • Effective for the partial degradation of crude oil • Displaces oil through bacterial growth between the oil and the surface of rock and water

Table 6. Effective agents for MEOR adapted from [14, 19].

Biosurfactants. Biosurfactants are biodegradable and more effective in emulsifying aqueous hydrocarbon mixtures than synthetic surfactants [152]. Biosurfactants can be produced in bioreactors *ex situ* and injected as an aqueous surfactant formulation into the reservoir. As surfactant migrates towards the oil-aqueous interface, IFT is reduced and capillary number increases displacing and recovering residual oil [19, 152].

The production of *in situ* biosurfactants takes place by injecting the biosurfactant-producing microbes into the formation ensuring proper propagation of the microbes into the oil reservoir [153]. Selected nutrients are also injected to stimulate the growth of the biosurfactant-producing indigenous microbes in the reservoir [152].

Biopolymers. Biopolymers are mainly used for selective plugging of high permeability thief zones. In this MEOR application, bacteria in aqueous solutions are injected into the formation that preferentially flows through the high-permeability pathways, where the growth of biomass plugs the pore throats, leading to permeability reduction [19]. Plugging of high permeability thief zones diverts waterflood towards the lower permeability oil saturated areas.

Bacterial consortia. Bacterial consortia are used for the selective production of biogases (i.e. methane, carbon dioxide and hydrogen), biosolvents (i.e. acetone, ethanol, 1-butanol, butanone, etc.) and bioacids (i.e. acetic, propionic, butyric, etc.). In a pressure-depleted formation, biogases assist in pressure build-up and at high pressures, biogases can dissolve within the oil phase reducing its viscosity [19]. Bioacids are capable of dissolving carbonate rocks leading to porosity and permeability increase in the oil formation [19, 147]

Process benefits. MEOR is environmentally friendly as the MEOR bioproducts are biodegradable [14], low oil production costs, MEOR is not dependent on oil price like the conventional CEOR processes and MEOR consumes less energy than the TEOR processes [19, 154]. MEOR is economically attractive for application in marginally producing oil fields because the injected bacteria and nutrients are low priced [14].

Process limitations. The MEOR process is complex because it depends on the reservoir chemistry for bacteria functionality and isolation. MEOR renders low incremental oil recovery [19].

2.4.4. MEOR field applications

MEOR field projects have been conducted worldwide in past decades. In Australia, MEOR was applied in the Alton field producing approximately 40% of incremental oil after 1 year of treatment application [155]. In the Asian region, MEOR has also been deployed in China, India and Malaysia [156, 157]. Notable MEOR successes with incremental oil productions ranging up to 204% at field trials have been reported in Argentina, US, Romania, India and Russia [158]. Other MEOR application successes at laboratory and field scale have been reported in Bulgaria, Canada, Former East Germany, Saudi Arabia, the Netherlands, Oman, Romania, Norway and Hungary [159].

2.4.5. Technological advancements in MEOR

MEOR has developed from laboratory studies between the 1940s and 1980s to successful field applications in the last two decades [19]. Several advances have been made in its application such as the injection of adapted mixed enrichment cultures (AMEC) into reservoirs [160, 161], the stimulation of indigenous microbiota through the use of salts and oxygen alongside water injection [162], and the selective plugging of high-permeability channels through the use of ultra-micro-bacteria formed by selective starvation [163]. Recently, the two notable advances in MEOR are genetically engineered micro-organisms EOR (GEMEOR), and the enzyme EOR (EEOR). Both advances involve the growing of microbes that can withstand extreme reservoir conditions using genetic engineering tools and techniques [19].

3. EOR techniques

3.1. Production performance

In thermal EOR, oil production is increased in heavy oil formations through several mechanisms such as oil viscosity reduction, oil swelling and steam flashing and stripping [1]. Among the TEOR techniques, steam flooding has the highest potential for additional oil recovery than CSS, SAGD and ISC. Steam flooding requires intensive heating and trillions of barrels of heavy oil are recovered as a result of this intense heating [29]. In chemical EOR, polymer flooding exhibits better oil production potentials in comparison to SP and ASP. Whereas ASP demonstrate better recovery efficiency than SP as it prolongs the production life of the formation [107]. In gas injection EOR, the most effective and promising method is CO_2 injection. Although CO_2 is capable of displacing oil by miscible and immiscible flooding, miscible flooding has proven to be more efficient. Although, immiscible flooding shows lower recovery factors, it may still be economical due to the lower cost of the immiscible gases, e.g. N_2 [164]. Microbial EOR is economically attractive; however, a longer time interval is a requirement to attain incremental oil production. More so, oil production rates are often low when compared to the oil production rates of TEOR, CEOR and GEOR processes [19].

3.2. Cost of EOR Implementation

TEOR projects are expensive ventures. A vast capital is required for project operations, specifically, steam generation and injection [26], which are often large scale and require high financial costs for multiple injection wells. Likewise, steam generators for such projects are usually high priced, yet essential components. CEOR is cost-effective in comparison to TEOR, since the chemicals for its operations are readily accessible and relatively cheap [3, 165], although surfactant injection remains an expensive undertaking [98]. Gas injection is again a relatively expensive practice when compared to CEOR and MEOR, but more cost-effective than the TEOR processes. However, the incremental oil production usually outweighs the production costs, especially for immiscible gas injection [2]. MEOR is a much cheaper alternative owing to the low energy requirements unlike TEOR. The application of MEOR is independent of oil price [19, 59], and thus it is considered economical. However, MEOR operations involve complex mechanisms [14, 15] that require proper technical understanding for its application. Therefore, cost should not be the only factor considered for adopting MEOR in the field.

3.3. Environmental friendliness

Thermal EOR, in comparison to microbial, chemical and gas EOR, is eco-unfriendly due to the generation of large volumes of greenhouse gas emissions. Specifically, the production of steam from the combustion of fossil fuels significantly increases emissions of carbon dioxide and nitrous oxide [26]. ISC also contributes to gas emissions such as CO_2, H_2S, CO and volatile hydrocarbons, which are generated during this process [41, 166]. Steam injection has fewer hydrocarbons, which are generated during this process [41, 166]. Steam injection has less environmental sustainability than ISC, since no current control measures over gas emissions during the steam generation process are in place [29]. MEOR is an eco-friendly method in comparison to thermal, chemical and gas methods [19] as MEOR does not release polluting and/or toxic gases such as H_2S and CO; thus, MEOR offers a better environmental sustainability.

4. Global EOR status and some case studies

EOR gas injection projects were stagnant in the mid-1908s [167], while thermal and chemical EOR processes experienced a decline in the 1980s [167]. However, since 2000, GEOR projects have been on the rise due to the growth in the implementation of CO_2-EOR projects [167]. Minor increases in thermal projects have been observed in recent times due to the increase in

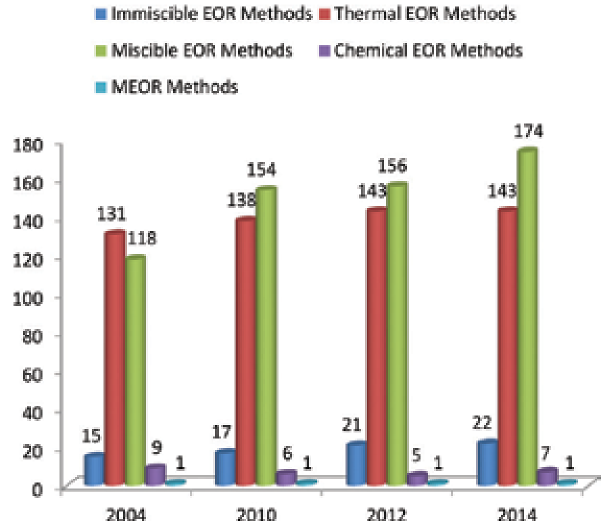


Figure 10. Global EOR project status [93].

the application of high-pressure air injection (HPAI) projects [167]. Between 2004 and 2014, gas EOR (i.e. miscible flooding) and thermal EOR techniques have been the most extensively applied EOR processes worldwide (**Figure 10**) [94].

The global oil demand has been steadily on the rise (**Figure 11**), with the exception of the temporary drop in oil demand between 1979 and 1983. Simultaneously, there has been a continuous decline in conventional oil resources. According to the U.S. Energy Information Administration, the worldwide oil consumption in 2014 increased by 1.2 million b/d, which on average corresponded to 92.4 million b/d [168]. At the end of year 2015, oil production reached approximately 97 million b/d [169], increase that was equivalent to a rise in oil consumption of 1.4 million b/d [170]. Expectations are that global oil consumption will grow by 1.4 million b/d in 2016 and 1.5 million b/d in 2017 (**Figure 11**). It is also important to mention that since 2014 to present, there is more oil supply than oil demand, which is clearly reflected by the drop in oil price. However, the current excess in oil supply comes from the exploitation of unconventional oil resources (i.e. tight reservoirs).

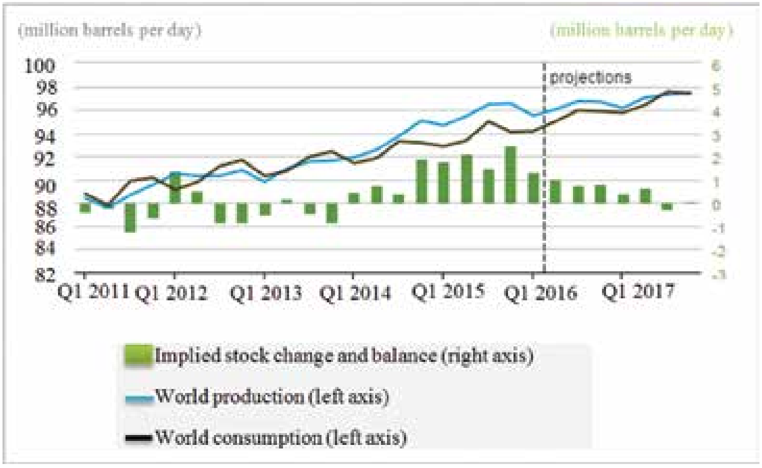


Figure 11. Global oil production and consumption [170].

The dramatic increase in oil demand over time has constantly prompted the quest for novel methods to enhance oil production. In 1998, global EOR projects achieved the production of 2.3 million b/d from steam flooding in the Duri field (Indonesia), which was the largest steam flooding project at the time [3]. EOR production of 480,000 b/d was further reported in Canada and China with an EOR production of 280,000 and 200,000 b/d, respectively [3].

In recent times, the EOR global market has experienced an unceasing progression in its growth pattern. In 2012, the global EOR market was 2095 million barrels [171]. By 2013, it further increased to 2681.6 million barrels. Globally, EOR contributes around 3.5% of daily oil production [172, 173], which corresponds to approximately 3 million barrels of oil per day [28]. A compound annual growth rate of 29.9% has been projected through 2014–2020; thus, a much higher growth above 16,000 million barrels is expected by 2020 that will amount to about US $ 283 billion [173].

4.1. Impact of EOR in the Kern River oil field (California)

The Kern River heavy oil field near Bakersfield, California, was discovered in 1899 [174]. In 1961, heavy oil production was approximately 19,000 b/d, which was considered low and prompted the introduction of steam flooding in 1964 and 1966 [174]. Steam flooding increased heavy oil production to 53,000 b/d in 1966 and production peaked at 141,000 b/d in 1985, followed by a lower production rate of 80,000 b/d [175]. After more than 100 years of production, the field is still producing and 60% of the oil output has been achieved by steam flooding EOR [176]. Kern River (a sandstone formation) has demonstrated the efficacy of thermal EOR for heavy oil reservoirs. In this field, a 60% recovery factor of the original oil-in-place (OOIP) has been achieved, which is significantly higher than the average global recovery factor of 32–35%. In the Kern River oil field, primary recovery and hot water injection produced around 5–10% to 15–25%, respectively, of the OOIP [176].

4.2. Impact of EOR on Russian oil fields

Russia, which is the second largest oil producer in the world, had an estimated ultimate oil production of 4.6 million b/d in 1988 [175, 177]. Russian's oil recovery factors have been on the decline in the last 30 years because of the depletion of giant fields [178]. The breakdown of the Soviet Union in 1991 also contributed to a production decrease of approximately 2.2 billion b/d [175]. In the 1960s, the oil recovery factor was 50%, but by 1993, the recovery factor dropped b/d [176]. In the 1960s, the oil recovery factor was 50%, but by 1993, the recovery factor dropped to 40% [178, 179]. Further decline (560 kb/d) in Russian's oil production is expected between 2014 and 2020. Projections indicate that the total production of liquid hydrocarbons in Russia will fall from 10.9 Mb/d in 2014 to 10.4 Mb/d by 2020. However, an increase in production of natural gas liquids (NGL) and condensate is expected by 2020 owing to the projected higher

Figure 12. IEA: The Oil Market Report (OMR) on current Russian oil production [180].

gas production rate with and average NGL output of 975 kb/d [180]. **Figure 12** shows the current Russian oil production and production projections up to 2020.

Several EOR techniques (TEOR, GEOR and MEOR) have been deployed in Russian oil fields, even though MEOR applications are restricted [181]. GEOR, specifically, miscible gas flooding, is considered the EOR process with the greatest potential [182]. Although, several EOR processes have been implemented in Russian oil fields, estimations of the actual number of implemented EOR projects are difficult to obtain. Based on oil companies' data, Russian oil production from 1996 to 2000 increased by 2.5–2.8 times [178]. Current Russian EOR oil production is approximately 17–18 MM tons with chemical EOR processes accounting for 81–82% of the incremental oil production and 0.35–0.4 MM tons of oil production from gas flooding and WAG applications [178]. Projections indicate that gas EOR technologies, WAG and combined technologies will be adopted in Russia in the near future [178].

4.3. Impact of EOR on the Cantarell oil field (Mexico)

Cantarell is the biggest oil field in Mexico [183]. Oil production commenced in 1979. Between 1980 and 1996, the production capacity of the Cantarell oil field was 1 MMbd. In 2000, nitrogen flooding was initiated and by 2005, the field responded to nitrogen flooding with an outstanding production increase [174]. The initial results were great, however, subsequently production dropped by approximately 400,000 bpd [183]. This oil production behaviour might indicate that nitrogen injection could be viewed as a method that accelerates oil recovery without upsurging ultimate recovery [174, 183].

4.4. Impact of EOR on the Oman oil field

Oman is the largest oil and natural gas producer in the Middle East outside the OPEC. Oil production peaked in year 2000 at 970,000 b/d and then declined to 710,000 b/d in 2007 [184]. The decline was prevented through the application of several EOR techniques, which increased production again to 919,000 b/d in 2012. Henceforth, Oman's incremental oil and natural gas

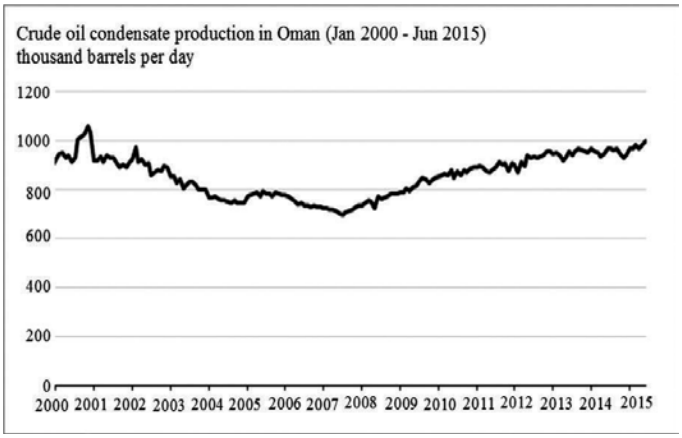


Figure 13. EOR impact on Oman Oil Production [186].

production is highly dependent on advanced extraction technologies [185]. EOR techniques such as polymer, miscible gas flooding and steam injection have been the main drivers of the country's rebounding oil production since 2007 [184]. In the Marmul oil field, polymer flooding produced about 75,000 b/d in 2012. Polymer flooding has been more effective than steam injection [184]. Miscible gas injection, which was deployed in the Harweel oil field cluster, improved the oil production rate to 23,000 b/d in 2012. Steam injection has also been deployed in the Mukhaizna, Marmul, Amal-East, Amal-West and Qarn Alam oil fields, among others [184]. Currently, oil production in Oman has remained on the increase since 2007 with a notable production increase of over a million b/d in 2015 (**Figure 13**) [186]. Projections indicate that the application of thermal EOR in the Amal-East and Amal-West oil fields will increase oil production by 23,000 b/d in 2018 [184]. In Oman's oil fields application of conventional and advanced EOR techniques will promote further production growth [185, 186]. Currently, expectations are that 16% of Oman's oil production will come from EOR projects this year (2016), which is more than five times the EOR production in 2012 [185].

4.5. Impact of EOR on the U.S. Permian Basin

The United States Permian Basin has shown successful deployment of EOR processes since the early 1970s [187], which started with two large CO_2-EOR projects [188]. In 1985, CO_2 was injected into the Denver Unit of the giant Wasson (San Andres) oil field to remediate the sharp decline of oil production that dropped from approximately 90,000 to 40,000 b/d. Upon deployment of the CO_2 flooding project, oil production increased to about 50,000 b/d [189]. In 2009, 105 miscible and 61 immiscible CO_2-EOR applications were implemented in the U.S. within the Permian Basin producing over 182,000 b/d [188]. In the United States, the number of CO_2-EOR projects has continuously increased over the years. In 2010, production rates of approximately 200,000 b/d in the Permian Basin were achieved using CO_2-EOR in oil fields ranging from the fieldwide CO_2 flood in the giant Wasson (San Andres) oil field to the small 160-acre pilot CO_2 flood at Dollarhide Clearfork reservoir [32, 190, 191]. **Table 7** presents details of several CO_2-EOR projects implemented in the Permian Basin [32].

Oil Fields	**Seminole**	**Means**	**Wasson**	**Slaughter****	**Kelly Snider**	**Total**
Primary operator	Hess	ExxonMobil	Occidental	Occidental	Kinder Morgan	
Total field production (b/d) year 2010	16,500	10,000	51,100	18,800	29,600	126,000
Incremental CO_2-EOR production (b/d) year 2010**	16,500	8,700	44,600	11,200	26,500	107,500

Note: *Joint recovery from six Wasson units and **Joint recovery from nine Slaughter units.

Table 7. CO_2-EOR oil recovery from the Permian Basin [32].

In 2012 and 2015, incremental oil production from CO_2-EOR operations in the Permian Basin was estimated at 186,000 and 241,000 b/d, respectively, with further projections of 301,000 b/d by 2020 [141].

5. Conclusions

Crude oil recovery takes place in three production stages primary, secondary and tertiary oil recovery processes. On average, oil recovery from the primary and secondary production stages is approximately one-third of the original oil-in-place (OOIP), while the remaining two-thirds of the oil, can be partially recovered through the application of tertiary processes also known as enhanced oil recovery (EOR) processes, which are key drivers for incremental oil recovery. EOR processes include thermal (TEOR), chemical (CEOR), gas flooding miscible and immiscible (GEOR) and microbial or MEOR processes.

- Thermal EOR techniques are applied for the recovery of heavy oils. In particular, steam-flooding is the dominant thermal EOR technique worldwide. Increase in oil productivity is achieved through viscosity reduction, oil swelling, steamstripping and thermal cracking [1].
- Chemical EOR techniques are suitable for application in mature oil fields. Globally, oil recovery using CEOR techniques have remained insignificant since the 1990s with the exception of China [79, 193]. Among the CEOR techniques, polymer/surfactant flooding through IFT reduction between the displacing liquid (i.e. water) and oil has the best potential for ultimate oil recovery [1]. However, polymer flooding is less complex and the most widely deployed technique for mobility control [83, 112].
- Miscible and immiscible gas injection or GEOR are suitable for application in light, condensate and volatile oil reservoirs [114]. CO_2 is considered the most widely used gas for GEOR injection especially in the US Permian Basin, where most of the CO_2 field projects have been deployed. In the US, continuous growth of CO_2 flooding projects is expected. N_2 and hydrocarbon gas injection projects have been deployed in Canada and the US, although incremental oil recovery from these processes has been negligible.
- MEOR is a promising and eco-friendly recovery process with potential for future incremental oil recovery [19]. The main downsides of MEOR are longer time intervals are required to attain incremental oil production and MEOR renders the lowest oil recovery in a given period in comparison to other EOR techniques.

Huge potentials for incremental oil recovery exist through the application of EOR processes; however, the volume of recoverable oil is greatly dependent on the implemented EOR technique. Among the key EOR techniques deployed in oil fields, miscible gas injection EOR and thermal EOR processes are currently the most commonly used techniques in the field. Continuous evolution of EOR processes in the near future should take a synergistic approach from different EOR technologies.

Nomenclature

AMEC	adapted mixed enrichment cultures
CEOR	chemical enhanced oil recovery
CSS	cyclic steam stimulation
EEOR	enzyme EOR
EOR	enhanced oil recovery
Fast-SAGD	fast-steam assisted gravity drainage
GAGD	gas assisted gravity drainage
GEMEOR	genetically-engineered microorganisms enhanced oil recovery
GEOR	gas enhanced oil recovery
GOGD	gas-oil gravity drainage
HPAI	high-pressure air injection
HPAM	hydrolysed polyacrylamide
HPAM-AMPS	hydrolysed polyacrylamide-acrylamide methyl propane sulfonic acid
ISC	*in situ* combustion
MEOR	microbial enhanced oil recovery
NCG- SAGD	non-condensable gas-steam assisted gravity drainage
NGL	natural gas liquids
OTSG	enclosed trough solar once-through steam generator
PAM	polyacrylamide
PWAG	polymer water alternate gas injection
SAGD	steam assisted gravity drainage
SAPc	superabsorbent polymer composite
ST-EOR	solar thermal enhanced oil recovery
SWAG	simultaneous water alternate gas injection
TAGOGD	thermally assisted gas-oil gravity drainage
TEOR	thermal enhanced oil recovery
TGD	tertiary gravity drainage
THAI	toe to heel air injection
WAG	water alternate gas injection

Author details

Lezorgia Nekabari Nwidee[1], Stephen Theophilus[2], Ahmed Barifcani[1,3],
Mohammad Sarmadivaleh[1] and Stefan Iglauer[1*]

*Address all correspondence to: stefan.iglauer@curtin.edu.au

1 Department of Petroleum Engineering, Curtin University, Perth, Western Australia

2 School of Energy, Construction and Environment, Coventry University, Coventry, United Kingdom

3 Department of Chemical Engineering, Curtin University, Perth, Western Australia

References

[1] Green D. W., Willhite G. P. (1998). Enhanced oil recovery. SPE Textbook Series. Richardson, TX: Society of Petroleum Engineers.

[2] Thomas S. (2008). Enhanced oil recovery—An overview. Oil and Gas Science and Technology, 63, 1, 9–19.

[3] Terry R. E. (2001). Enhanced oil recovery. Encyclopedia of Physical Science and Technology, 18, 503–518.

[4] Sheng J. (2011). Modern chemical enhanced oil recovery: Theory and practice. Amsterdam: Elsevier Publication Inc.

[5] Stegemeier G. L. (1977). Mechanisms of Entrapment and Mobilization of Oil in Porous Media in Improved Oil Recovery by Surfactant and Polymer Flooding. D.O. Shah and R.S. Schechter, eds., pp. 55–91. New York: Academic Press.

[6] Sydansk R. D., Romero-Zerón L. (2011). Reservoir conformance improvement. Richardson, TX: Society of Petroleum Engineers.

[7] Cohen D. (2007). Exaggerated oil recovery. Peak watch. Available from http://peakwatch.typepad.com/peak_watch/2007/07/exaggerated-oil.html. 10 Jan, 2016.

[8] Habermann B. (1960). The efficiencies of miscible displacement as a function of mobility ratio. Petroleum Transactions, AIME, 219, 264–272; Miscible processes, reprint series, SPE Dallas, (1965) 8, 106–114.

[9] Lyons W., Plisga B. S. (eds.) (2005). Standard handbook of petroleum & natural gas engineering (Second edition). Burlington, MA: Elsevier Inc.

[10] Satter A., Iqbal G. M., Buchwalter J. L. (2008). Practical enhanced reservoir engineering: Assisted with simulation software. Pennwell: Oklahoma.

[11] Shrimali H. V. (2015). Developments in enhanced oil recovery technologies: A review. International Journal of Research in Advent Technology, 3(6), 2321–2963.

[12] Donaldson E. C., Chilingarian G.V., Yen T.F. (1989). Enhanced oil recovery 11: Processes and operations. Amsterdam: Elsevier Science Publications, Inc.

[13] Yen T. F. (1990). Microbial enhanced oil recovery: Principle and practice. Boca Raton, FL: CRC Press.

[14] Lazar I., Petrisor I. G., Yen T. F. (2007). Microbial enhanced oil recovery (MEOR). Petroleum Science and Technology, 25(11), 1353–1366.

[15] Ollivier B., Magot M. (2005). Petroleum microbiology. Herndon, VA: ASM Press.

[16] McInerney M. J., Nagle D. P., Knapp R. M. (2005). Microbially enhanced oil recovery: Past, present, and future. Petroleum Microbiology, 215–23. Washington, DC: ASM Press.

[17] Belyaev S. S., Borzenkov I. A., Nazina T. N., Rozanova E. P., Glumov I. F., Ibatullin R. R., Ivanov M. V. (2004). Use of microorganisms in the biotechnology for the enhancement of oil recovery. Microbiology, 73, 590–598.

[18] Brock V., Christman P., Morell J., Shahi G. (2009). Well recovered. [online] Available from http://www.worldexpro.com/articles/014mar09/WEX014 wellrecovered.pdf. 14 Dec, 2015.

[19] Sen R. (2008). Biotechnology in petroleum recovery: The microbial EOR. Progress in Energy and Combustion Science, 34(6), 714–724.

[20] Van Hamme J. D., Singh A., Ward O. P. (2003). Recent advances in petroleum microbiology. Microbiology, 67(4), 503–549.

[21] Iglauer S., Favretto S., Spinelli G., Schena G., Blunt M. J. (2010). X-ray tomography measurements of power-law cluster size distributions for the nonwetting phase in sandstones. Physical Review E, 82, 056315.

[22] Hirasaki G. J., Miller C. A., Puerto M. (2011). Recent advances in surfactant EOR. Society of Petroleum Engineering, 16(4), 889–907.

[23] Jack T. R. (1988). Microbially enhanced oil recovery. Biorecovery, 1, 59–73.

[24] Donaldson E. C. (1991). Microbial enhancement of oil recovery—Recent advances. New York: Elsevier.

[25] Khire J. M., Khan M. I. (1994). Microbially enhanced oil recovery (MEOR). Part 1: Importance and mechanism of MEOR. Enzyme Microbial Technology, 16, 170–172.

[26] Potts G. D. (2011). Integrating renewable energy resources within the oil industry: Concentrated solar power & enhanced oil recovery. [Online] available from http://www.gdpcapital.co.uk/docs/thermal_EOR_CSP.pdf. 20 December, 2015.

[27] Latil M. (1980). Enhanced oil recovery. Paris: Technip, Gulf Publishing.

[28] Kokal S., Al-Kaabi A. (2010). Enhanced oil recovery: Challenges & opportunities. [Online] available from http://www.world-petroleum.org/docs/docs/publications/2010yearbook/P64-69_Kokal-Al_Kaabi.pdf.10 November, 2015.

[29] Kovscek A. R. (2012). Emerging challenges and potential futures for thermally enhanced oil recovery. Journal of Petroleum Science and Engineering, 99, 130–143.

[30] Veld K. V., Philips O. R. (2010). The economics of enhanced oil recovery: Estimating incremental oil supply and CO_2 demand in the powder river basin. The Energy Journal, 31(4)31–55.

[31] Tunio S. Q., Tunio A. H., Ghirano N. A., El Adawy Z. M. (2011). Comparison of different enhanced oil recovery techniques for better oil productivity. International Journal of Applied Science and Technology, 1(5), 143–153.

[32] National Energy Technology Laboratory. (2011). Improving domestic energy security and lowering CO_2 emissions with “next generation” CO_2-enhanced oil recovery (CO_2-EOR). [Online] available from http://www.netl.doe.gov/energy-analyses/pubs/storing%20co2%20w%20eor_final.pdf .12 November, 2015.

[33] Iglauer S., Wu Y., Shuler P., Tang Y., Goddard III W. A. (2010). New surfactant classes for enhanced oil recovery and their tertiary oil recovery potential. Journal of Petroleum Science and Engineering, 71(1–2), 23–29.

[34] Prats M. (1986). Thermal recovery. 2nd edition. Dallas, TX: SPE.

[35] U.S. Department of Energy (DOE/EIA 2014). Annual energy outlook 2014 with projections to 2040. [Online] available from http://www.eia.gov/forecasts/aeo/pdf/0383(2014).pdf. 30 January, 2016.

[36] Moritis G. (2002). Report on enhanced oil recovery. Oil and Gas Journal, 15 April.

[37] Moritis G. (2010). CO_2, miscible, steam dominates EOR processes. Oil and Gas Journal, 20 April.

[38] Stovall S. (1934). Recovery of oil from depleted sands by means of dry steam injection. Oil Weekly, 17–24.

[39] De Haan H., Schenk L. (1969). Performance and analysis of a major steam drive project in the Tia Juana field, Western Venezuela. Journal of Petroleum Technology, 21(1), 111–119.

[40] Slider H. C. (1983). Worldwide practical petroleum reservoir engineering methods. Tulsa, OK: Penn Well Publications, Inc.

[41] Sarathi S. P. (1999). Handbook of in-situ combustion. US: National Department of Energy.

[42] Moore R. G., Laureshen C. J., Belgrave J. D., Ursenbach M. G., Mehta S. A. (1994). In-situ combustion in Canadian heavy oil reservoirs. Journal of Petroleum Science and Engineeering, 74(8), 1169–1175.

[43] Farouq Ali S. M. (2003). Heavy oil-evermore mobile. Journal of Petroleum Science and Engineering, 37, 5–9.

[44] Akkutlu I. Y., Yortsos Y. C. (2003). The dynamics of in-situ combustion fronts in porous media. Combustion and Flame, 134, 229–247.

[45] Lake L. W., Walsh M. P. (2008) Enhanced oil recovery (EOR) field data literature search. [Online] available from http://www.ens.dk/sites/ens.dk/files/undergrund-forsyning/

olie-gas/felter-produktion-danmark/foroeget-indvinding- eor/EOR_Report_Final.pdf. 12 December, 2015.

[46] Shafiei A., Dusseault M. B., Zendehboudi S., Chatzis I. (2013). A new screening tool for evaluation of steamflooding performance in naturally fractured carbonate reservoirs. Fuel, 108(2013), 502–514.

[47] Baibakov N. K., Garushev A. R. (1989). Thermal methods of petroleum production. Amsterdam: Elsevier.

[48] Nabipour M. A. (2006). Laboratory investigation of thermally-assisted gas-oil gravity drainage for secondary and tertiary oil recovery in fractured models. Journal of Petroleum Science and Engineering, 55(2), 74–82.

[49] Baibakov N. K., Garushev A. R., Cieslewicz W. J. (2011). Thermal methods of petroleum production. Amsterdam: Elsevier.

[50] Lei T., Zhaomin L., Yiquan B., Li B., Zhang J. (2010). Multi-combination exploiting technique of ultra-heavy oil reservoirs with deep and thin layers in Shengli Oilfield. Petroleum Exploration and Development, 37(6), 732–736.

[51] Yanbin C., Dongqing L., Zhongping Z., Shantang W., Quan W., Daohong X. (2012). Steam channeling control in the steam flooding of super heavy oil reservoirs, Shengli Oilfield. Petroleum Exploration and Development, 39(6), 785–790.

[52] Chilingarian G. V., Robertson J. O., Kumar S. (1989). Surface operations in petroleum production, II. Amsterdam: Elsevier.

[53] Johannes A., Han S. (2013). Current overview of cyclic steam injection process. Journal of Petroleum Science Research, 2(3), 116.

[54] Zhao D. W., Wang J., Gates I. D. (2013). Optimized solvent-aided steam-flooding strategy for recovery of thin heavy oil reservoirs. Fuel, 112, 50–59.

[55] Liu C. Z., Cheng L. S., Liu Y., Pang Z. X. (2008). Calculating models for heating radius of cyclic steam stimulation and formation parameters in horizontal well after soaking. Acta Petrolei Sinica, 29(1), 101–115.

[56] Hashemi-Kiasari H., Hemmati-Sarapardeh A., Mighani S., Mohammadi A. H., Sedaee-Sola B. (2014). Effect of operational parameters on SAGD performance in a dip heterogeneous fractured reservoir. Fuel, 122, 82–93.

[57] Gates I. D., Adams J. J., Larter S. R. (2008). The impact of oil viscosity heterogeneity on the production characteristics of tar sand and heavy oil reservoirs. Part II: Intelligent, geotailored recovery processes in compositionally graded reservoirs. Journal of Canadian Petroleum Technology, 47(9), 40–49.

[58] Elliott K. T., Kovscek A. R. (1999). Simulation of early–time response of single–well steam assisted gravity drainage (SW-SAGD). Society of Petroleum Engineers Journal.

[59] Giacchettaa G., Leporinia M., Marchetti B. (2015). (SAGD) facility for oil recovery from Canadian oil sands. Applied Energy, 142, 1–9.

[60] Shin H., Polikar M. (2006). Experimental investigation of the fast-SAGD process. In: Canadian International Petroleum Conference. Calgary, Alberta: Petroleum Society of Canada.

[61] Edmunds N., Chhina H. (2001). Economic optimum operating pressure for SAGD projects in Alberta. Journal of Canadian Petroleum and Technology, 40(12), 13–17.

[62] Adasania A. A., Bai B. (2011). Analysis of EOR projects and updated screening criteria. Journal of Petroleum Science and Engineering, 79(2), 10–24.

[63] Iglauer S., Rahman T., Sarmadivaleh M., Al-Hinai A., Ferno M., Lebedev M. (2016). Influence of wettability on residual gas trapping and enhanced oil recovery in three-phase flow: A pore-scale analysis using micro-computed tomography. SPE Journal, in press.

[64] Bierman B., Treynor C., O'Donnell J., Lawrence M., Chandra M., Farver A., von Behrens P., Lindsay W. (2014). Performance of an Enclosed Trough EOR system in South Oman. Energy Procedia, 49, 1269–1278.

[65] Nabipour M., Escrochi M., Ayatollahi S., Boukadi F., Wadhahi M., Maamari R., Bemani A. (2007). Laboratory investigation of thermally-assisted gas–oil gravity drainage for secondary and tertiary oil recovery in fractured models. Journal of Petroleum Science and Engineering, 55, 74–82.

[66] Wever D. A. Z., Picchioni F., Broekhuis A. A. (2011). Polymers for enhanced oil recovery: A paradigm for structure–property relationship in aqueous solution. Progress in Polymer Science, 36(11), 1558–1628.

[67] Baviere M. (2007). Basic concepts in enhanced oil recovery processes. London: Elsevier Applied Science.

[68] Petros Group. (2010). Modern EOR review. [Online] available from http://petros.ru/eng/worldmarketoil/?action=show&id=287. 10 December, 2015.

[69] Iglauer S., Wu Y., Shuler P., Tang Y., Goddard III, W. A. (2009). Alkyl polyglycoside surfactant–alcohol cosolvent formulations for improved oil recovery. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 339(2009), 48–59.

[70] Goddard W. A., Tang Y., Shuler P. J., Blanco M., Jang S. S., Lin S. T., Maiti P., Wu Y., Iglauer S., Zhang X. (2004). Lower cost methods for improved oil recovery (ior) via surfactant flooding. DOE Project DE-FC 26-01BC15362, Final Report, September.

[71] Iglauer S., Wu Y., Shuler P., Blanco M., Tang Y., Goddard III, W. A. (2004). Alkyl polyglycoside Surfactants for improved oil recovery. SPE/DOE Symposium.17–21 April. Tulsa, Oklahoma, USA.

[72] Schramm L. (2000). Surfactants: Fundamentals and application in petroleum industry. Cambridge: Cambridge University Press.

[73] Lake L. W. (2010). Enhanced oil recovery. SPE ATCE. Training Courses. Florence, Italy: Society of Petroleum Engineers, September 23, 2010.

[74] Wu Y., Iglauer S., Shuler P., Tang Y., Goddard III W. A. (2010). Alkyl polyglycoside sorbitan ester formulations for improved oil recovery. Tenside Surfactants Detergents, 47(5), 280–287.

[75] Iglauer S., Wu Y., Shuler P., Tang Y., Goddard III W. A. (2010). Alkyl polyglycoside sorbitan ester formulations for improved oil recovery. Tenside Surfactants Detergents, 47(5), 280–287.

[76] Iglauer S., Salamah A., Sarmadivaleh M., Liu K., Phan C. (2014). Contamination of silica surfaces: Impact on water–CO2–quartz and glass contact angle measurements. International Journal of Greenhouse Gas Control, 22, 325–328.

[77] Wei B., Romero-Zero′N L., Rodrigue D. (2014). Oil displacement mechanisms of viscoelastic polymers in enhanced oil recovery (EOR): A review. Journal of Petroleum Exploration Production Technology, 4, 113–121.

[78] Iglauer S., Wülling W., Pentland C. H., Al-Mansoori S., Blunt M. J. (2011). Capillary trapping capacity of sandstones and sandpacks. Society Petroleum Engineering Journal, 16(4), 778–783.

[79] Chang H. L., Zhang Z. Q., Wang Q. M., Xu Z. S., Guo Z. D., Sun H. Q., Cao X. L., Qiao Q. (2006). Advances in polymer flooding and alkaline/surfactant/polymer processes as developed and applied in the People's Republic of China. Journal of Petroleum Technology, 58, 84–89.

[80] Zargartalebi M., Kharrat R., Barati N. (2015). Enhancement of surfactant flooding performance by the use of silica Nanoparticles. Fuel, 143, 21–27.

[81] Curbelo F. D. S., Santanna V. C., Barros Neto E. L., Dutra Jr. T. V., Castro Dantas T. N., Dantas Neto A. A., Garnica A. I. C. (2007). Adsorption of nonionic surfactants in sandstones. Colloids Surfurces A, 293, 1–4.

[82] Trabelsi S., Argillier J. F., Dalmazzone C., Hutin A., Bazin B., Langevin D. (2011). Effect of added surfactants in an enhanced alkaline/heavy oil system. Energy Fuels, 25, 1681–1685.

[83] Pope G. A. (2011). Recent developments and remaining challenges of enhanced oil recovery. [Online] Available from http://www.spe.org/jpt/print/archives/2011/07/15RDGrandChallenges.pdf. 28 December, 2015.

[84] Watkins C. (2009). Chemically enhanced oil recovery stages a comeback. In International News on Fats, Oils and Related Materials. Boulder, IL: The American Oil Chemists' Society.

[85] Abidina A. Z., Puspasaria T., Nugroho W. A. (2012). Polymers for enhanced oil recovery technology. Procedia Chemistry, 4, 11–16.

[86] Hou C. T., Barnabe N., Greaney K. (1986). Biodegradation of xanthan by salt-tolerant aerobic microorganisms. Journal of Industrial Microbiology, 1, 31–37.

[87] Cadmus M. C., Jackson L. K., Burton K. A., Plattner R. D., Slodki M. E. (1982). Biodegradation of xanthan gum by Bacillus sp. Applied Environmental Microbiology, 44, 5–11.

[88] Sutherland I. W. (1982). An enzyme system hydrolysing the polysaccharides of Xanthomonas species. Journal of Applied Bacteriology, 53, 385–393.

[89] Leela J. K., Sharma G. (2000). Studies on xanthan production from Xanthomonas campestris. Bioprocess Engineering, 23, 687–689.

[90] Zu H., Luo J., New Polymers for EOR. (2008). A laboratory study. Research Institute of Petroleum Exploration & Development, Petrochina, Beijing, China.

[91] Wang H., Cao X., Zhang J., Zhang A. (2009). Development and application of dilute surfactant–polymer flooding system for Shengli oilfield. Journal of Petroleum Science and Engineering, 65, 45–50.

[92] Wang H., Miller B. (2013). Development of a new surfactant-polymer system and its implementation in Dagang oilfield. Journal of Petroleum Gas and Engineering, 4, 118–126.

[93] Abu El Ela M., Sayyouh H., El Tayeb S. (2014). An integrated approach for the application of the enhanced oil recovery projects. Journal of Petroleum Science Research, 3(4), 176–188.

[94] Shah D. O., Schechter R. S. (1977). Improved oil recovery by surfactant and polymer flooding. New York: Academic Press.

[95] Wu Y., Iglauer S., Shuler P., et al. (2011). Experimental study of surfactant retention on kaolinite clay. Tenside Surfactants Detergents, 48(5), 346–358.

[96] Bourrel M., Schechter R. S. (1988). Microemulsions and related systems, formulation solvency and physical properties. New York, NY: Marcel Dekker, Inc.

[97] Kamari A., Sattari M., Mohammadi A. H., Ramjugernath D. (2015). Reliable method for the determination of surfactant retention in porous media during chemical flooding oil recovery. Fuel, 158, 122–128.

[98] Mayer E. H., Breg R. L., Carmichael J. D., Weinbrandt R. M. (1983). Alkaline injection for enhanced oil recovery—A status report. Journal of Petroleum Technolology, 35 (1), 209–221.

[99] Johnson C. E. (1976). Status of caustic and emulsion methods. Journal of Petroleum Technology, 28 (1), 85–96.

[100] Froning H. R., Leach R. O. (1967). Determination of chemical requirement and applicability of wettability alteration flooding. Journal of Petroleum Technology, 19(6), 839–843.

[101] Huang S., Dong, M. (2004). Alkaline/surfactant/polymer (ASP) flood potential in Southwest Saskatchewan oil reservoirs. Journal of Canadian Petroleum Technology, 43(12), 56–61.

[102] Nicholas P., Jeffrey H. (1997). Case studies for the feasibility of sweep improvement in surfactant-assisted water flooding. Journal of Petroleum Science and Engineering, 17(1–2), 41–62.

[103] Shah D. O. (1981). Fundamental aspects of surfactant-polymer flooding process. Amsterdam: Elsevier.

[104] Rai K., Johns R. T., Delshad M., Lake L. W., Goudarzi A. (2013). Oil-recovery predictions for surfactant polymer flooding. Journal of Petroleum Science and Engineering, 112, 341–350.

[105] Lau K. S. Y. (2014). High-performance polyimides and high temperature resistant polymers. Handbook of Thermoset Plastics. California, USA: Elsevier.

[106] Choi B., Sik M., Lee K. S. (2014).Temperature-dependent viscosity model of HPAM polymer through high-temperature reservoirs. Journal of Degradation and stability, 110, 225–231.

[107] Gregersen C. S., Kazempour M., Alvarado V. (2012). ASP design for the minnelusa formation under low-salinity conditions: Impacts of anhydrite on ASP performance. Fuel, 105, 368–382.

[108] Needhan R. B., Peter H. D. (1987). Polymer flooding review. Journal of Petroleum Technology, 12, 1503–1507.

[109] Panthi K., Sharma H., Mohanty K. K. (2016). ASP flood of a viscous oil in a carbonate rock. Fuel, 164, 18–27.

[110] Manrique E. J., Muci V. E., Gurfinkel M. E. (2007). EOR field experiences in carbonate reservoirs in the United States. SPE Reservoir Evaluation Engineering, 10(6), 667–686.

[111] Alagorni A. H., Yaacob Z. B., Nour A. H. (2015). An overview of oil production stages: Enhanced oil recovery techniques and nitrogen Injection. International Journal of Environmental Science and Development, 6, 9.

[112] Manning R. K., Pope G. A., Lake L. W., Paul G. W., Wesson T. C. (1983). A technical survey of polymer flooding projects. Report no. DOE/BC/10327-19; U.S. Department of Energy, Tulsa, OK, USA. p. 329.

[113] Alvarado V., Manrique E. (2010) Enhanced oil recovery: Field planning and development strategies. Burlington: Gulf Professional Publications, Inc.

[114] Zhu Y., Yi Z., Jialing N., Weidong L., Qingfeng H. (2012). The research progress in the alkali-free surfactant-polymer combination flooding technique. Petroleum Exploration and Development, 39(3), 371–376.

[115] Sheng J. J. (2013). Enhanced oil recovery field case studies. New York: Gulf Publishing Elsevier.

[116] French T. (1999). Evaluation of the Sho-Vel-Tum Alkali-Surfactant-Polymer (ASP) Oil Recovery Project. DOE/SW/45030-1; U.S. Department of Energy, Tulsa, OK, USA.

[117] Parker M. E., Meyer J. P., Meadow S. R. (2009). Carbon dioxide enhanced oil recovery injection operations technologies. Energy Procedia, 1(1), 3141–3314.

[118] Ferguson R. C., Christopher N., Leeuwen T. V., Kuuskraa V. A. (2009). Storing CO_2 with enhanced oil recovery. Energy procedia, 1(1), 1989–1996.

[119] Knight J. (2011). Enhanced oil recovery techniques [online]. Available from http://www.articlesnatch.com/Article/Enhanced-OiRecoveryTechniques/1039088. 24 November, 2015.

[120] Sahimi M., Rasaei M. R., Haghighi M. (2006). Gas injection and fingering in porous media. Gas transport in porous media. Springer, pp. 133–168.

[121] U.S. Department of Energy. (2009). Carbon dioxide enhanced oil recovery untapped domestic energy supply and long term carbon storage solution. [Online] Available from https://www.netl.doe.gov/file%20library/research/oil-gas/small_CO2_EOR_Primer.pdf. 20 Feb, 2016.

[122] Flood L. (1947). Inventory of gas-drive projects in West Texas and New Mexico. Drilling and production practice. New York. American Petroleum Institute.

[123] Intergovernmental Panel on Climate Change (IPCC). (2005). Special Report. Carbon dioxide capture and storage. Cambridge University Press. [Online] available from https://www.ipcc.ch/pdf/specialreports/srccs/srccs_wholereport.pdf. 30 October, 2015.

[124] Zhang L., Ren B., Huang H., Li Y., Ren S., Chen G., Zhang H. (2015). CO_2 EOR and storage in Jilin oilfield China: Monitoring program and preliminary results. Journal of Petroleum Science and Engineering, 125, 1–12.

[125] Iglauer S., Pentland C. H., Busch A. (2015). CO_2 wettability of seal and reservoir rocks and the implications for carbon geo-sequestration. Water Resources Research, 51(1), 729–774.

[126] Department of Energy & Climate Change (DECC). (2010). Optimization of CO_2 storage in CO_2 enhanced oil recovery projects. [Online] available from https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/47992/1006-optimization-of-co2-storage-in-co2-enhanced-oil-re.pdf. 30 November, 2015.

[127] Al-Anazi B.D. (2007). Enhanced oil recovery techniques and nitrogen injection. [Online] Available from http://memberfiles.freewebs.com/50/69/68186950/documents/Enhanced%20Oil%20Recovery%20Techniques-1.pdf. 28 November, 2015.

[128] Fath A. F., Pouranfard A. R. (2014). Evaluation of miscible and immiscible CO_2 injection in one of the Iranian oil fields. Egyptian Journal of Petroleum, 23(3), 255–270.

[129] Sarapardeh H. A., Ayatollahi S., Ghazanfari M.-H., Masihi M. (2014). Experimental determination of interfacial tension and miscibility of the co2–crude oil system; temperature, pressure, and composition effects. Journal of Chemical Engineering Data, 59(1), 61–69.

[130] Han J., Lee M., Lee W., Lee Y., Sung W. (2016). Effect of gravity segregation on CO_2 sequestration and oil production during CO_2 flooding. Applied Energy, 161, 85–91.

[131] Evolution Petroleum Corporation (EPC). (2012). Solutions: gas flooding.[Online] available from http://www.evolutionpetroleum.com/solutions_flooding.html. 20 December, 2015.

[132] Oren P. E., Billiote J., Pinczewski W. V. (1992). Mobilization of waterflood residual oil bygas injection for water-wet conditions. SPE Formal Evaluation, 7, 70–78.

[133] Iglauer S., Paluszny A., Blunt M. J. (2013). Corrigendum to ‘'Simultaneous oil recovery and residual gas storage: A pore-level analysis using in situ X-ray microtomography”. Fuel, 103, 905–914.

[134] Zhang Y., Huang S. S., Luo P. (2010). Coupling immiscible CO_2 technology and polymer injection to maximize EOR performance for heavy oils. Journal of Canadian Petroleum Technology, 49(5), 25–33.

[135] Hou Y. L., Yue X. A. (2010). Research on a novel composite gel system for CO_2 breakthrough. Petroleum Science, 7(2) 245–250.

[136] Heidari P., Kharrat R., Alizadeh N., Ghazanfari M. H. (2013). A comparison of WAG and SWAG processes: Laboratory and simulation studies. Energy Sources Part A, 35(23), 2225–2232.

[137] Pingping S., Chen X. L., Qin J. S. (2010). Pressure characteristics in CO_2 flooding experiments. Petroleum Exploration and Development, 37(2), 211–215.

[138] Shen Z. H., Wang H. Z., Li G. S. (2010). Feasibility analysis of coiled tubing drilling with supercritical carbon dioxide. Petroleum Exploration and Development, 37(6), 743–747.

[139] Energy Information Administration (EIA, 2014). Oil prices drive projected enhanced oil recovery using carbon dioxide. [Online] available from http://www.eia.gov/todayinenergy/detail.cfm?id=17331. 20 January, 2016.

[140] U.S. Department of Energy (DOE/NETL, 2014). Near-term projections of CO_2 utilization for enhanced oil recovery. [Online] available from https://www.netl.doe.gov/energy-analyses/temp/FY14_NearTermProjectionsofCO$_2$UtilizationforEnhancedOilRecovery_040114.pdf. 22 February, 2016.

[141] Siregar S., Hidayaturobbi A. D., Wijaya B. A., Listiani S. N., Adiningrum T., Pratomo A. I. (2007). Laboratory experiments on enhanced oil recovery with nitrogen injection. Journal of Engineering and Technological Sciences, 39(1), 20–27.

[142] Hudgins D. A., Llave F. M., Chung F. T. (1990). Nitrogen miscible displacement of light crude oil: A laboratory study. SPE Reservoir Engineering, 5(1), 100–106.

[143] Syed F. I., Tunio A. H., Ghirano N. A. (2011). Compositional analysis and screening for enhanced oil recovery processes in different reservoir and operating conditions. International Journal of Applied, 1(4), 143–160.

[144] Moritis G. (2008). Worldwide EOR survey. Oil and Gas Journal, 106(41–42), 44–59.

[145] Brown L. R. (2010). Microbial enhanced oil recovery (MEOR). Current Opinion in Microbiology, 13, 1–5.

[146] Bryant R. S., Burchfield T. E. (1989). Review of microbial technology for improving oil recovery. SPE Reservoir Engineering Journal, 4, 151–154.

[147] Zobell C. (1947). Bacterial release of oil from sedimentary materials. Oil and Gas Journal, 46, 62–65.

[148] Kalish P. J., Stewart J. A., Rogers W. F., Bennett E. O., (1964). The effect of bacteria on sandstone permeability. Journal of Petroleum Technology, 805–813.

[149] Nazina T. N., Sokolova D. S., Grigoryan A. A., Xue Y. F., Belyaev S. S., Ivanov M. V. (2003). Production of oil-releasing compounds by microorganisms from the Daqing oil field, China. Microbiology, 72, 173–178.

[150] Sarkar A. K., Goursaud J. C, Sharma M. M, Georgiou G. (1989). Critical evaluation of MEOR processes. In Situ, 13(4), 207238.

[151] Zobell C. (1946). Action of microorganisms on hydrocarbons. Bacterial Reviews, 10, 1–49.

[152] Banat I. M. (1995). Biosurfactants production and possible uses in microbial enhanced oil recovery and oil pollution remediation: A review. Bioresource Technology, 51, 1–12.

[153] Bubela B. (1985). Effect of biological activity on the movement of fluids through porous rocks and sediments and its application to enhanced oil recovery. Geomicrobiology Journal, 4, 313–327.

[154] Youssef N., Simpson D. R., Duncan K. E. (2007). In-situ biosurfactant production by bacillus strains injected into a limestone petroleum reservoir. Environmental Microbiology, 73, 1239–1247.

[155] Sheehy A. J. (1990). Field studies of microbial EOR. Society Petroleum Engineering/ Department of Energy-20254. Enhanced oil recovery symposium, Tulsa, 13–17 April.

[156] Hamdan M. K., Darman N., Hussain D., Ibrahim Z. (2005). Enhanced oil recovery in Malaysia: Making it a reality. Society Petroleum Engineering-93329. Asia Pacific Oil and Gas Conference and Exhibition, Jakarta, 5–7 April.

[157] He Z., Mei B., Wang W., Sheng J., Zhu S., Wang L. (2003). A pilot test using microbial paraffin removal technology in Liaohe oilfield. Petroleum Science Technology, 21, 201–210.

[158] Hong G. C., Zekri A., El K. (2009). MEOR applications—1: Microbes enhance oil recovery through various mechanisms. Oil and Gas Journals.

[159] Shibulal B., Al-Bahry S. N., Al-Wahaibi Y. M., Elshafie A. E., Al-Bemani A. S., Joshi S. J. (2014). Microbial enhanced heavy oil recovery by the aid of inhabitant spore-forming bacteria: An insight review. Scientific World Journal, 309159, 1–12.

[160] Lazar I. (1991). MEOR field trials carried out over the world during the past 35 years. In: Microbial enhancement of oil recovery—Recent advances, Donaldson E. C. (ed.). Amsterdam: Elsevier Science, pp. 485–530.

[161] Lazar I. (1998). International MEOR applications for marginal wells. Pakistan Journal of Hydrocarbon Research, 10, 11–30.

[162] Ivanov M. V., Belyaev S. S., Borzenkov I. A., Glumov I. F., Ibatulin P. B. (1993). Additional oil production during field trials in Russia. In: Microbial Enhancement of Oil Recovery —Recent Advances, Premuzic E. and Woodhead A. (eds.). Amsterdam: Elsevier, pp. 373–381.

[163] Cusak F. M., Singh S., Novosad J., Chmilar M., Blenkinshapp S., Costerton W. J. (1992). The use of ultramicrobacteria for selective pluggingin oil recovery by waterflooding. The Society of Petroleum Engineers.

[164] Thomas F. B., Okazawa T., Erian A., Zhou X. L., Bennion D. B., Bennion D. W. (2001). Does miscibility matter in gas injection?' Petroleum Society of CIM and Canmet, 95 (51), 1–12.

[165] Sahay B. (2001). Petroleum exploration and exploitation practise. New Delhi: Allied Publication Inc.

[166] Pahlavan H., Rafiqul I. (1994). Laboratory simulation of geochemical changes of heavy crude oils during thermal oil recovery. Journal of Petroleum Science and Engineering, 12 (3), 219–231.

[167] Alvarado V., Manrique E. (2010). Enhanced oil recovery: An update review. Energies, 3, 1529–1575.

[168] U.S. Energy Information Administration. (2015). Global petroleum and other liquids consumption. Short-term energy outlook. [Online] available from https://www.eia.gov/forecasts/steo/report/global_oil.cfm.2 February, 2016.

[169] U.S. International Energy Agency. (2015). The oil market report. [Online] available from http://www.iea.org/aboutus/faqs/oil/. 4 February, 2016.

[170] U.S. Energy Information Administration. (2015). Global petroleum and other liquids consumption. Short-term energy outlook. [online] Available from https://www.eia.gov/forecasts/steo/report/global_oil.cfm. 10 May, 2016.

[171] Grand View Research. (2015). Global enhanced oil recovery (EOR) market by technology (thermal, gas injection, chemical) expected to reach USD 283 billion by 2020. [Online] available from http://www.grandviewresearch.com/press-release/global-enhanced-oil-recovery-eor-market. 2 January, 2016.

[172] Abu El Ela M., Samir M., Sayyouh H., El Tayeb S. (2008). Thermal heavy-oil recovery projects succeeded in Egypt, Syria. Oil and Gas Journal, 106, 48.

[173] Taber J. J., Martin F. D., Seright R. S. (1997). EOR screening criteria revisited—Part 1: Introduction to screening criteria and enhanced recovery field projects. SPE Reservoir Engineering Journal, 12(3), 189.

[174] Cobb K. (2010). Will enhanced oil recovery be an oil supply savior. [Online] available from http://scitizen.com/future-energies/will-enhanced-oil-recovery-be-an-oil-supply-savior-_a-14-3424.html. 20 December, 2015.

[175] SBI Energy. (2010). EOR enhanced oil recovery worldwide. [Online] available from http://www.sbireports.com/EOR-Enhanced-Oil-2523826/. 10 December, 2015.

[176] Nelder C. (2011). Heavy oil of the Kern River oil field. [Online] available from http://www.getreallist.com/heavy-oil-of-the-kern-river-oil-field.html. 15 December, 2015.

[177] Manicore. (2015). A peak in oil production, have you seen any? [Online] Available from http://www.grandviewresearch.com/press-release/global-enhanced-oil-recovery-eor-market. 20 February, 2016.

[178] Shandrygin A. N., Lutfullin A. (2008). Current status of enhanced oil recovery techniques in the fields of Russia. SPE Annual Technical and Exhibition, Denver, Colorado, USA.

[179] Dzhavadyan A. A., Gavura V. E. (1993). Modern methods of enhanced oil recovery and new technologies for the fields of the Russian federation. Journal Neftyanoye Khozyaistvo, 10, 6–13.

[180] U.S. International Energy Agency. (2015). Oil medium-term market report: Russian oil production. [Online] available from https://www.iea.org/publications/freepublications/publication/MTOMR_2015_Final.pdf. 5 May, 2016.

[181] Iskhakov I.A., et al. (2003). Perspectives of oil production and recovery enhancement in exhausted reef fields of Pre Urals flexure of bashkortoostan. Oil Industry Journal, 4, 49–54.

[182] Degtyarev N. M. (1993). Results of study and implementation of gas EOR. Oil Industry Journal, 4, 19–21.

[183] Millikin M. (2005). Mexico's largest oil field in premature decline. [Online] available from http://www.greencarcongress.com/2005/03/mexicorsquos_la.html. 22 January, 2016.

[184] U.S. Energy Information Administration. (2013). Enhanced oil recovery techniques helped Oman reverse recent production declines. [Online] available from http://www.eia.gov/todayinenergy/detail.cfm?id=13631. 28 December, 2015.

[185] U.S. Energy Information Administration. (2016). Oman international energy data and analysis. [Online] available from http://www.eia.gov/beta/international/analysis.cfm?iso=OMN. 10 March, 2016.

[186] U.S. Energy Information Administration. (2016). Oman is the largest non-OPEC oil producer in the Middle East. [Online] available from http://www.eia.gov/todayinenergy/detail.cfm?id=24632. 30 April, 2016.

[187] U.S. Department of Energy. (2006). Basin oriented strategies for CO_2 enhanced oil recovery: Permian Basin. Advanced Resources International for the US. Department of Energy, pp. 1–8.

[188] Global CCS Institute. (2009). U.S.-Permian basin. [Online] available from https://hub.globalccsinstitute.com/publications/co2-storage-depleted-oilfields-global-application-criteria-carbon-dioxide-enhanced-o-11. 15 February, 2016.

[189] Kuuskraaa V. A., Godeca M. L, Dipietro P. (2013). CO_2 utilization from “next generation” CO_2 enhanced oil recovery technology. Energy Procedia, 37, 6854–6866.

[190] Melzer L. S. (2012). Carbon dioxide enhanced oil recovery (CO_2 EOR): Factors involved in adding carbon capture, utilization and storage (CCUS) to enhanced oil recovery. CO_2 Consultant and Annual CO_2 Flooding Conference Director Midland, TX. [Online] available from http://neori.org/Melzer_CO2EOR_CCUS_Feb2012.pdf. 20 February, 2016.

[191] World Research Institute (WRI). (2012). CO_2-enhanced oil recovery. [Online] available from http://www.wri.org/publication/content/8355. 18 December, 2015.

[192] U.S. Department of Energy (DOE/NETL, 2014). *Near-term projections of CO_2 utilization for enhanced oil recovery*. Online available from https://www.netl.doe.gov/energy-analyses/temp/FY14_NearTermProjectionsofCO2UtilizationforEnhancedOilRecovery_040114.pdf. 12 Feb, 2016.

[193] Han D. K., Yang C. Z., Zhang Z. Q., Lou Z. H., Chang Y. I. (1999). Recent development of enhanced oil recovery in China. Journal of Petroleum Technology and Engineering, 22, 181–188.

[194] Guo S., Wang H., Shi J., Pan., Cheng Y. (2015). Synthesis and properties of a novel alkylhydroxyl-sulfobetaine zwitterionic surfactant for enhanced oil recovery. Journal of Petroleum Exploration and Production Technology, 5, 321–326.

Section 2

Chemical Enhanced Oil Recovery (cEOR)

Polymer Flooding

Antoine Thomas

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/64623

Abstract

The focus of this chapter is on polymers and their use to enhance oil recovery through the process known as polymer flooding. Emphasis is given to practical information relevant to field application(s) of polymer flooding. Therefore, the purpose of this chapter is to provide a brief but thorough overview of key concepts necessary to understand this technology for its successful implementation in the field.

Keywords: polymer flooding, polymers, polyacrylamide, chemical enhanced oil recovery, viscosity, sweep efficiency, pilot

1. Introduction

Among all the chemical-enhanced oil recovery methods (cEOR), polymer flooding is a straightforward technique with a lengthy commercial history and proven results. This technology by far outnumbers other chemical technologies because the risk of polymer flooding application is indeed very low and the envelope of application has greatly widened over the past years, with field cases in high temperature and high salinity reservoirs. Polymer flooding consists of injecting polymer-augmented water into a subterranean oil formation in order to improve the sweep efficiency in the reservoir. The increased viscosity of the water causes a better mobility control between the injected water and the hydrocarbons within the reservoir.

The early pioneering work on polymers was carried out by Pye [1], Sandiford [2], Mungan [3], and Gogarty [4] with later studies performed by Mungan et al. [5], Smith [6], Szabo [7], and others. The first "large" commercial uses of polymers to increase oil recovery date back to the 1960s and 1970s in the United States during a crude oil price control period. Economic incentive programs have played an important role in the development of chemical EOR processes in the

United States. ERDA (Energy Research and Development Association), DOE (Department of Energy), and the Cost-sharing Program provided direct financial support to oil companies for the implementation of EOR processes from 1974 through 1980. The DOE-EOR Incentive Program launched from 1979 to 1981 allowed frontend recoupment of expenses by allowing companies to sell oil at higher prices. The Crude Oil Windfall Profit Tax Act of 1980 reduced tax rates for EOR projects. The Economic Recovery Tax Act of 1981 provided research and experimentation tax credits. However, that program had a loophole which allowed EOR project incentives to be ring-fenced with full field production, which was exploited by oil companies. The result was higher "Tier 3" oil prices for projects that barely used EOR techniques, bringing economic successes but technical failures. For polymer flooding, few studies were carried out at the time and a number of projects used minute amounts of polymer, being totally inefficient at improving the sweep efficiency in reservoirs. In the end, the misconception that the technology did not work remained in the minds of petroleum engineers.

The number of projects abruptly decreased in the 1980s for several reasons including oil prices and poor global understanding of the technology. However, research has continued over the years and polymer flooding regained interest in China in the mid-1990s.

The largest polymer injection aimed at improving the mobility ratio was implemented in 1996 in the Daqing oilfield. As of 2004, more than 31 commercial projects were implemented, involving approximately 2427 injection wells and 2916 production wells. Polymer injection in the Shengli and Daqing oilfields yielded incremental oil recoveries ranging from 6 to 12%, contributing to 250,000 barrels per day in 2004. At the end of 2006, water consumption had decreased by 21.8 m^3 per cubic meter of oil produced, with a water-cut reduction of one-fourth resulting in important savings in regards to produced water treatment and disposal.

Another example of successful polymer injection in the 1990s was in Courtenay, France, where extra oil recoveries from 5 to 30% have been reported after the technology was conducted in a secondary recovery mode as augmented waterflooding. Other examples will be discussed later in this chapter.

The objective of the following work is to give a summarized overview of the key concepts necessary to understand this technology, which would allow its successful implementation in the field. Other chemical-enhanced oil recovery techniques that involve the use of polymers such as surfactant-polymer flooding and alkali-surfactant-polymer flooding are not discussed in detail here. There has been a wealth of papers and books published in recent years that the reader can refer to for further clarifications or details on polymer flooding and other cEOR techniques, part of which are cited in the following sections of this chapter.

2. Introduction to polymer flooding

2.1. History and concepts

Muskat [8] first recognized in 1949 that fluids mobility would affect waterflood performance. In 1950, Stiles [9] used permeability and capacity distribution in waterflood calculations; while

Dykstra and Parsons showed the effect of mobility ratio and permeability variations on oil recovery. The mobility ratio concept was then discussed by Aronofsky and Ramey as well as its influence on flood patterns, injection, and production histories in a five-spot waterflood in 1956. Dyes et al. [10] presented studies of the influence of mobility ratio on oil production after breakthrough. Following these studies, it was suggested to increase water viscosity to improve reservoir sweep efficiency. It was established a couple of years later by Pye and Sandiford [1, 2] that the mobility of the injected brine could be effectively reduced by the addition of small quantities of water-soluble polymers. More recently, studies have focused in essence on polymers and their behavior in reservoirs. This will be discussed in more detail shortly.

If waterflooding of an oil reservoir proves to be inefficient, due to premature water production and low oil recovery factor at water breakthrough, polymer flooding may be considered as a possible option. The value of adding polymer to a conventional waterflood can be explained by the mobility ratio which is defined by the following relationship:

$$M = \frac{\lambda_o}{\lambda_w} = \frac{\mu_o / k_o}{\mu_w / k_w}$$

where λ, μ, and k are the mobility, viscosity, and effective endpoint permeabilities, respectively, and where the subscripts w and o refer to water and oil. Effective permeabilities are considered since it allows considering the selective reduction of (usually) water permeability by polymer retention and pore-blocking mechanisms.

Oil is left behind in a waterflood either because it is trapped by the capillary forces (residual oil) or because it is bypassed [11]. The mobility ratio improvement associated with the use of polymers minimizes the bypassing effect.

Polymer flooding is often implemented in two cases [12]:

- When the mobility ratio during a waterflood is not favorable, continuous polymer injection can improve the sweep efficiency in the reservoir.
- Even with a favorable mobility ratio, if the reservoir has some degree of heterogeneity, polymer injection can help to reduce the water mobility in the high-permeability layers supporting the displacement of oil from the low-permeability layers [13].

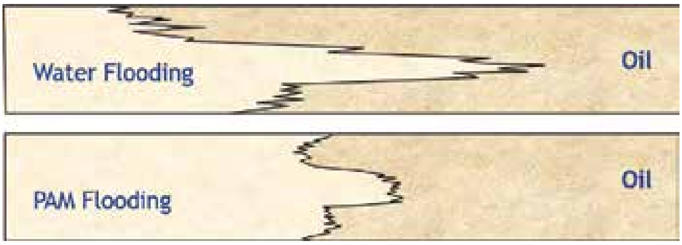


Figure 1. Water breakthrough can be delayed and sweep efficiency improved by increasing the viscosity of the injected fluid with polyacrylamide polymers (PAM) (modified with permission from Sorbie [11]).

In the first case, there is an inefficient macroscopic displacement that promotes early water breakthrough followed by a long period of two-phase production with increasing water-cuts. This situation can simply be illustrated by the viscous fingering concept which occurs especially in heavy oil reservoirs or when the mobility ratio M is larger than 1 ($M > 1$) (**Figure 1**). Fractional flow calculations extensively described in the literature can be useful to visualize the benefits of polymer injection and compare simple cases.

The second case is often overlooked. It appears that, even if the mobility ratio is equal or below 1, the presence of high-permeability channels or large-scale reservoir layering and heterogeneities can greatly impair the areal and vertical sweep efficiencies during water injection. The presence of high-permeability layers will also lead to early water breakthrough, in these cases significant improvement can be gained using polymers to increase the viscosity of the injected water. This aspect should be remembered when screening the candidates for polymer injection to not overlook reservoirs that contain very light oils. The mechanisms of oil recovery using polymers in heterogeneous systems are quite complex and a detailed explanation of those mechanisms is beyond the scope of this chapter. A proper overview is given in Sorbie's Polymer Improved Oil Recovery [11].

An important parameter in polymer flooding is how the improvement in oil recovery can be assessed compared to waterflooding. For this, two approaches can be used. The first one considers that polymer flooding produces only the moveable oil and does not change the residual oil saturation. In this case, the final amount of oil recovered should be the same between a waterflood and a polymer flood: the only difference would be the timescale to produce the same amount of oil for each case with polymer essentially accelerating oil production (**Figure 2**). However, this approach is highly dependent on reservoir characteristics since the presence of important heterogeneities would greatly hinder water from sweeping the entire reservoir, leaving some mobile oil behind.

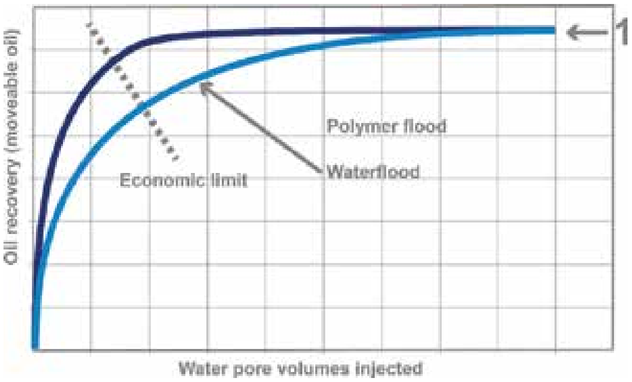


Figure 2. Production profiles for waterflood and polymer flood showing the economic limit [11].

Some recent studies [14, 15] have discussed the possible impact of polymers on residual oil saturation bringing forward the notion of viscoelasticity. In this case, in addition to pushing mobile oil, polymers would be able to decrease the residual oil saturation therefore recovering more oil than a simple waterflood, whatever the timescale considered.

The definition of incremental oil is therefore linked to the mechanisms behind polymer injection and the timescale considered for the project. For the latter, it would be necessary to compare water injection and polymer injection scenarios over the practical reservoir development period and the corresponding economic limits. This can be done with simulation studies which are not discussed in detail here.

2.2. Polymer flooding plan

There is no general rule defining the quantity of polymer that should be injected into a reservoir. The number generally given, based on experience, is a minimum of 30% of the reservoir pore volume, with the following sequence:

- Viscosity ramp-up at the beginning of the project to observe the reservoir response and possible pressure increases.
- Viscosity plateau with a minimum of 30% reservoir pore volume (the worldwide average is approximately 50% of pore volume injected). The larger the slug, the better the efficiency during polymer injection and after. The maximum efficiency will be reached after 1 PV injected.
- Viscosity ramp-down over the last 5% of pore volume injected, which serves to decrease the viscosity contrast between the polymer slug and the water chase.

As previously indicated, the larger the volume of polymer injected expressed as reservoir pore volume, the higher the efficiency of the process. This is explained by looking at what is happening when the injection of polymer is switched back to water injection at the end of the process: if the polymer slug volume is too small, there is a high probability that the chase water will again finger through the polymer slug, thereby decreasing the efficiency of the whole process.

Another technique described in the literature in regards to the application of polymer flooding in the Daqing oilfield is the sequential injection of high-viscosity polymer slugs to improve reservoir conformance and redistribute the flow inside the reservoir by decreasing the flow in the high-permeability zones [16].

The vast majority of polymer floods inject concentrations of active polymer between 1000 and 2000 parts per million (ppm), whatever the reservoir characteristics and oil viscosity. These "magic" numbers do not always have a scientific basis: normally, if the oil viscosity is very high or the reservoir heterogeneities are important, a higher viscosity should be considered at least for the pilot stage to check the acceptable reservoir pressure limits; while the final viscosity of the polymer solution to be injected is often dictated by the economics and the oil price at the time of the project approval.

Finally, the incremental oil recovery from polymer injections averages an extra 10% of oil originally in place (OOIP). The Courtenay oil field in France yielded from 5 up to 30%, the

Daqing oil field showed approximately 12%, and the Marmul field roughly 10% of incremental oil recovery.

2.3. Timing

The paradox with enhanced oil recovery methods is that they are often classified as tertiary recovery methods, even if it is well-known that primary recovery followed by water injection is, for a significant number of reservoirs, not able to produce more than 35% OOIP on average. The question that pops up is therefore: why do we wait to change the field development approach and implement the so-called enhanced oil recovery techniques from the very beginning? There are probably multiple answers to this question:

- Lack of knowledge on the green field: geometry, fluid distributions, pressure responses to a viscous fluid injection, optimal well placement, and connectivity between zones, etc.
- How to quantify the efficiency of an EOR method and incremental oil without baseline data for comparison?

The appropriate timing for a polymer injection can be summarized in a simple statement: the earlier the better! The economics of secondary EOR application will always be better than the economics of tertiary (and late) EOR, knowing that polymer flooding brings forward the oil production profile, delays water breakthrough and the overall handled water volumes and associated costs of water treatment and disposal. Nevertheless, there is still a significant benefit of implementing the technology even in watered-out reservoirs and especially for heavy oil pools [17].

2.4. Screening criteria for polymer application

Historically, it appears that sandstones were preferred over carbonates when considering polymer injection. For instance, when looking at the projects in the USA between 1971 and 1990, 320 pilot projects or field wide chemical floods have been identified in the literature among which 57 were conducted in carbonate reservoirs. This preference can probably be explained by the fact that anionic polymers present several advantages: they have a high viscosifying power, very high molecular weights, and are cheap to produce by opposition to synthetic cationic polymers which are expensive to produce, highly shear sensitive, and display lower molecular weights on average. For sandstone and clayey reservoirs, which are negatively charged, the injection of anionic macromolecules is obviously preferred to limit ionic interactions.

Papers published in the 1960s, 1970s, or even 1980s indicate that polymers for EOR were limited to a narrow range of oil field conditions (**Tables 1** and **2**). A literature review on polymer field applications shows that the maximum reservoir temperature was 200°F (90°C), crude oil viscosity had to be below 200 cP, and injection water must not exceed a certain amount of divalent ions (300–500 ppm).

Reservoir temperature (°F)	<200
Polyacrylamide	<160
Xanthan gums	<200
Crude oil viscosity (cP)	<200
Water-oil mobility ratio	>1
Mobile oil saturation (%PV)	>10
Water-to-oil ratio (WOR)	<15 preferred
Average reservoir permeability (mD)	>20
Lithology	Sandstone preferred
Reservoirs with strong natural water drive, large gas caps, gross channeling, or major natural fractures should be avoided	

Table 1. Screening criteria for polymer flooding according to Chang [18].

In 1991, Sorbie described some limits which were within the same range, i.e., T_{max} = 95°C, oil viscosity < 70 cP, and reservoir permeability above 20 mD (**Table 2**).

Seright [17] proposed several explanations for these screening criteria considering the state of the technology and oil prices at that time:

- Considering an oil price of $20, 150 cP was viewed as the most viscous oil that could be recovered economically using polymers.
- For oil viscosities above 150 cP, the viscosity requirements to achieve a favorable mobility ratio were expected to decrease injectivity.

Many improvements have widened the range of polymer applicability for polymers in cEOR. In addition to a better understanding of polymer flow behavior through the rock formation and a better knowledge of the geology and dynamics of the reservoirs, many developments in chemistry have allowed manufacturing polymers that are more stable to high temperatures, tolerant to high salinity and hardness concentration, and shear resistant polymers. The addition of protective additives to prolong the chemical stability of the polymers has been also performed. Furthermore, new equipment has been designed to maximize the injection efficiency of polymer solutions while decreasing the overall risk of degradation before entering the reservoir. For instance, Vermolen et al. [19] described the stability of *N*-vinyl pyrrolidone (NVP)-based ter-polymers for 1 year at 120°C in 180 g/L TDS brine. Gaillard et al. [20] tested the efficiency of protective additives on temperature and salinity resistant polymers. Seright et al. described the implementation of polymers in a field with 500 cP oil. Kulawardana et al. [21] demonstrated the efficient propagation of NVP ter-polymers in 50 mD cores at 100°C. This is just a very small view into the work that has been conducted in the past years to validate the polymer technology for EOR applications. Many references are given for further reading at the end of the chapter.

Some unchanging parameters that must be considered before the implementation of polymer flooding are:

- Water injectivity: obviously, good water injectivity will ensure appropriate polymer injectivity. Several guidelines will be provided later on.
- Clays: a high percentage of clays can be detrimental to polymer propagation (adsorption and retention).
- Presence of aquifers: to avoid dilution and chemical losses, injection should occur outside of the aquifer zone.

Screening criterion	Viscosity control polymer flood	Heterogeneity control polymer flood	Comment
Oil viscosity	Usually 5 cP < μ_o < 30 cP Max 70 cP	Usually 0.4 cP < μ_o < 10 cP Max 20 cP	The indicator in both cases is early water breakthrough and low sweep efficiency
Level of large -scale heterogeneity	Low formation should be as homogeneous as possible	Some heterogeneity by definition 4 < horizontal perm. /average permeability/ k_{av} < 30	For heterogeneity control less severe contrast does not require polymer and more severe is too high for normal polymer
Absolute permeability	>20 mD		To avoid excessive polymer retention
Temperature	Lower temperature best Best <80°C Max <95°C		Polymers degrade at higher temperatures
Water injectivity	Should be good preferably with some spare injection capacity—fracturing may help		If there are some problems with water, they will be worse with polymer
Aquifer/oil/water contact	Injection not deep in aquifer or far below oil/water contact		Additional retention losses in transport to oil leg
Clays	Should be generally low		Tend to give high polymer retention
Injection brine salinity/ hardness	Not critical but determine which polymer can be used		High salinity/hardness biopolymer Low salinity/hardness = PAM

Table 2. Screening criteria for polymer flooding according to Sorbie [11].

Table 3 presents updated screening criteria for polymer flooding, in which only the upper values of the respective ranges are provided for the most important criteria.

Parameter	Year 1970s and 1980s	After 2000
Oil viscosity	<200 cP	<10,000 cP
Temperature	<95°C	<140°C
Permeability	>20 mD	>10 mD
Salinity	Low (<30 g/L TDS)	<200 g/L TDS

Table 3. Current screening criteria for polymer flooding application (updated after [11] and [18]).

2.5. Other technologies

- Surfactant-polymer (SP) and alkali-surfactant-polymer (ASP)

Capillary forces cause large quantities of oil to be bypassed in well-swept zones of water-flooded oil reservoirs [13, 22]. Surfactant injection (surface active agents) can reduce the interfacial tension between the oil and water and release trapped oil; while the injection of a large polymer slug provides mobility control. However, it is often necessary to inject significantly higher dosages of costly surfactants to balance their adsorption onto the rock surface. This effect can be offset by addition of alkali to the solution. The latter will adsorb onto rocks (decreasing surfactant adsorption), increase the pH, and generate *in situ* soaps. This process often requires expensive water treatment facilities, and combined with the surfactant, can generate difficulties to break the produced emulsion. Surfactant-polymer and alkali-surfactant-polymer require a careful design and should be monitored cautiously [13].

- Gels and derivatives

As discussed by Seright et al. [23], the preliminary discussion is to point out the main differences between a gel used for reservoir conformance control and a polymer flood. Conventional gels used in "conformance control" are intended to block or reduce the flow capacity of high-permeability channels without damaging the less-permeable hydrocarbon-productive zones. It is therefore compulsory to minimize penetration of gelants into the less-permeable zones. Any gel or blocking agent that enters the less-permeable zones can hinder or even shut off any subsequent injected fluids from entering and displacing oil from those

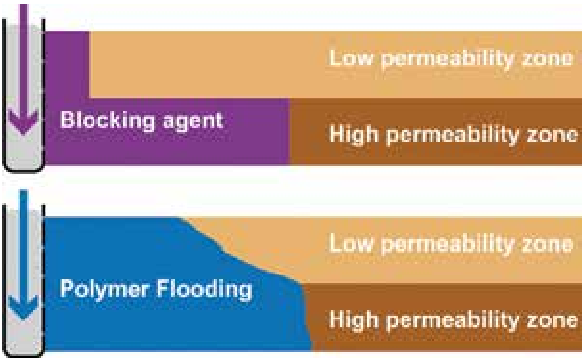


Figure 3. Comparison between polymer flood and gel systems (modified with permission from Seright [23]).

zones. In contrast, polymer floods are designed to directly displace oil from lower permeability zones. As a matter of fact, a viscous polymer solution should enter as much as possible into these lower permeability zones to displace oil from these poorly swept areas (**Figure 3**, [23]).

Particularly, colloidal dispersion gels—low polymer concentration with a metallic cationic cross-linker—are often claimed to be more efficient and cost-effective than conventional polymer floods. Several questions arise in regards to this claim and are as follows:

- Does the cross-linker propagate inside the reservoir without any retention on the negatively charged clays and sandstone? Obviously, the answer would be probably no in this case.
- Are these gels plugging mainly the high-permeability layers allowing the chase fluid to go into the low-permeability zones? This statement defies basic reservoir engineering laws including Darcy's law.

Some positive results have been reported from field applications of this technology. However, the extra-oil recovery observed might be caused by:

- A decreased mobility ratio obtained by the added polymer within the colloidal dispersion gel formulation, even at low polymer concentrations. It should be noticed that increasing the water viscosity from 1 to 2 cP divides the mobility ratio expression by 2.
- A decreased relative permeability to water that could be induced by both: overall polymer retention (mechanical retention and adsorption) and the formation of gel in all zones of the reservoir, with a temporary effect on the oil recovery.

In any case, laboratory studies involving coreflooding using long reservoir core plugs should be performed to ensure that the entire system propagates through the core plug prior to implementation in the field.

3. Polymer characteristics

Polymers are chemical compounds composed of repeating units called monomers. Biopolymers and synthetic polymers are the two families of polymers usually considered by the oil industry when attempting to increase water viscosity and to improve the sweep efficiency of the reservoir. These types of polymers will be briefly described in the following paragraphs. However, a particular focus will be directed to synthetic polymers, which are the most commonly used polymers by the oil industry, primarily due to their availability and favorable costs.

3.1. Biopolymers

Xanthan gum and more recently schizophyllan are the main biopolymers considered for applications in the oil industry.

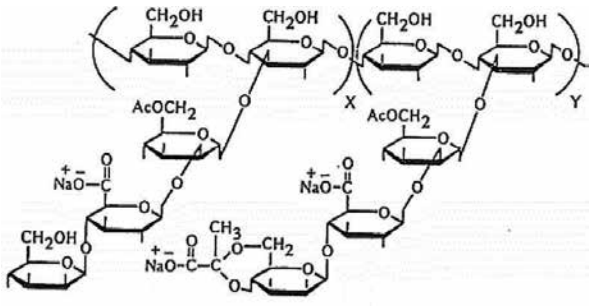


Figure 4. Molecular structure of Xanthan gum [24].

Xanthan gum is a fermentation product produced by a mutant of *Xanthamonas campestris*. Xanthan gum is a polysaccharide made from saccharide monomer units which are D-glucose, D-mannose, and D-glucuronic acid. This biopolymer has a cellulose-like backbone composed of repeating β -D- (1-4) glucose units with mannose and glucuronic acid side chains, and the mannose partially modified with acetyl and pyruvate ketal groups (**Figure 4**). The rigid structure of xanthan gum provides good shear and brine tolerance when compared to polyacrylamides. However, some drawbacks still remain such as cost and availability and the fact that the biopolymer should be protected from any biological attack with biocides.

Xanthan gum is available in different forms:

- Broth: from 5 to 13% active content in an aqueous medium that contains a biocide.
- Powder: dry form with an active content >90%.

Schizophyllan is a homo-glucan with an average molecular weight of 2–3 million Dalton produced by a fungus in a fermentation process from a carbon source (**Figure 5**) [13]. The polymer has a linear structure without charged functional groups which yields high viscosity as well as salt tolerance. The rigidity of the structure is also responsible for the mechanical and temperature stabilities.

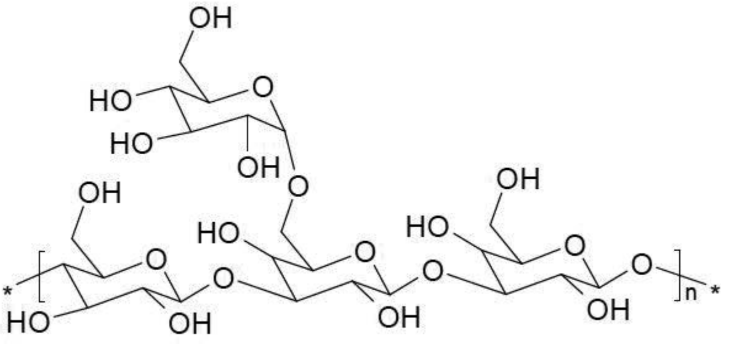


Figure 5. Chemical structure of β-1, 3:β-1,6 glucan [13].

A critical step for the development of this biopolymer was the biotechnological process required to separate the fungus from the biopolymer and make it viable at large scales.

3.2. Partially hydrolyzed polyacrylamide

The most common synthetics polymers used in polymer flooding are partially hydrolyzed polyacrylamides (HPAMs) and synthetic flexible straight chains of acrylamide monomers.

HPAMs are prepared with a typical degree of hydrolysis of 30%, but it can be adjusted to be higher or lower. These polymers are usually delivered in two forms:

- Powder: >90% active content.
- Emulsion: as a water-in-oil emulsion with 30% active content, which must be properly inverted to release the polymer (**Figure 6**).

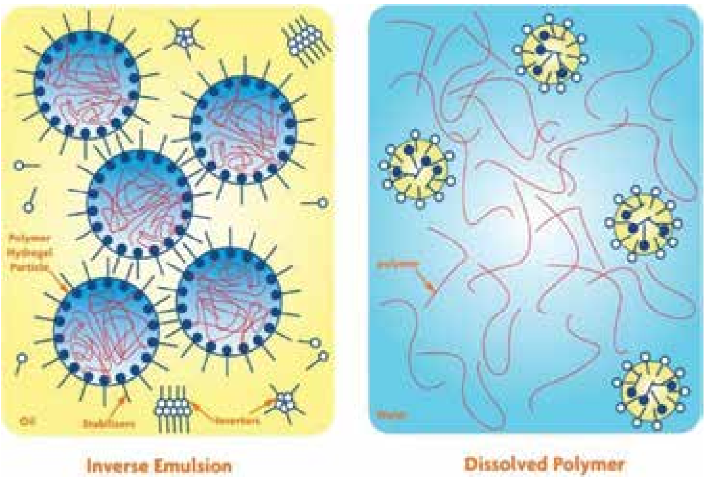


Figure 6. Inverse emulsion system [25].

3.2.1. Polymerization processes

These polymers can be manufactured using different chemical paths as follows:

- Copolymerization of acrylamide and sodium acrylate (or/and sodium acrylamido-tertiary-butyl sulfonate (ATBS)) (**Figure 7**).
- Cohydrolysis or posthydrolysis of a polyacrylamide (**Figure 8**).
- Copolymerization or terpolymerization of acrylamide with other ionic or nonionic functional monomers. Functional monomers can enhance the resistance to temperature and salinity (example of *N*-vinylpyrrolidone for improved thermal and salinity resistance) [26].

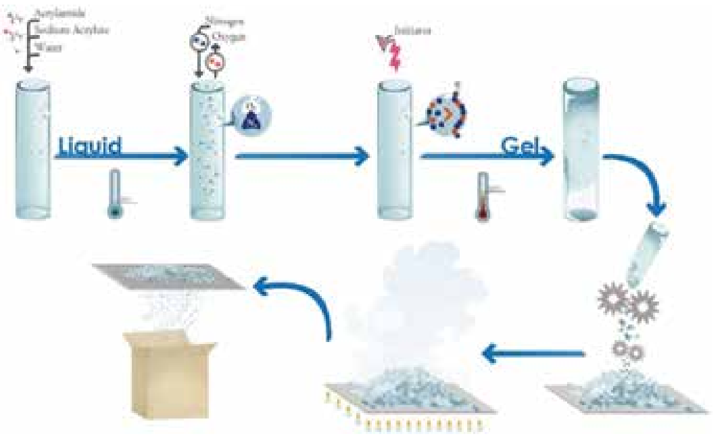


Figure 7. Overview of the copolymerization process [25].

Figure 8. Overview of the posthydrolysis process [25].

Depending upon the manufacturing process, the distribution of the anionic charges along the polymer chain differs, which induces different physical properties during and after hydration. Posthydrolyzed polyacrylamides are composed of a wide range of anionic chains, some being highly charged and others less charged. The copolymerization of acrylamide and sodium acrylate produces a polymer with a more even charge distribution along the backbone. These properties are paramount for the behavior of the polymers in an aqueous solution, especially in the presence of divalent cations such as calcium and magnesium [13].

There are several ways to characterize anionic polyacrylamides including their molecular weight (M_w) and molecular weight distribution or polydispersity index (PDI). The range of M_w typically lies between 4 and 30 million g/mol and it is often determined using intrinsic viscosity measurement. As of today, PDI cannot be determined since neither standards with low PDIs nor GPC (gel permeation chromatography) techniques exist today for such high M_w. However, as with the anionicity, a relatively wide range of molecular weights is present in one given product. Moreover, the structure of copolymers is more easily controlled than the post-hydrolyzed molecules. **Figures 9** and **10** show some common polymer structures [26].

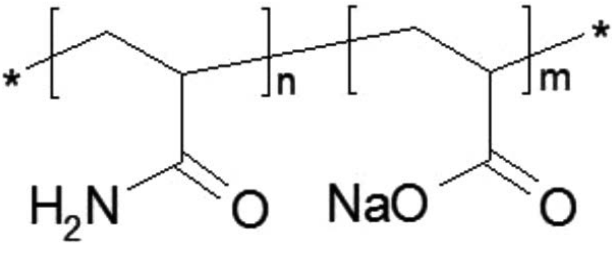


Figure 9. Example of acrylamide and sodium acrylate copolymer [26].

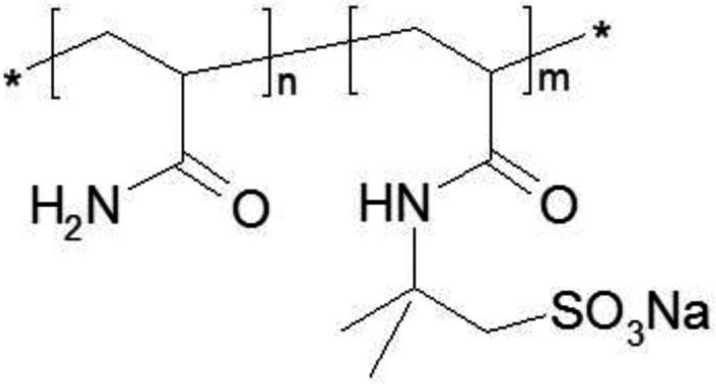


Figure 10. Example of acrylamide-ATBS copolymer [26].

3.2.2. Viscosity

The thickening or viscosifying capability of anionic polyacrylamides is linked to the level of entanglement of the high molecular weight macromolecules and also to the intra- and intermolecular electrostatic repulsions between polymer coils. When polyelectrolytes are dissolved in water containing electrolytes (salts), a reduction in viscosity is observed [27]. This is attributed to the shielding effect of the charges leading to a decreased electrostatic repulsion and therefore to a minimum expansion of the polymer coils in the aqueous solution. The result is a lower hydrodynamic volume and consequently a lower viscosity [28]. In addition to the salt dependency, other factors influencing the viscosity of partially hydrolyzed polyacrylamide solutions are the degree of hydrolysis, solution temperature, molecular weight (**Figure 11**), tridimensional structure, and solvent quality [29].

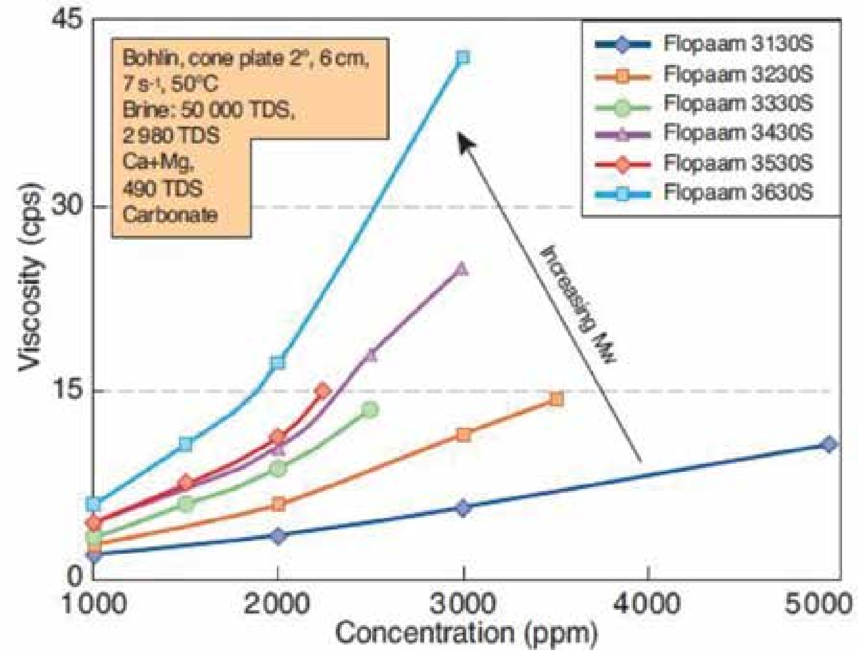


Figure 11. Viscosity of several polymers as a function of concentration. The average molecular weight increases from Flopaam 3130S to 3630S [25].

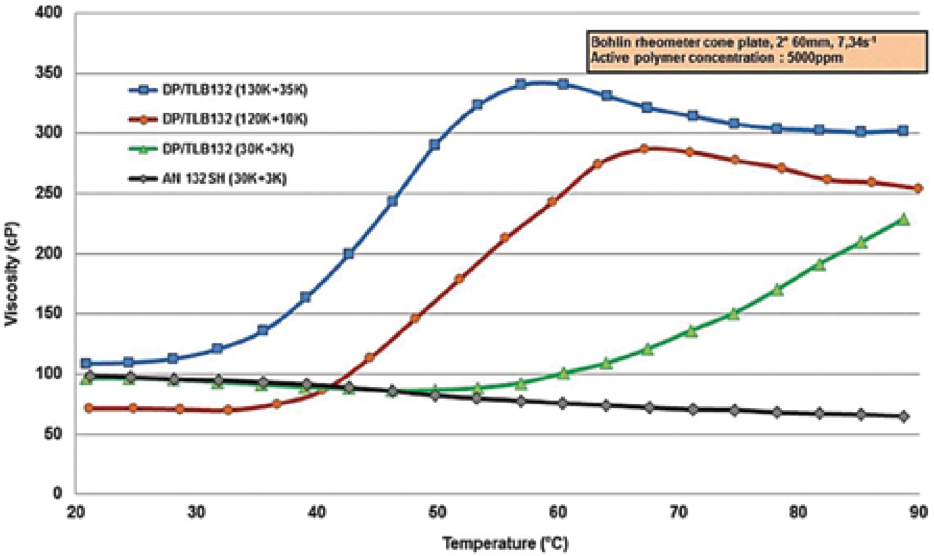


Figure 12. Viscosity versus temperature for several polymers including thermoresponsive (DP/TLB) and conventional polymers (AN132SH). Brines are displayed as 130K + 35K meaning 130 g/L NaCl + 35 g/L $CaCl_2$ (from Leblanc et al. [31]).

At isomolecular weight and at isoconcentration conditions, polyelectrolytes are likely to behave differently depending on their chemistry and on the composition of the aqueous media. For instance, if the polymer is compatible with the injection and/or formation brine, the polymer molecule will uncoil allowing interchain interactions. In the other case, if the polymer is not compatible with the injection and/or formation brine, the polymer molecule will coil up resulting in intramolecular associations.

Other strategies exist to enable intermolecular associations independently of the molecular weight of the polymer. One approach is the incorporation of hydrophobic moieties within a hydrophilic molecule in the polymer backbone—leading to segments that associate. A concise overview of this technology including the chemistry of these so-called associative polymers is given by Wever et al. [30]. More recently [31], thermosensitive polymers have been developed (**Figure 12**). The thermosensitive concept involves water-soluble main chains with blocks or side groups which possess lower critical solution temperature or LCST moieties [32]. These thermosensitive polymers display viscosity increase as a function of salinity and temperature. Other advantages of these thermosensitive polymers would include the highly improved injectivity of the viscous polymer solutions inside oil-bearing formations since the viscosity would build progressively with temperature and/or salinity.

3.2.3. Rheology

Polyacrylamide fluids behave as non-Newtonian fluids meaning that the viscosity is dependent on the applied shear (**Figure 13**). They show a pseudo-plastic (or shear thinning) behavior: viscosity decreases as shear stress increases following a power-law model (**Figure 14**). The viscosity is dependent upon the concentration and the molecular weight of the polymer in the aqueous solution. Moreover, the rheological behavior of synthetic polymers in porous media is quite different from their rheological behavior in bulk (in a viscometer measuring device). This topic is beyond the scope of this chapter and it will not be discussed here.

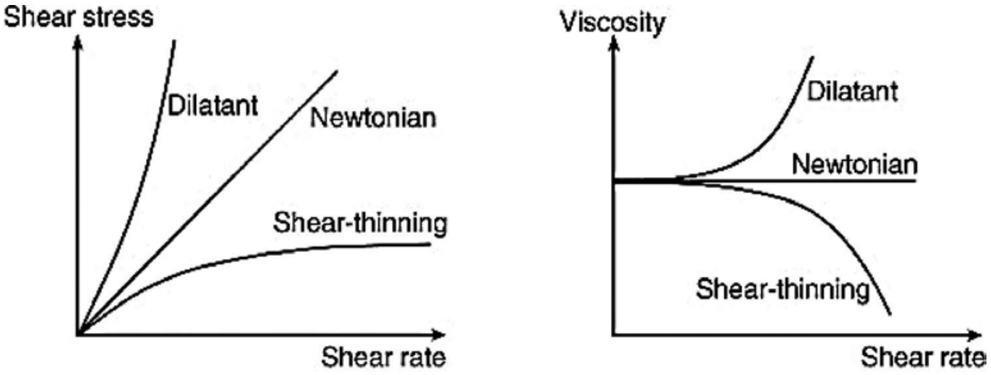


Figure 13. Types of fluids and their characteristics [25].

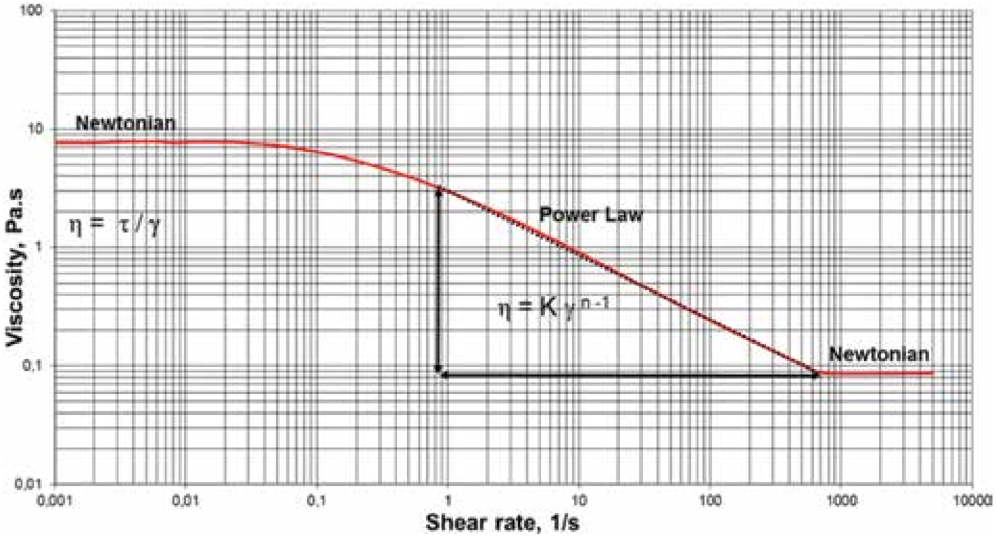


Figure 14. Viscosity profile for a typical non-Newtonian polyacrylamide fluid as a function of shear rate fitted using a power law equation [33].

3.2.4. Solubility

In the field, polyacrylamides are solubilized in injection brine which contains dissolved salts. Total dissolution of the polyacrylamide in the brine is achieved when no insoluble or swollen particles remain in the solution, as determined by the filtration test. If high molecular weight polymers with $M_w > 1$ million g/mol or even higher molecular weight ($M_w \approx 18$ million g/mol) polymers are used in the field, injectivity issues can be observed if total dissolution of the polymer in the brine is not achieved. Furthermore, polymers may contain low concentration of partially soluble species (i.e., branched or cross-linked chains) due to the manufacturing process. Therefore, it is necessary to ensure that minute undissolved polymer clusters known as fish-eyes are not formed during the polymer dissolution process, in order to limit potential damages to the formation during polymer injection.

3.2.5. Stability tests

Long-term stability tests are useful to ensure that polymer degradation will not occur within the reservoir during the transit time between the injection and production wells. Polymer solutions are prepared under anaerobic conditions inside a glove (**Figure 15**) and stored in specially designed stainless steel ampoules which are stored in oven at the specific reservoir temperature. Viscosity is checked on a regular basis inside the glove box using concentric cylinder Brookfield rheometers. Some stability studies can last several years for offshore projects where the spacing between the injector and producer is large and transit times are significant.

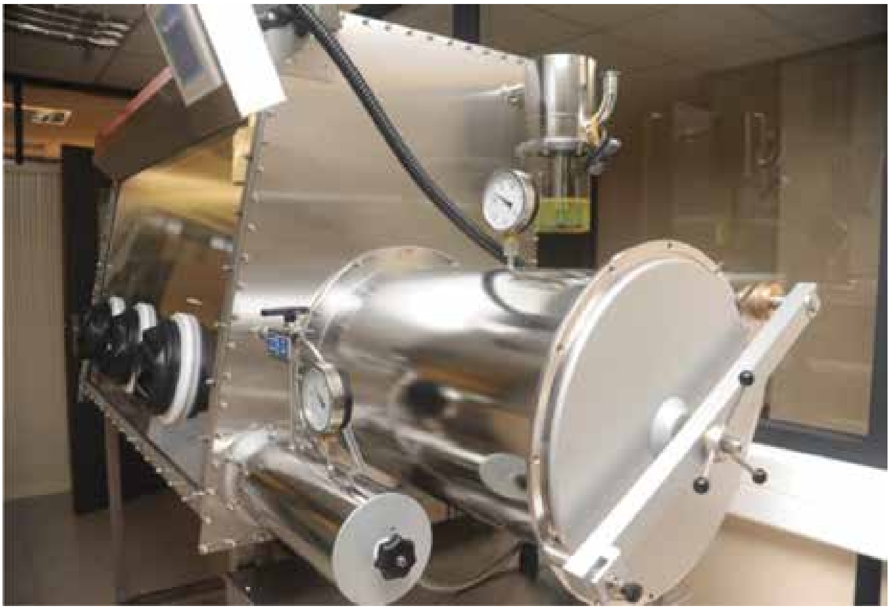


Figure 15. Typical glove box set-up to perform tests in anaerobic conditions [25].

3.2.6. Coreflooding

Polymer injection into porous medium (i.e., coreflooding tests) is a useful testing procedure to check the propagation of the macromolecules through core plugs from the reservoir to ensure that irreversible damage to the formation will not occur. However, it is necessary to be mindful that a core plug will never be representative of what will happen in a field application, in particular at the harsh conditions near the injection wellbore. Therefore, it is important to define the goal of coreflooding testing, such as the establishment of face plugging and the verification of proper polymer propagation along the core plug. Likewise, it is important to understand that coreflooding testing will not provide information on the following aspects:

- Polymer coreflooding testing does not provide information of the actual injectivity of the polymer in the field. Wellbore effects (even if radial corefloods are performed) on polymer flooding, such as completion, flow rates, the presence of microfractures, and damage formation, among others, cannot be evaluated during coreflooding testing. An example is the polymer shear-thickening behavior observed in the laboratory that will probably never occur in the field when considering the presence of microfractures created after completing the well (i.e., perforations, stress changes) or during the waterflooding stage.
- Polymer coreflooding testing does not provide information on true polymer overall retention values. Even if it seems obvious, it is important to remember that every reservoir have some degree of heterogeneity, therefore, polymer retention in the field will be likely greater than polymer retention observed in the laboratory [34].

More realistic objectives for polymer coreflooding testing are:

- To compare several polymers in terms of propagation and pressure drop stabilization.
- To compare the relative retentions of several polymers as well as residual resistance factors (permeability reduction).
- To established the efficiency of oil recovery as a function of polymer type and viscosity injected.
- To gather data to use (wisely) in simulation models for upscaling (resistance factors and retention, among others).

Preliminary screening can be performed using analog core plugs before using the actual reservoir core plugs to obtain more realistic retention and mobility reduction values.

Two important parameters are usually evaluated, the mobility reduction (or resistance factor) and the permeability reduction (or residual resistance factor). The mobility reduction (*FR*) is the apparent relative viscosity of polymer solution during its flow through the porous medium, defined by:

$$FR = \frac{\Delta P_{\text{polymer solution}}}{\Delta P_{\text{brine}}} \; \alpha \; \frac{\mu_{\text{polymer solution}}}{\mu_{\text{brine}}}$$

where $\Delta P_{\text{polymer solution/brine}}$ is the pressure drop during polymer injection and brine, respectively, and μ is the viscosity of the fluid considered.

The permeability reduction or residual resistance factor, *FRR*, is the reduction of permeability due to several mechanisms such as polymer adsorption onto the rock surface, mechanical retention of polymers in pore constrictions that are of smaller size than the polymer macromolecules, and any other condition that retains polymer in the porous media (i.e., polymer precipitation due to interactions with divalent cations present in the reservoir brines). The residual resistance factor (*FRR*) is defined as:

$$FRR = \frac{\Delta P_{\text{post polymer}}}{\Delta P_{\text{brine}}} \; \alpha \; \frac{k_{\text{brine}}}{k_{\text{post polymer}}}$$

Polymer retention would be a more appropriate wording since it includes adsorption, mechanical, and hydrodynamic entrapment as explained for instance in Sorbie [11] (**Figure 16**). Retention can be determined using several methods, either in static or dynamic conditions, the latter being the most relevant. Common acceptable values for polymer retention by sandstones range from 10 to 50 μg of lost polymer per gram of rock. Polymer retention depends on the lithology of the rock (i.e., the presence of clay, clay content, and types of clays) and on the polymer characteristics (i.e., molecular weight, chemistry, degree of hydrolysis, etc.).

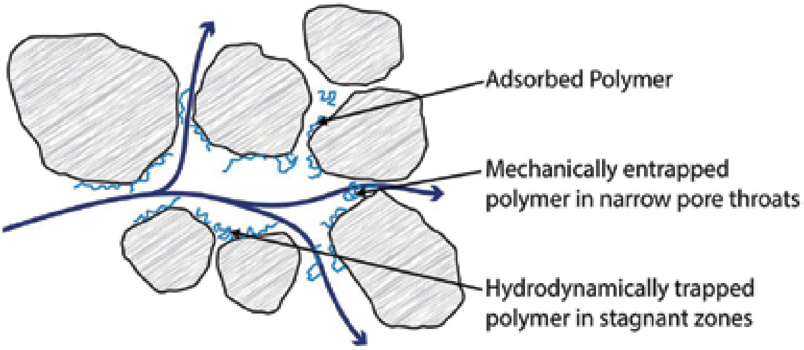


Figure 16. Mechanisms of polymer retention (modified with permission from Sorbie [11]).

Polymer retention in the porous media can be controlled by manipulating the polymer chemistry (i.e., the addition of ATBS is known to favor polymer propagation), the molecular weight (lower molecular weight means less hydrodynamic retention), and by adding sacrificial agents upfront to condition the reservoir before polymer injection, such as low molecular weight polyacrylates [35]. Determining a "true" residual resistance factor often requires the injection of many pore volumes of water. Injecting water behind a polymer slug creates an unstable displacement front and cleaning the core from any residual polymer in this case could take a long time. It is therefore recommended to take a value of FRR equal to 1 for simulation purposes to be conservative.

3.2.7. Polymer degradation

The stability and chemical reliability of polymers used for cEOR are significant factors for oil field applications. Polymers can undergo chemical, mechanical, and thermal degradation during EOR flooding operations.

Currently, there are limited data available from actual polymer oil field applications in regards to the degree of degradation endured by the polymer injected during the flooding operation. Internal reports and papers published on polymer floodings carried out at the Daqing and Shengli oil fields (China), indicate that the viscosity of the produced polymer solution was low [36, 37]. Additionally, polymer concentration in the produced solution was 50% lower than the concentration of the injected polymer, the anionicity of the polymer was increased, and the produced polymer average molecular weight was much lower compared to the molecular weight of the injected polymer. For field applications, it is also important to determine where polymer degradation occurs—at the surface facilities, down hole of the injection well, or inside the reservoir. In any case, it is paramount to minimize any potential degradation to maintain a reasonable viscosity of the polymer solution injected during the duration of the cEOR flooding to maximize the extra oil recovery.

A brief review on the chemical, mechanical, and thermal degradation of polymers within the context of cEOR is presented in the following paragraphs.

- Chemical degradation

Chemical degradation is related to the formation of free radicals that can react with the polymer backbone resulting in a drop of molecular weight [38, 39] and viscosity loss. Redox reactions are often involved in the formation of free radicals [40]. The presence of chemicals or contaminants such as oxygen contributes to the formation of such radicals. For example, iron II and/or H_2S in contact with oxygen cause polymer degradation. Stabilizer compounds are added to some commercial grade polymers to delay the unavoidable occurrence of chemical degradation. **Figure 17** shows the percentage of viscosity loss of the polymer solution as a function of iron and oxygen concentration. The viscosity loss can reach 50% with the addition of only 1 ppm of iron and 300 ppb of oxygen.

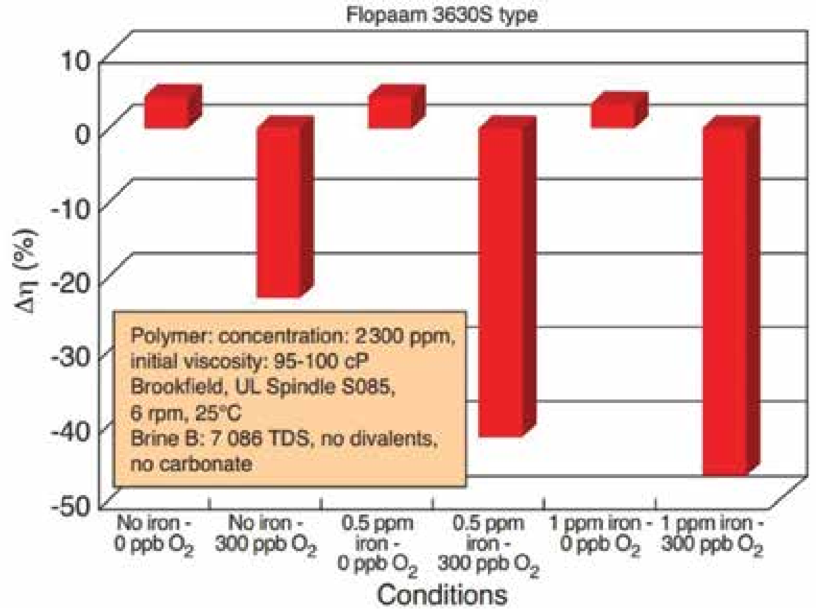


Figure 17. Polymer degradation in presence of oxygen and iron 2 in 7.086 g/L TDS brine [26].

Oxygen. A concentration of oxygen below 5 ppb allows for good stability of a polyacrylamide solution up to 120°C for more than 200 days [41, 42]. The addition of oxygen scavengers such as dithionite and sodium sulfite [41, 43] to the brine is beneficial to maintain the concentration of free oxygen at a low level in the brine. However, any reexposure to any trace of oxygen in the presence of residual oxygen scavenger will act to break the polymer chains. It is therefore compulsory to keep the oxygen content as well as the presence of oxygen scavenger in the brine under control.

Iron. To limit the effect of polymer degradation due to the presence of iron in the injection brine, several complexing agents can be added to the solution such as EDTA (ethylene diamine tetra-acetic acid). However, using a chelating agent to complex iron can lead to an increase of the degradation of the polymer [44]. Another approach is to partially precipitate the iron contained in the injection brine by increasing the pH of the solution with sodium carbonate [42].

- Mechanical degradation

Mechanical degradation occurs when the polymer backbone is subjected to a large shear rate, high velocity (i.e., flow rate), and singular pressure drop. The critical points which must be assessed along the injection facilities are chokes, valves, and certain types of pumps, as well as the well completion [26, 45].

In every case, choosing the right polymer is paramount: the higher the average molecular weight, the higher the sensitivity to shear. Breaking a high molecular weight polymer can possibly improve the injectivity with a minor viscosity loss. A drawback to this method can be the loss of the viscoelastic effect which is mainly given by the highest molecular weight fraction of the polymer [46]. **Figure 18** shows the impact of shear degradation on polymers with different molecular weights. This experiment was carried out using a pipe of 0.875 mm internal diameter and a pipe length of 200 mm. As mentioned previously, the higher the molecular weight, the higher the irreversible viscosity loss. Large-scale studies and field cases (especially dealing with the effect of well completion on the mechanical degradation of polymer) can be found in the following references [47–49].

- Thermal degradation

Thermal degradation varies with the type of polymer and reservoir conditions. For typical HPAM polymers, a temperature increase will lead to an increase in the hydrolysis of acryla-

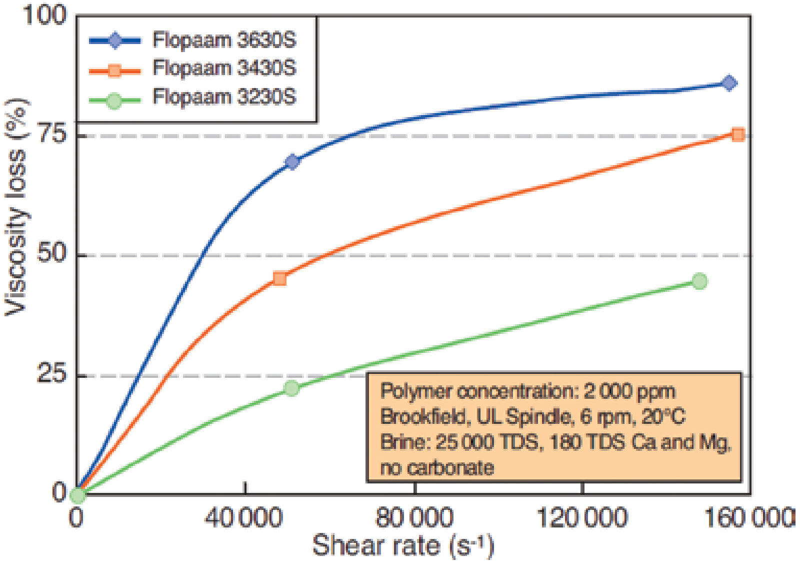


Figure 18. Shear degradation and percentage of viscosity loss for polymers having the same chemistry but different molecular weights (from high molecular weight polymer, Flopaam 3630S, to lower molecular weight polymer, Flopaam 3230S) [26].

mide moieties generating a higher charge density of anionic functionalities along the polymer backbone (**Figure 19**).

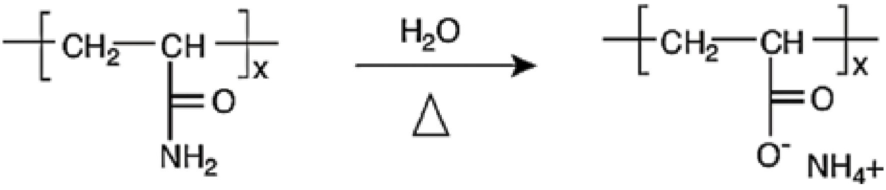


Figure 19. Hydrolysis of acrylamide moieties along the polymer backbone [25].

If the brine contains significant amounts of divalent cations such as calcium and magnesium, a viscosity drop is observed due to ionic bridges that can ultimately result in precipitation of the polymer [50]. The incorporation of sulfonate monomer (ATBS) to the polymer backbone improves its tolerance to calcium (AN125SH) at high temperature but in general with an increased polymer cost (**Figure 20**). An optimal polymer composition (i.e., addition of ATBS monomers) can be customized in the laboratory for a particular reservoir and its unique conditions.

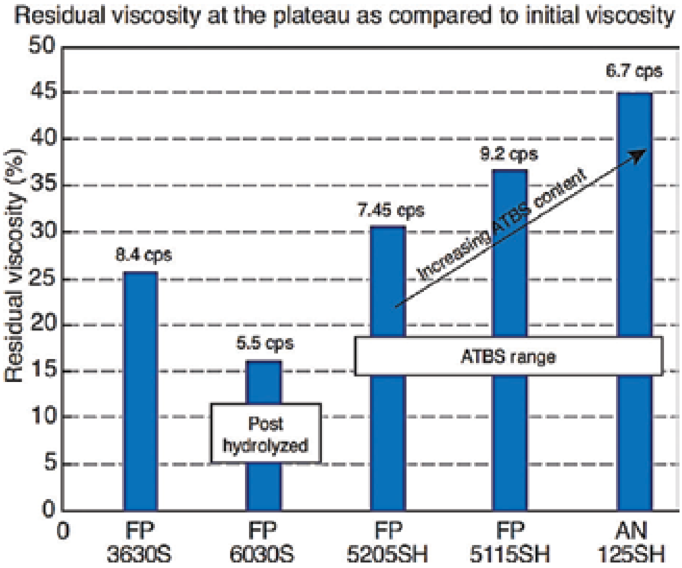


Figure 20. Salt tolerance of different polymer chemistries. The three polymers on the right side of the graph have increasing ATBS content [25].

It is clear that fine-tuning the polymer chemical structure (i.e., composition and molecular weight) is crucial to optimize the polymer stability for application at specific reservoir conditions. The selection of the best reservoir for polymer flooding application must take into consideration the analysis of the following three reservoir parameters: reservoir temperature, brine composition (salinity, divalent cations, dissolved oxygen, iron, and hydrogen sulfide), and permeability. Polymer stability tests can be carried out over several months or years to ensure that viscosity loss is not observed during ageing in the presence of contaminants [26]. It is mandatory to perform these experiments under controlled anaerobic conditions (in glove box for instance) to quantify the level of degradation.

4. Polymer flooding: design and implementation

4.1. Reservoir screening

The objective of any reservoir screening process is to identify the best technology to improve oil recovery at a reasonable cost. Several criteria can be used during the screening process. General guidelines are provided in the following paragraphs. However, very often, a variety of parameters are assessed and obtaining a clear depiction of what would be the best technology-reservoir duo could be difficult.

Two general screening rules for polymer flooding are:

- The selection of reservoirs which have poor waterflooding sweep efficiency due to high oil viscosity and/or large-scale heterogeneity.
- The review of the overall conditions of the selected reservoir to determine if polymer flooding implementation will fix the poor sweep efficiency problem.

Specific parameters that need to be checked to determine if polymer flooding would be a viable option for the selected reservoir(s) are as follows:

- Lithology: sandstone
- Temperature: below 140°C (preferred below 100°C)
- Permeability: above 10 mD
- Oil viscosity: below 10,000 cP
- Current oil saturation: above residual oil saturation or presence of mobile oil
- Salinity of injection water: <200 g/L total dissolved salts. For salinity, another parameter called R^+ is usually considered. It is defined as the weight ratio of cationic divalent ions divided by the total of cationic ions as in following equation:

$$R^+ = \frac{\sum(Divalent\,cations)}{\sum(Cations)}$$

The above list can appear to be quite short and simple, when indeed there are many other factors related to the oil field that should be considered. However, if these criteria are met, there is already a good chance that injecting polymer would, technically speaking, increase the recovery factor. The next question would be: is it economically viable?

Obviously, among the mentioned parameters, the most important is probably the oil saturation and the corresponding remaining oil in place. If it is considered (and generally accepted) that polymer flooding does not displace residual oil saturation, then the presence of moveable oil is compulsory to make the injection viable. The *in situ* oil viscosity is a secondary criterion: even in those cases where oil viscosity is low and the mobility ratio of the displacement process (i.e., waterflooding) appears to be favorable, oil formations are generally heterogeneous by nature. Therefore, there is a good chance that even in those cases of favorable mobility ratio, sweep efficiency can be improved by the implementation of a polymer flooding.

Other parameters for consideration are linked to the choice of the most suitable polymer chemistry and the polymer concentration needed to reach a reasonable target viscosity. The higher the temperature and salinity, the higher the polymer concentration needed to obtain a sufficient viscosity to improve the recovery factor and, therefore, the higher the cost of the polymer flooding.

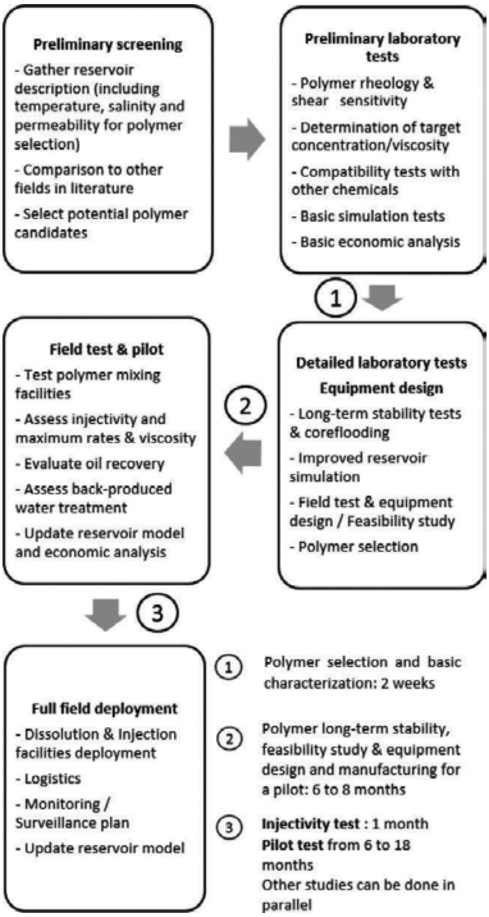


Figure 21. Example of workflow for polymer flooding implementation [25].

After the first selection has been made, more conventional reservoir studies can be performed before the implementation of a pilot test (**Figure 21**). The engineers should look at the reservoir geology (large-scale sand body connectivity and heterogeneity), distribution of target oil, presence and location of faults, shales, aquifers, and distribution of clays. The simultaneous analysis of the reservoir production history helps to understand and refine the current knowledge of the reservoir and the behavior of the injected and produced fluids to avoid chemical dispersion and polymer losses during polymer flooding.

Tracer test. Tracer flooding testing aids in improving the reservoir description using a range of techniques. This test provides information on well-to-well communication and transit time, data on large-scale layering, and an approximate estimate of areal sweep, and in-layer dispersion. Frequently, it is not necessary to perform an explicit tracer flood since there is virtually always a difference in the composition of each ion in the injection and formation brines (Na^+, Ca^{2+}, Cl^-, SO_4^{2-}, etc.). Therefore, a careful analysis of the breakthrough composition of the produced brine would provide very useful information. However, it can be complicated by ion exchanges within the reservoir, especially for Ca^{2+}. It should be pointed out that the polymer is in itself a good tracer, with its detection in producing wells during the pilot using the kaolinite flocculation method. This will provide additional input regarding the flow streams.

In some cases, profile modification before polymer injection has been reported [51]. Another approach would be to start polymer injection with high-viscosity slugs in an attempt to seal the high-permeability zones without plugging them irreversibly. This approach has been demonstrated successfully in both the Daqing and Kazakhstan oil fields.

4.2. Importance of water quality

Field observations showed that a well-performing waterflood with “clean water” and good injectivity will translate into a well-performing polymer flood. The composition of a “clean water” provided here is a common guideline found in the oil industry when considering injecting water in order to maintain a decent injectivity during the life of a project [52, 53]. The recommended composition of “clean water” is:

- Oil content <100 ppm (to minimize reservoir plugging)
- Solids content <20 ppm
- Solid particle size <5 μm (to minimize reservoir plugging)
- Consistent salinity over the life of a project to minimize viscosity variations
- Oxygen content <20 ppb (to avoid polymer degradation if iron II or H_2S are present)

The composition of a “clean water,” except for oxygen content, do not have a major impact on the polymer behavior or stability, but it could affect the overall performance of surface facilities and injection wells.

The viscosity of the polymer solution is designed to reduce the overall mobility ratio of the fluids in the reservoir. Other than minimizing polymer degradation, it is important to inject the polymer consistently at the target viscosity. This can be achieved with periodic polymer sampling or by inline viscosity monitoring of the polymer injected. Since water quality can change, a target concentration of polymer shall not be considered. Inversely, polymer concentration must be adapted to obtain the target viscosity, depending on water quality changes.

4.3. Pilot injection and monitoring

The objectives of a pilot polymer injection are to:

- Check the efficiency of the entire polymer injection process;
- Gather information on the reservoir response during polymer injection (pressure, flow rate, viscosity, injectivity, etc.). This information is useful to upgrade the reservoir model, if one exists; and
- Quantify the incremental oil recovery necessary to calculate the economics of polymer flooding in a view of a full-field extension.

The most important goal of a pilot polymer injection test is to determine the maximum flow rates and viscosities that can be accepted by the reservoir. Some guidelines for consideration during the implementation and monitoring of a pilot polymer flooding test are given below:

- Polymer injection should be ramped up over a period of days in order to initiate the flow of polymer into the reservoir.
- Injection rate, wellhead pressure, bottom-hole pressure, and cumulative injection should be recorded throughout the pilot.
- Polymer viscosity must be monitored by proper sampling or use of inline viscometers.
- Proper control of the formation parting pressure can be helpful to improve injectivity and minimize overall polymer mechanical degradation. The Hall Plot is a useful tool to follow the reservoir response during polymer flooding [54] (**Figure 22**). For instance, if the formation parting pressure is reached, it is recommended to slightly decrease the polymer injection rate to avoid changing the viscosity of the polymer due to mechanical degradation.
- The more viscous the polymer solution injected, the better the polymer flooding sweep efficiency (a mobility ratio <1 takes into account reservoir heterogeneity).
- Step-rate tests should be conducted to gather information on the maximum allowed injection rates, pressure, and polymer viscosity.
- Maintaining good water quality is paramount to ensure success.
- No real consensus exist on how should polymer injection be stopped: with or without tapering. Most probably, in any case, water will finger again through the slug in the high-permeability zones.

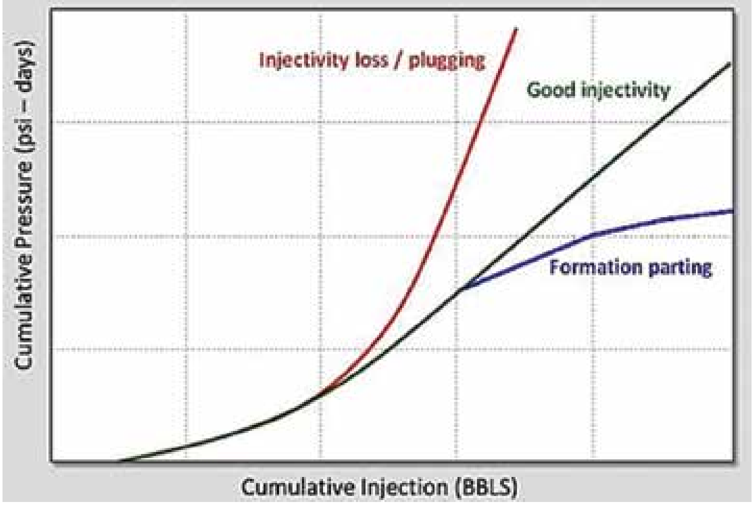


Figure 22. Hall Plot indicating different injection profiles and their interpretation (modified after [55]).

Continuous viscosity monitoring can be achieved by the use of an inline viscometer and periodic sampling at the wellhead to make sure the viscosity of the injected solution is the targeted one. This fluid sampling process must be carried out carefully to ensure the measured viscosity corresponds to the produced solution and not to a degraded polymer sample. An inaccurate sampling method can induce shearing or oxygen entry into the polymer sample, which will trigger chemical reactions between oxygen and potential reducers such as iron II and H_2S. This will lead to the formation of free radicals that act to chemically degrade the polymers, with an immediate polymer viscosity drop. This issue is also valid in the laboratory, where viscosity measurements in the presence of contaminants must be performed under an inert atmosphere, such as a nitrogen-blanketed glove box.

Injectivity. Injectivity is a hot topic among reservoir engineers and projects managers. Large polymer injection projects that have been successful in injecting high polymer viscosities are the polymer flooding implemented in the Daqing, Suriname, and Kazakhstan oil fields.

Interestingly, there are very few cases of bad injectivity reported in the literature during polymer flooding. Injectivity failures during polymer injection are usually linked to a flaw flooding design including improper polymer dissolution systems or polymer protection against degradation (chemical, mechanical, and thermal degradation), issues with water quality, well completion, injection of polymer solutions having very low viscosities, and/or polymer injection out of the target zone. Another possible reason is near-wellbore effects. If the near wellbore area is not modeled properly, or not understood at all, it is easy to overlook this area and to misinterpret what really happens in this zone.

Engineers from Oman Petroleum Development [56] have brought forward ideas to explain why the observed injectivity was better than the injectivity expected and predicted by models:

- Polymer degradation during injection. This hypothesis is very often discarded when polymer viscosity and concentrations are measured in the production fluids. Also, a significant viscosity loss would translate into a bad sweep efficiency and low extra oil recovery which is not the case.
- Polymer rheology: shear thinning and drag reduction effects are often not considered in the injection well before entering the reservoir. These effects will impact positively polymer injectivity. Shear thickening is possible but highly improbable considering the existence of microfractures.
- Uncharacterized reservoir heterogeneities.
- Dilution mechanisms in surrounding aquifers.
- Radial versus linear flow. A better understanding of the flow regimes is important, especially when considering the different well completion types (cased and perforated, gravel packs, vertical vs. horizontal wells, microfractures, and the skin factor, etc.).
- In addition, injecting a higher viscosity polymer induces a more stable displacement front that would translate into enlarged swept surface and therefore less pressure drop per linear meter. In other words, if the swept area is enlarged for the same amount of fluid, the pressure drop over a certain distance decreases.
- Most of the wells are injecting under fracturing conditions.

The last hypothesis is probably the most plausible explanation of the observed remarkable polymer injectivity that has been confirmed by other authors [37]. If this is the case, then it is important to understand the type of “fractures” that has been induced in terms of fracture geometry and extension. In this regards, some thoughts are given as follow:

- Well drilling and completion will change the stress repartition around the wellbore and create instabilities which, in addition to natural reservoir heterogeneities, will set favorable conditions for microfracture creation and extension.
- There is a great deal to learn from the nonconventional segment of oil and gas production and especially from the use of hydraulic fracturing to produce hydrocarbons from low-permeability reservoirs. In particular, regarding fracture creation, extension, and orientation. Geomechanics can be a useful tool to understand formation of fracture in the context of conventional oil reservoirs. It is well known that it is quite difficult to propagate long fractures even at high pumping rates. Additionally, the newly created or reactivated fractures can easily be contained in the formation which presents the most favorable stress orientation (this is important when discussing over cap rock integrity) [57, 58].
- Prolonged reservoir waterflooding will aggravate the near-wellbore formation damage. Especially, if the injected water is not at reservoir temperature.

All in all, it is important to characterize the near-wellbore area as best as possible and to work with the local heterogeneities to improve the overall chemical injection. Higher area for flow means less pressure drop and therefore less mechanical degradation. Using common reservoir monitoring methods (step-rate tests, interference tests, and Hall plots, etc.), controlling injection rates and pressure to open up or close microfractures can bring significant improvement to the polymer flooding field operation. Another simple tool consists in analyzing the value of $q/\Delta P$:

If $q/\Delta P \leq (\Sigma\, k\, h)/[141.2\, \mu \ln (r_e/r_w)]$, radial flow is probable (matrix injection)

If $q/\Delta P \geq (\Sigma\, k\, h)/[141.2\, \mu \ln (r_e/r_w)]$, linear flow is probable (fracture-dominated regime)

where q is the injection or production rate (BPD), P pressure drawdown (psi), k permeability (md), h formation height (ft), μ fluid viscosity (cP), r_e external drainage radius (ft), and r_w wellbore radius (ft).

Last but not the least, it is paramount to translate these findings into the reservoir simulation models, which often give pessimistic results when injecting a viscous solution into the ground, especially when pressure constrains are set without a clear picture of polymer injectivity as obtained after a pilot test.

Numerical modeling and simulation. 3D modeling is a useful tool to predict the efficiency of a polymer flooding, assuming that the user has the proper understanding of the polymer characteristics and polymer flow properties. The most critical issue is modeling the near-wellbore area to duplicate the results observed during the field pilot injection. Polymer rheology regimes such as shear-thinning or shear-thickening properties should be used carefully, together with a suitable understanding of the well completion, formation damages, and reservoir fractures.

The most important parameters that can be obtained from the laboratory experiments that are useful during numerical simulation of polymer flooding are resistance factors, such as retention and residual resistance factors. If coreflooding experiments were not performed, it is possible to use the low shear viscosity information obtained from conventional rheometers for simulation purposes. Polymer degradation inside the reservoir is usually limited since the chemistry of the polymer is always selected to ensure the stability of the polymer during polymer injection and propagation throughout the reservoir. However, useful information can be gathered from long-term polymer stability tests.

4.4. Quality control

Routine quality control procedures are available to check the quality of the polymer to be injected. The main parameters for polymer quality controls are:

- Active content of the polymer: active material of the solid powder.
- Yield viscosity: definition of the polymer concentration needed in the injection brine to reach the target viscosity.
- UL viscosity: viscosity of polymer solution at 0.1% active in 1 mole NaCl.
- Filterability of the polymer solution: it is important to determine polymer dissolution issues, such as the formation of undissolved polymer clusters and/or fish-eyes (**Figure 23**).

Figure 23. Typical set-up used to perform filter ratio tests with vessels (top) and graduated cylinders connected to a stopwatch (bottom) [25].

Some of the laboratory procedures commonly used for polymer quality control are described in the API procedure RP63. Discussions with suppliers can also bring important inputs on the proper handling of the products and control of the overall quality.

As previously indicated, during reservoir polymer flooding, the main parameter to be monitored is polymer solution viscosity, which can be performed via an inline viscometer or by manual and careful polymer solution sampling for bench-scale viscosity analysis.

5. Back-produced polymer

A pilot injection can bring important information on the quality and quantity of back-produced polymer, as well as its impact on the existing water treatment facilities if the effluents can be isolated and polymer dilution limited.

For an extended field project, the crude and produced water separation stage and the produced water treatment stage must be considered as an important part of the polymer flooding implementation design. The treated water can be either reused or disposed of. The main aspects of the treatment of back-produced polymer are the following:

- Anionic polymer can interact with the oil emulsions breaker system, possibly resulting in an inefficient oil-water separation. Service companies generally select the most appropriate and compatible oil-water breaker through several tests including bottle testing. Since polyacrylamide polymers are water soluble, they are considered absent from the oil phase [26].

- Anionic polyacrylamides are used widely in water treatment processes as flocculating agents. If the TSS (total suspended solids) is relatively high in the produced fluid, some agglomerates can appear and precipitates can deposit on the surface of process equipment (i.e., heating units). These deposits have to be periodically removed.

Equipment for back-produced water treatment is usually sized to operate with water viscosities below 4 cP. An increase in water viscosity after polymer breakthrough will reduce the efficiency of the treating devices in separating hydrocarbons and wetted suspended materials. For example, if the viscosity of the water produced reaches 10 cP, the residence time required for treatment is five times longer and the size of the devices are five times larger [26].

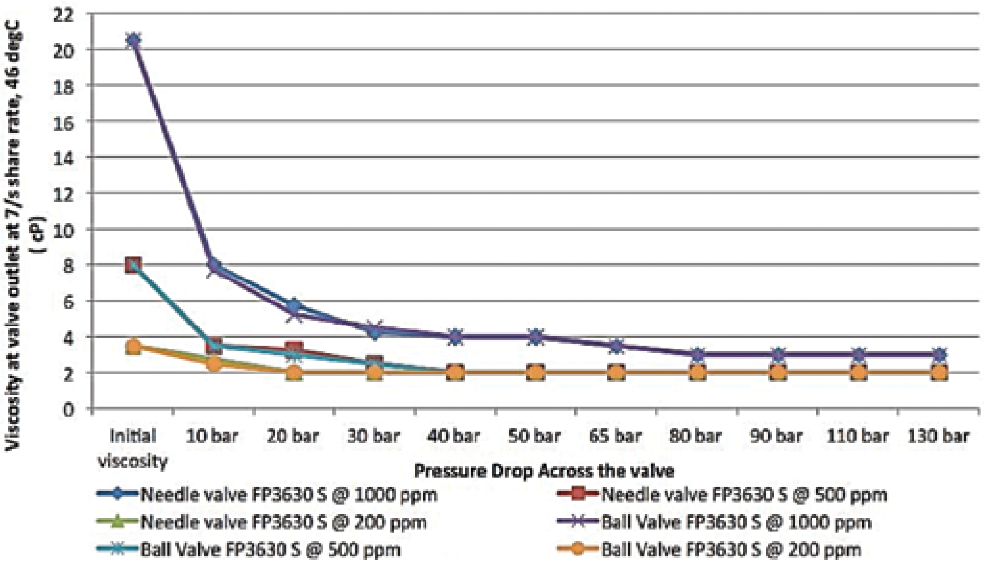


Figure 24. Mechanical degradation of polymer solutions at different concentrations (Flopaam 3630S) [25].

Several methods (mechanical, chemical, and filtration, etc.) can be used to decrease the viscosity of the produced effluent in order to maintain the efficiency of the water treatment process [59] as follows:

- Mechanical degradation is often a viable and efficient method to decrease the molecular weight of the polymer and thereby to decrease the viscosity of the solution (**Figure 24**). A shearing pump or a choke valve can be used to achieve the required degradation to decrease the viscosity of the polymer solution produced. However, too much shear can stabilize oil in water (O/W) emulsions.

- Polyacrylamides experience chemical degradation in the presence of oxidizers that generate free radicals that react with the polymer backbone chain, resulting in a decrease of the molecular weight and viscosity of the polymer solution. A preferred oxidizer is sodium hypochlorite (NaClO). However, if the treated water needs to be reused to hydrate polymer for a further injection, any remaining excess of oxidizer must be neutralized with a reducing agent to prevent any excess of oxidizer from degrading the new batch of dissolved polymer.

- Polymer precipitation: can be performed by using trivalent metal salts (i.e., aluminum sulfate, polyaluminum chloride, ferric chloride, etc.). However, this method entails several disadvantages: the reagents acidify the water, which must be corrected to prevent equipment corrosion. In addition, the formed colloidal precipitate would require a large settler-flocculator and a centrifugation/filtration sludge system. This sludge would then require disposal in a landfill, when permitted by local regulation or incinerated. Additionally, the recovery of any adsorbed oil on the precipitate would be very difficult.

The back-produced polymer can also have several benefits:

- It can be reused to possibly decrease the amount of fresh polymer added, reducing the operational expenditures. This does not impact standard dissolution facilities.

- Polymer remaining in the water will act as a drag reducing agent when pumping the water for reinjection or disposal, thereby reducing the pumping energy and increasing injection rates for the same pressure drop.

- If water is injected into a virgin part of the reservoir, the polymer present in the water phase will act as a sacrificial agent by adsorption onto the rock surface. Therefore, if chemical injection is envisaged, less chemicals will be lost to retention.

- Anionic polymers have other benefits such as clay stabilizers, sand control, and even anticorrosion (passivation).

6. Equipment and surface facilities

6.1. Process examples

Depending on the polymer form (emulsion or powder), two different approaches can be considered. When the polymer is supplied in powder form, it should be dissolved into the injection water prior to being pumped for dilution and injected into the reservoir at the target viscosity. A typical set-up for powder dissolution is presented in **Figure 25**. The polymer in powder form is stored in a hopper and distributed with a dosing screw into a nitrogen-blanketed polymer slicing unit (PSU) where it is hydrated. The solution will then pass into a maturation tank where it will achieve full hydration/dissolution. Finally, the mother solution is pumped and diluted to the target concentration (**Figure 25**).

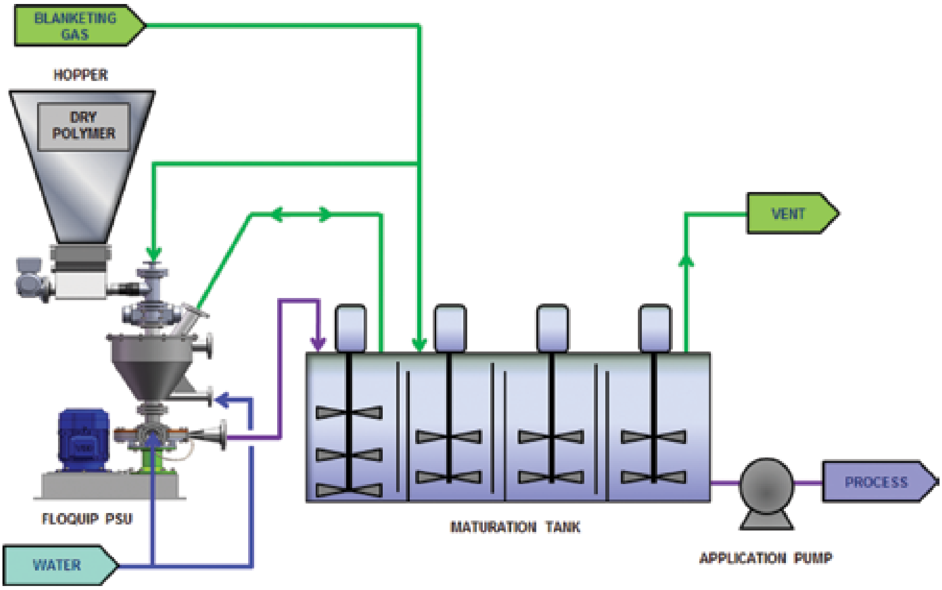


Figure 25. Typical dissolution process for polymers in powder form [25].

Skid-mounted systems are widely used onshore: the polymer dissolution and hydration systems as well as the pumps are placed inside 20 or 40 feet containers that are adapted to the local field conditions (weather, accessibility). As discussed previously, it is recommended to blanket the main equipment with nitrogen to avoid any oxygen ingress and further degradation of the polymer solution viscosity. This type of system with a slicing unit allows for quick and proper hydration of the polymer, avoiding fish-eyes and gels formation, which would require filtration of the polymer solution.

Two configurations can be considered based on the water supply:

- If high pressure water is available, then the configuration shown in **Figure 26** is recommended.
- If low pressure water is available, the configuration displayed in **Figure 27** should be used to ensure the proper hydration of the polymer.

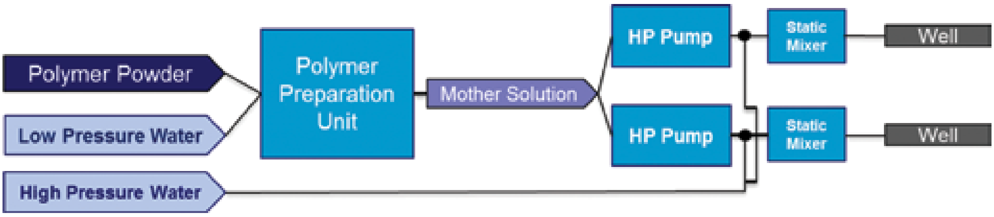


Figure 26. Configuration for polymer preparation when high pressure water is available [25].

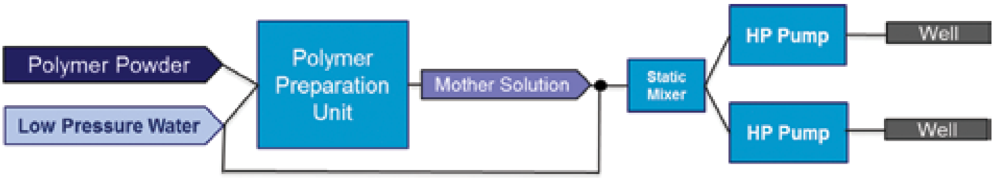


Figure 27. Configuration for polymer preparation when low pressure water is available [25].

When using polymer in emulsion form, inline static mixers (with a sufficient pressure drop) are required to invert the water-in-oil emulsion (W/O) into an oil-in-water emulsion (O/W) which is then injected in the reservoir. The footprint for the process is much less extensive than in the case of polymer in powder form. Nevertheless, due to the active content and the density of the emulsion, the volume of the tank necessary to store the emulsion is often twice the volume of the tank used to prepare polymer in powder form. **Figure 28** presents a simplified flow diagram for the dilution process of polymer in inverse emulsion form.

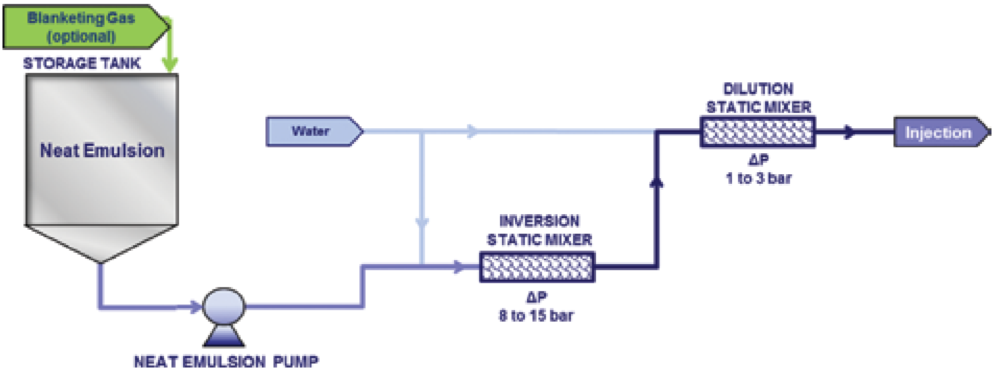


Figure 28. Typical inversion and dilution process for the preparation of polymer in inverse emulsion form [25].

Among the three main types of degradation, chemical and mechanical polymer degradations are susceptible to occur at surface facilities.

Chemical degradation can be minimized by blanketing the equipment with nitrogen or by adding specific scavengers in the flow stream. It is also possible to remove as many contaminants as possible or to add protective additives to the polymer.

Specific guidelines should also be applied to minimize mechanical degradation in dissolution and surface equipment or in the injection lines if restrictions or chokes are present. Progressive cavity or rotary lobes pumps are recommended for low pressure processes. For high pressure, plunger or diaphragm pumps (Triplex or Quintuplex) are preferred. The maximum velocity of the fluid must remain below a critical value, wherever the fluid is moved such as in the agitation process with impellers or in pipes (short distance). For example, in a 2-inch pipe, it must be kept below 7 m/s.

Chokes must be removed, bypassed, fully opened, or replaced by nonshearing systems to avoid any uncontrolled shearing that would be detrimental to the final viscosity of the polymer solution. Well completion influences the amount of degradation; for example, the density and number of perforations must be taken into account and correlated to the flow rate of the fluid to assess the potential shearing occurring at this step (a value of 12 shots per foot is usually recommended) [26].

6.2. Key points for offshore polymer flooding implementations

The constraints are very different when designing an offshore or an onshore polymer flooding project. Equipment footprint is the key in offshore operations, therefore it is necessary to know the space and load limits of the Floating Production Storage Offloading (FPSO) or the offshore platform. Logistics and local weather conditions can also dictate the form of the product to be used. Polymer in inverse emulsion form is easier to handle offshore, especially when the weather conditions are particularly unfavorable. It does not require specific systems, the inversion is performed on the fly with sufficient energy and the solution can then be diluted and injected into the reservoir. However, polymer in powder form, with a higher active content (up to 90% compared to the 30 or 50% for an emulsion), is cheaper to implement and requires less logistics.

The main points to consider during the design of polymer flooding for offshore applications are the following:

- Specific design considering footprint limitations and loads constraints.
- Modular solution to limit the installation activities on the FPSO, platform, or any offshore vessel. Those modules should also comply with lifting/handling constrains such as crane limitation and specific offshore procedures, among others.
- Sensitivity to vibrations during operations (pumps running, conveying, etc.). Specific attention shall be paid on loads interaction and structural issues.
- Hazardous classified area: specific design is to be provided to adapt equipment and modules to the hazardous classification constrains, especially for the control room, motor control center, and utilities shelters.
- Environmental conditions: consideration of the vessel motions (rolling, sagging, pitching, heaving), wind loads, and blast loads on structural and equipment design.
- Corrosion: protection against the corrosive atmosphere (stainless steel equipment, specific painting procedures, nitrogen blanketing, greasing).
- Waste management and back produced water: use of chemicals offshore and possible waste to be handled. Specific cleaning procedures have to be foreseen as well.
- Subsea: polymer is a shear sensitive chemical. For offshore projects, nonshearing injection pumps should be used to transfer the injected solution through the main risers up to the several subsea Christmas trees dedicated to each well. Choke valves will then be used to

control the flow and the pressure at each wellhead. Specific solutions shall be selected to minimize viscosity degradation.

- Logistics: for chemical EOR, a large quantity of chemicals has to be handled either in liquid or powder form. Therefore, the supply chain has to be secured accordingly.

7. Field cases and economics

7.1. Economics

Three areas of expenses can be defined when considering polymer injection:

- Laboratory studies and simulation.
- Equipment design, fabrication, installation, and other costs associated with the start-up of the flooding process.
- Chemical costs.

Out of the three aforementioned sections, the first one represents approximately 1% of the overall costs while the following two represent 25% and 70–75%, respectively. It is obvious that the bulk of the cost is linked to the injection of the chemicals. An important aspect is the field development plan and the deployment of the injection facilities. Two approaches are often encountered:

- Centralized polymer dissolution and injection plants.
- Modular skid-based polymer dissolution and injection systems.

The latter helps to optimize the deployment of the facilities in the field by adding modules for polymer dissolution or polymer injection modules, minimizing the capital expenditures upfront. It also allows moving the systems to other parts of the field for short-term tests.

The average cost of polymer per incremental barrel ranges from $1 to $4. The cost of polymer per incremental barrel of oil produced at the Daqing oil field polymer flooding has been estimated at approximately $2.7/barrel. In this case, it was shown that polymer injection was less expensive than water injection considering the average capital costs per well and the volumes of fluids injected and produced which are significantly less for polymer injection than for water injection.

Another example is the Brintnell polymer flood project (CNRL, Canada) where the average incremental cost for polymer flooding was $13, but including incremental wells, mixing facilities, water-treating facilities, additional production facilities, maintenance capital, and the polymer itself, whereas the cost of the polymer alone was $4 per incremental barrel of oil produced.

7.2. Field cases of polymer flooding

In 2015, there were more than 50 polymer injections running worldwide, excluding the projects still in the design phase or about ready to start in the field.

It would be hard to summarize the entirety of field cases here, so only few examples will be addressed, highlighting some important design aspects and some key learnings. Also, only publicly available information will be discussed in the upcoming paragraphs.

7.2.1. Canada

Canadian operators have gained significant experience in the last years on polymer injection for heavy oils. Interestingly, the vast majority of the cases are publicly released in corporate presentations, providing a wealth of information on the efficiency of the process. The constant here is the benefit of injecting viscous solutions to improve recovery from heavy-oil pools. The list of fields is extensive: Pelican Lake, Brintnell, Mooney, Horsefly, Countess, Bodo, Suffield Caen, Wainwright, Giltedge, Seal, Taber, Wildmere, Wrentham, Provost, Edgerton, etc. [60–62]. These wells are mainly horizontal, with a short-spacing often between 50 and 100 m and oil viscosities up to 10,000 cP. **Table 4** presents a summary of reservoir properties of three typical Canadian oil fields in which polymer flooding has been implemented. The incremental oil recovery obtained from each polymer flooding project is also indicated in **Table 4**.

Project	Pelican Lake	Mooney	Seal
Company	CNRL & Cenovus	Black Pearl	Murphy
Average depth	300–450	900–950	610
Average net pay	1–9	2.5	8.5
Permeability	300–5000	100–10,000+	300–5800
Reservoir temperature	12–17	29	20
API gravity	12–14	12–19	10–12
Dead oil viscosity	800–80,000	300	5000–12,000
Live oil viscosity	800–80,000	1000–3000	3000–7000
Incremental oil recovery	10–25%	~10%	9%

Table 4. Summary of reservoir properties of three typical Canadian oil fields in which polymer flooding has been implemented (modified after [60]).

7.2.2. China

The Daqing polymer flooding case has been extensively discussed previously in this chapter. Incremental oil recovery as a result of polymer injection is approximately 12% OOIP. Other successful polymer flooding projects in Chinese oil fields such as the Shengli and Bohai Bay have been described in the literature [65]. Additionally, some papers report the use of high-viscosity polymer slug to further improve oil recovery: the objective is to inject very high viscosity slugs followed by a regular polymer flooding with possible repetition in order to account for reservoir heterogeneities [62–64].

7.2.3. Europe and Middle East

The number of polymer flooding pilot tests and projects has greatly increased in the past years in Europe, some examples are as follows:

- Bockstedt oil field in Germany where Wintershall has injected the schizophyllan biopolymer.
- Matzen oil field in Austria operated by the OMV Group.
- Patos-Marinza oil field (heavy oil reservoir) operated by Bankers Petroleum in Albania.
- Other polymer flooding pilots in the North Sea, Eastern Europe, Russia, and Kazakhstan whose oil field names are often protected by nondisclosure agreements.
- Polymer flooding pilots in Egypt and the Marmul field polymer flooding project in Oman.

In the Marmul oil field, Petroleum Development Oman (PDO) implemented a pilot polymer injection in 2010. A polyacrylamide polymer and a protective additive were injected in 27 wells. The high-permeability (multi-Darcy) reservoir contains a 22° API crude oil with a viscosity of around 90 cP; injection patterns are inverted 9- and five-spot patterns. The polymer solution (15 cP) was injected at an average flow rate of 13,000 m^3/day. Preliminary results as of 2012 are presented in **Figure 29** [56].

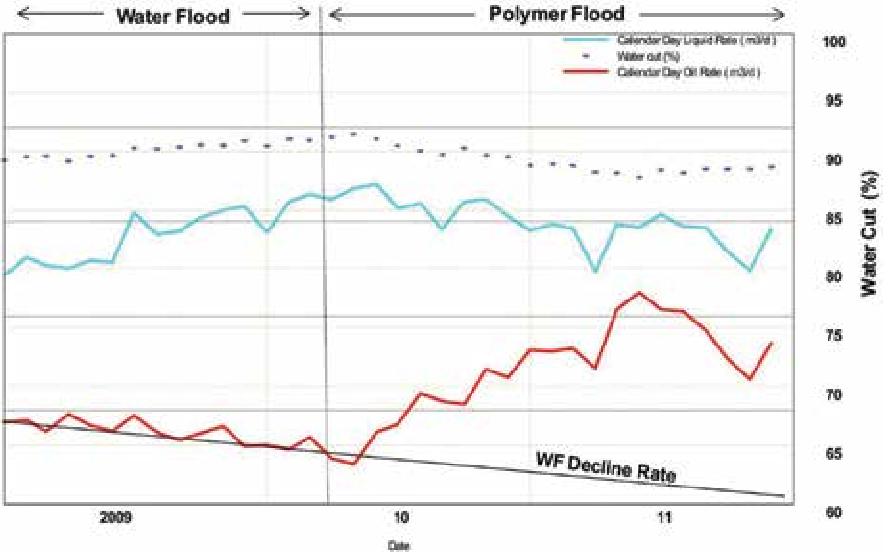


Figure 29. Water-cut and oil production rate from the Marmul oil field before and after the start-up of polymer injection [56].

7.2.4. South America

Polymer flooding pilot injections are on-going in Argentina, Suriname, and Colombia with polymer flood projects in Brazil and Venezuela. An interesting case is the Sarah Maria field operated by Staatsolie [37] in Suriname. This reservoir is a heterogeneous sandstone, with permeabilities of several Darcie's and a live oil viscosity around 500 cP. Moe Soe Let et al. (2012) have reported the first observations of this polymer flooding. In this project, reservoir fractures have been used to improve the injectivity of the highly viscous polymer solutions (up to 160 cP). The creation and extension of fractures have been monitored through pressure profiles, interwell tracer tests, water-cut variations, salinity, and polymer breakthrough: the aim was to increase water injection and oil production rates without risking irreversible reservoir damages.

Acknowledgements

The author would like to acknowledge Kimberley McEwen, Nicolas Gaillard, and Olivier Braun for their careful review.

Author details

Antoine Thomas

Address all correspondence to: athomas@snf.fr

SNF Floerger, Andrezieux-Boutheon, France

References

[1] Pye, D.J., 1964. Improved secondary recovery by control of water mobility. J. Pet. Tech., vol. 16, issue 08, 911–916. AIME, 231.

[2] Sandiford, B.B., 1964. Laboratory and field studies of waterflood using polymer solutions to increase oil recoveries. J. Pet. Tech., vol. 16, issue 08, 917–922, AIME, 211.

[3] Mungan, N., 1969. Rheology and adsorption of aqueous polymer solutions. J. Can. Pet. Tech., April–June, 8, 45.

[4] Gogarty, W. B., 1967. Mobility control with polymer solutions. Soc. Pet. Eng. J., June, vol. 07, issue 02, 161–170.

[5] Mungan, N., Smith, F.W., Thompson, J.L., 1966. Some aspects of polymer floods. J. Pet.Tech., vol. 18, issue 09, September, 1143.

[6] Smith, F.W., 1970. The behaviour of partially hydrolysed polyacrylamide solutions in porousmedia. J. Pet. Tech., 22, 148–156.

[7] Szabo, M.T., 1975. Some aspects of polymer retention in porous media using a 14C - tagged hydrolysed polyacrylamide. Soc. Pet. Eng. J., vol.15, issue 04, August, 323.

[8] Muskat, M., 1949. Physical Principles of Oil Production. McGraw-Hill Book Co., New York City.

[9] Stiles, W.E., 1949. Use of permeability distribution in waterflood calculations. Trans. AIME, 186, 9–13.

[10] Dyes, A.B., Caudle, B.H., Erickson, R.A., 1954. Oil production after breakthrough as influenced by mobility ratio. Trans. AIME, 201, 81–86.

[11] Sorbie, K.S., 1991. Polymer-Improved Oil Recovery. CRC Press, Inc., Boca Raton, FL.

[12] Willhite, G.P., Green, D.W., 1998. Enhanced Oil Recovery. SPE Textbook Series, 6. Henry, L. Doherty Memorial Fund of AIME, Society of Petroleum Engineers, Richardson, TX.

[13] Leonhardt, B., Visser, F., Lessner, E., Wenzke, B., Schmidt, J., 2011. From Flask to Field – The Long Road to Development of a New Polymer. Paper presented at the 16th European Symposium on Improved Oil Recovery Cambridge, UK, 12–14 April.

[14] Wang, D., Gang, W., Huifen, X., 2011. Large Scale High Viscous-Elastic Fluid Flooding in the Field Achieves High Recoveries. SPE 144294 presented at the SPE Enhanced Oil Recovery Conference held in Kuala Lumpur, Malaysia, 19–21 July.

[15] Delshad, M., Kim, D.H., Magbagbeola, O.A., Huh, C., Pope, G.A., Tarahhom, F., 2008. Mechanistic Interpretation and Utilisation of Viscoelastic Behavior of Polymer Solutions for Improved Polymer-Flood Efficiency. Paper SPE 113620 presented at the SPE/DOE Improved Oil Recovery Symposium held in Tulsa, Oklahoma, USA, 19–23 April.

[16] Wang, L., Wang, Y., Zhang, C., Yin, D., Wang, L., 2012. Study on High-Concentration Polymer Flooding in Lamadian Oilfield, Daqing. Paper SPE 154625 presented at the SPE EOR Conference at Oil & Gas West Asia held in Muscat, Oman, 16–18 April.

[17] Seright, R.S., 2010. Potential for polymer flooding viscous oils. SPE Reservoir Eval. Eng., 13(6), 730–740.

[18] Chang, H. L., 1978. Polymer Flooding Technology: Yesterday, Today and Tomorrow. Paper SPE7043 presented at the Fifth Symposium on Improved Methods for Oil Recovery, Tulsa, OK, 16-19 April.

[19] Vermolen, E.C.M., Van Haasterecht, M.J.T., Masalmeh, S.K., Faber, M.J., Boersma, D.M., Gruenenfelder, M., 2011. Pushing the Envelope for Polymer Flooding towards High-temperature and High-salinity Reservoirs with Polyacrylamide Based Ter-polymers.

Paper SPE 141497 presented at SPE Middle East Oil and Gas Show and Conference, Manama, Bahrain, 25–28 September, 2011.

[20] Gaillard, N., Giovannetti, B., Favero, C., 2010. Improved Oil Recovery using Thermally and Chemically Stable Compositions Based on Co and Ter-polymers Containing Acrylamide. Paper SPE 129756 presented at SPE Improved Oil Recovery Symposium, Tulsa, Oklahoma, USA, 24–28 April, 2010.

[21] Kulawardana, E., Koh, H., Kim, D., Liyanage, P., Upamali, K., Huh, C., Weerasooriya, U., Pope, G., 2012. Rheology and Transport of Improved EOR Polymers under Harsh Reservoir Conditions. Paper SPE 154294 presented at the Eighteenth SPE Improved Oil Recovery Symposium in Tulsa, Oklahoma, USA, 14–18 April, 2012.

[22] Lake, L.W., 1989. Enhanced Oil Recovery, 323-324, 396-400. Prentice Hall, Englewood Cliffs, New Jersey.

[23] Seright, R.S., Zhang, G., Akanni, O.O., Wang, D., 2011. A Comparison of Polymer Flooding with In-Depth Profile Modification. Paper SPE 146087 presented at the Canadian Unconventional Resources Conference held in Calgary, Alberta, Canada, 15–17 November.

[24] Wyatta, N.B., Liberatore, M.W., 2010. The effect of counterion size and valency on the increase in viscosity in polyelectrolyte solutions. Soft Matter, 2010, 6, 3346–3352.

[25] SNF Internal Support for Training. Confidential document, issue 05, 2014.

[26] Thomas, A., Gaillard, N., Favéro, C., 2013. Some key features to consider when studying acrylamide-based polymers for chemical enhanced oil recovery. Oil Gas Sci. Technol. – Rev. IFP Energies nouvelles, vol. 67, Number 6, November-December 2012. Dossier: Challenges and New Approaches in EOR.

[27] Borthakur, A., Rahman, M., Sarmah, A., Subrahmanyam, B., 1995. Partially hydrolyzed polyacrylamide for enhanced oil recovery. Res. Industry, 40, 90–94.

[28] Ellwanger, R.E., Jaeger, D.A., Barden, R.E., 1980. Use of the empirical hill equation for characterization of the effect of added cations on the viscosity of aqueous solutions of partially hydrolyzed polyacrylamide. Polymer Bull., 3, 369–374.

[29] Sukpisan, J., Kanatharana, J., Sirivat, A., Wang, Y., 1998. The specific viscosity of partially hydrolyzed polyacrylamide solutions: Effects of degree of hydrolysis, molecular weight, solvent quality and temperature. J. Appl. Polymer Sci. B: Polymer Phys., 36, 743–753.

[30] Wever, D.A.Z., Picchioni, F., Broekhuis, A.A., 2011. Polymers for enhanced oil recovery: A paradigm for structure-property relationship in aqueous solution. Progress Polymer Sci., 36(11), 1558–1628.

[31] Leblanc, T., Braun, O., Thomas, A., Divers, T., Gaillard, N., Favéro, C., 2015. Rheological Properties of Stimuli-Responsive Polymers in Solution to Improve the Salinity and Temperature Performances of Polymer-Based Chemical Enhanced Oil Recovery

Technologies. Paper SPE 174618 presented at the SPE Enhanced Oil Recovery Conference held in Kuala Lumpur, Malaysia, 11–13 August.

[32] Bokias, G., Hourdet, D., Iliopoulos, I., 1997. Hydrophobic interactions of poly (N-isopropylacrylamide) with hydrophobically modified poly (sodium acrylate) in aqueous solution. Macromolecules, 26, 8293.

[33] Bonnier, J., Rivas, C., Gathier, F., Quillien, B., Thomas, A., 2013. Inline Viscosity Monitoring of Polymer Solutions Injected in Chemical Enhanced Oil Recovery Processes. Paper SPE 165249 presented at the SPE Enhanced Oil Recovery Conference held in Kuala Lumpur, Malaysia, 2–4 July.

[34] Manichand, R.N., Seight, R.S., 2014. Field vs. Laboratory Polymer Retention Values for a Polymer Flood in the Tambaredjo Field. Paper SPE presented at the SPE Improved Oil Recovery Symposium held in Tulsa, Oklahoma, USA, 12–16 April.

[35] Shamsijazeyi, H., Hirasaki, G., Verduzco, R., 2013. Sacrificial Agent for Reducing Adsorption of Anionic Surfactants. SPE 164061 presented at the SPE International Symposium on Oilfield Chemistry, The Woodlands, Texas, USA, 8–10 April.

[36] Xie, J., Liu, F.P., 2007. Degradation and protection of polymer used for enhanced oil recovery. J. Shandong Univ. Sci. Technol., 26, 16–20.

[37] Manichand, R.N., Moe Soe Let, K.P., Gil, L., Quillien, B., Seright, R.S. 2013. Effective Propagation of HPAM Solutions Through the Tambaredjo Reservoir During a Polymer Flood. Paper SPE 164121 presented at the SPE International Symposium on Oilfield Chemistry, The Woodlands, Texas, USA, 8-10 April.

[38] Grollman, U., Schnabel, W., 1982. Free radical-induced oxidative degradation of polyacrylamide in aqueous solution. Polym. Degrad. Stab., 4, 203–212.

[39] Wellington, S.L., 1983. Biopolymer solution viscosity stabilization-polymer degradation and antioxidant use. SPEJ, vol. 23, issue 6, 901–912.

[40] Fenton, H.J.H., 1894. Oxidation of tartaric acid in presence of iron. J. Chem. Soc., 65, 899–910.

[41] Seright, R.S., Campbell, A.R., Mozley, P.S., Han, P., 2010. Stability of partially hydrolyzed polyacrylamides at elevated temperatures in the absence of divalent cations. SPEJ., vol. 15, issue 2, June, 341–348.

[42] Levitt, D.B., Pope, G.A., 2008. Selection and Screening of Polymers for Enhanced-Oil Recovery. Paper SPE 113845 presented in Tulsa, Oklahoma, 19–23 April.

[43] Seright, R.S., Skjevrak, I., 2014. Effect of Dissolved Iron and Oxygen on Stability of HPAM Polymers. Paper SPE 169030 presented at the SPE Improved Oil Recovery Symposium held in Tulsa, Oklahoma, USA, 12–16 April.

[44] Kheradmand, H., Francois, J., Plazanet, V., 1990. Effect of additives on the degradation of acrylamide-acrylic acid co-polymers in aqueous solution. J. Appl. Polymer Sci., 39, 1847–1857.

[45] Maerker, J.M., 1975. Shear degradation of partially hydrolyzed polyacrylamide solutions. SPE J., 15(4), 311–322; Trans. AIME, 259. SPE-5101-PA. DOI: 10.2118/5101-PA.

[46] Wang, D.M., Jiecheng, C., Qingyan, Y., Wenchao, G., Qun, L., 2000. Viscous-Elastic Polymer Can Increase Microscale Displacement Efficiency in Cores. Paper SPE 63227 presented at the Annual Technical Conference and Exhibition, Dallas, Texas, 1–4 October, 2000.

[47] Jouenne, S., Anfray, J., Cordelier, P.R., Mateen, K., Levitt, D., Souilem, I., Marchal, P., Lemaitre, C., Choplin, L., Nesvik, J., Waldman, T.E., 2014. Degradation (or Lack thereof) and Drag Reduction of HPAM During Transport in Pipelines. Paper SPE 169699 presented at the SPE EOR Conference at Oil and Gas West Asia held in Muscat, Oman, 31 March–2 April.

[48] Morel, D.C., Zaugg, E., Jouenne, S., Danquigny, J.A., Cordelier, P.R., 2015. Dalia/Camelia Polymer Injection in Deep Offshore Field Angola Learnings and In Situ Polymer Sampling Results. Paper SPE 174699 presented at the SPE Enhanced Oil Recovery Conference held in Kuala Lumpur, Malaysia, 11–13 August.

[49] Bouts, M. N., Rijkeboer, M.M., 2014. Design of Horizontal Polymer Injectors Requiring Conformance and Sand Control. Paper SPE 169722 presented at the SPE EOR Conference at Oil & Gas West Asia held in Muscat, 31 March–2 April.

[50] Moradi-Araghi, A., Doe, P.H., 1987. Hydrolysis and precipitation of polyacrylamides in hard brines at elevated temperatures. SPE Res. Eng., vol. 02, issue 02, May, 189–198.

[51] Wang, D., Seright, R.S., Shao, Z., Wang, J., 2007. Key Aspects of Project Design for Polymer Flooding. Paper SPE 109682 presented at the SPE Annual Technical Conference and Exhibition held in Anaheim, California, USA, 11–14 November.

[52] Willhite, G.P., 1986. Waterflooding. Textbook Series, 3, SPE, Richardson, Texasm, USA.

[53] Craig, F.F., Jr., 1971. The reservoir engineering aspects of waterflooding. Monograph Series, 3, SPE, Richardson, Texas, USA.

[54] Hall, H.N., 1963. How to analyze waterflood injection well performance. World Oil, vol. 156, October, 128–130

[55] http://fekete.com/SAN/TheoryAndEquations/WellTestTheoryEquations/index.htm

[56] Al-Saadi, F.S., Amri, A.B., Nofli, S., Van Wunnik, J., Jaspers, H.F., Harthi, S., Shuaili, K., Cherukupali, P.K., Chakravarthi, R., 2012. Polymer Flooding in a Large Field in South Oman – Initial Results and Future Plans. Paper SPE 154665 presented at the SPE EOR Conference at Oil and Gas West Asia held in Muscat, Oman, 16–18 April.

[57] Economides, M.J., Martin, T., 2007. Modern Fracturing: Enhancing Natural Gas Production. ET Pusblishing, Houston, Texas, USA, 509 pp.

[58] Economides, M.J., Nolte, K.G., 2000. Reservoir Stimulation. 3rd edition, Wiley, 856 pp.

[59] Al Kalbani, H., Mandhari, M.S., Al-Hadrami, H., Philip, G., Nesbit, J., Gil, L., Gaillard, N., 2014. Treating Back Produced Polymer to Enable Use of Conventional Water Treatment Technologies. Paper SPE 169719 presented at the SPE EOR Conference at Oil and Gas West Asia held in Muscat, Oman, 31 March–2 April.

[60] Delamaide, E., Bazin, B., Rousseau, D., Degré, G., 2014. Chemical EOR for Heavy Oil: the Canadian Experience. SPE 169715 presented at the SPE EOR Conference at Oil and Gas West Asia held in Muscat, Oman, 31 March–2 April 2014.

[61] Delamaide, E., Zaitoun, A., Renard, G., Tabary, R., 2013. Pelican Lake Field : First Successful Application of Polymer Flooding in a Heavy Oil Reservoir. Paper SPE 165234 presented at the SPE Enhanced Oil Recovery Conference held in Kuala Lumpur, Malaysia, 2–4 July.

[62] Liu, J.Z., Adegbesan, K., Bai, J.J., 2012. Suffield Area, Alberta, Canada – Caen Polymer Flood Pilot Project. Paper SPE 157796 presented at the SPE Heavy Oil Conference Canada held in Calgray, Alberta, Canada, 12–14 June.

[63] Fulin, Y., Demin, W., Xizhi, Y., Xinguang, S., Qinghai, C., Lei, Z., 2004. High Concentration Polymer Flooding is Successful. SPE paper 88454 presented at the SPE Asia Pacific Oil and Gas Conference and Exhibition held in Perth, Australia, 18–20 October.

[64] Wang, D., Han, P., Shao, Z., Weihong, H., Seright, R.S., 2008. Sweep improvement options for the Daqing oil field. SPE Reservoir Eval. Eng., vol. 11, issue 01, February, 18–26.

[65] Chang, H.L., Zhang, Z.Q., Wang, Q.M., Xu, Z.S., Guo, Z.D., Sun, H.Q., Cao, X.L., Qiao, Q., 2006. Advances in polymer flooding and alkaline/surfactant/polymer processes as developed and applied in the People's Republic of China. JPT, 58(2), 84–89.

Chapter 3

New Insight from Visualization of Mobility Control for Enhanced Oil Recovery Using Polymer Gels and Foams

Bergit Brattekås and Martin A. Fernø

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/64586

Abstract

Several enhanced oil recovery (EOR) methods have been designed and developed in the past decades to maintain economic production from mature reservoirs with declining production rates. This chapter discuss mitigation of poor sweep efficiency in layered or naturally fractured reservoirs. EOR methods designed for such reservoirs all aim to reduce flow through highly conductive pathways and delay early breakthrough in production wells. Two approaches within this EOR class, injection of foam and polymer, specifically aim to improve the mobility ratio between the injected EOR fluid and the reservoir crude oil. Reduction in fracture conductivity may be achieved by adding a crosslinking agent to a polymer solution to create polymer gel. This may also be combined with water or chemical chasefloods (e.g. foam) for integrated enhanced oil recovery (iEOR). Polymer gel and foam mobility control for use in fractured reservoirs are discussed in this chapter, and new knowledge from experimental work is presented. The experiments emphasized visualization and in situ imaging techniques: CT, MRI and PET. New insight to dynamic behaviour and local variations in fluid saturations during injections was achieved through the use of complementary visualization techniques.

Keywords: polymer gel, foam, fractured reservoirs, iEOR, *in situ* imaging

1. Introduction

Polymer gel as a conformance control technique is frequently applied in fractured reservoirs to reduce fracture conductivity close to production wells, but may also be applied to enhance oil recovery when used in the injection well to divert subsequent fluids injected from the fracture network into unswept matrix blocks. Fluid injection following a gel injection is here referred to as a *chaseflood*, and constitutes a range of EOR fluids depending on the reservoir and availability. Waterflooding was used as the standard chaseflood in this work, and the reader may assume that water is injected if not otherwise specified.

Generally, polymer gels are mixed in fresh water before injection to the field to achieve long-term stability of the solution. In this work, polymer gels are made from saline brines and offer a significant advantage compared with fresh water gels because less interaction is expected between the gel and reservoir fluids when the gel solvent (most commonly water) is comparable to the formation brine, and gel blocking performance is significantly improved when combined with low-salinity waterfloods in *integrated EOR*—iEOR, a term used here to describe the process where two or more proven EOR techniques are combined or performed in a smart sequence. In heterogeneous and fractured reservoirs, the iEOR approach is particularly effective when polymer gels are combined with mobility control techniques such as foam. The conformance control offered by polymer gels reduces flow in the largest fractures, whereas foam reduces gas mobility and increases the volumetric sweep efficiency of the reservoir resulting in incremental oil recovery. Gas mobility is reduced when bubbles are formed to make the gas phase discontinuous and separated by thin liquid films called lamellae. Foam application is particularly suited for heterogeneous reservoirs and is a field scale proven technique for EOR at both immiscible and miscible conditions and for aquifer remediation.

To successfully apply polymer gels or foams their behaviour and flow properties in porous media must be accurately predicted on a variety of scales. New insight to dynamic behaviour and local variations in fluid saturations during injections may be achieved through the use of complementary visualization techniques. Three imaging techniques are reviewed in this chapter: X-ray computed tomography (CT), magnetic resonance imaging (MRI) and positron emission tomography (PET). The imaging techniques are used separately or combined to closely monitor flow processes and improve the understanding of EOR techniques and their underlying principles on core plug scale, and new results are discussed in this chapter.

2. Polymer gel placement in fractured systems

From a reservoir engineering point of view, achieving high sweep efficiency in the reservoir to maximize oil recovery represents a challenge when fractures are present. The fractures generally have permeabilities that exceed the rock matrix by several orders of magnitude and therefore represent thief zones for the injected EOR fluid. Rather than displacing oil from the oil-saturated rock matrix, the injected fluids channel through the fracture network towards the producer, resulting in low sweep efficiency and excess production of water or injected chemicals.

2.1. Gel or gelant injection

Polymer gel is usually injected to the field as a *gelant* solution—a mixture containing all chemical components, but not yet crosslinked to form a rigid and highly viscous polymer gel. Gelant in many ways resembles the standard polymer solution, but transforms into a gel depending on temperature conditions and time—the time it takes for a gelant to transform into a rigid gel at a given temperature is known as the *gelation time*. Gelant may flow both in the porous matrix and the fractures as a result of the lower viscosity and smaller particles relative to gel. When formed, long polymer chains in the gel structure prevent the gel from flowing through the small pores of the porous media, thus gel is contained to fractures during injection. In field applications, gelant is generally pumped from the surface and enters the reservoir either as a gelant or as a weak gel, depending on reservoir temperature and pumping time. The placement process must be carefully designed because the two fluids deposit differently in the fracture volume, which influences the ability of the gel to reduce fracture conductivity and impact its performance during conformance control operations. Gel blocking capacity as a function of gel state (gelant or gel) has therefore been thoroughly investigated at core plug scale [1–7].

2.2. The leakoff process

Although formed gel cannot flow through porous media due to its structure, the gel solvent (a range of solvents may be used, here we discuss water only) may leave the gel and progress through the pore network if the viscous forces become high enough. This fluid transport, called *leakoff*, increases the concentration of the gel in the fracture, resulting in a more rigid gel structure with a higher resistance to pressure during chasefloods. When the gel loses water due to leakoff its mobility decreases compared to the continuously injected (″fresh″) gel; fresh gel propagates through internal conduits within the concentrated gel called *wormholes* [3, 8–10]. The transport of water from the gel depends mainly on gel strength and differential pressures across the gel slug, in addition to rock wettability and two-phase flow functions, therein capillary forces. Reduction of flow in fractures or high permeability zones after placement of polymer gels have been reported [2, 10–15].

2.3. Gel mechanical strength-dependency on gel state during placement

The mechanical strength of a gel in a fracture is an indication of its blocking ability and is often determined in the laboratory by measuring the gel *rupture pressure*—the pressure at which the gel in the fracture breaks apart and permits fluids to pass through it. If the injection pressure exceeds, the rupture pressure of the gel during a chaseflood, the gel-filled fracture will be partially re-opened to flow and fluid channelling through the blocked fracture will start again [4, 5, 7, 16]. Measurements of rupture pressures in open fractures with defined geometries have shown that gel mechanical strength after placement is dependent on the gel state during placement [7]. Rupture pressures measured after formed gel placement with leakoff were often to be consistent and predictable. It is assumed that water mobilizes gel from the wormholes during chasefloods and is thereafter contained in the narrow flow channels constituting the wormholes. Because of this, efficient gel blocking may also be achieved after gel rupture and significant water throughput. Rupture pressures measured after gelant injection and subsequent *in situ* gel formation, a process referred to as *gelation*, were comparable to measurements during gel injection, but with more inconsistency. It was suggested that gelation did not always occur [7], because gelant may experience compositional changes that interfere with gelation upon contact with the reservoir rock and fluids [5, 17], e.g. cross-linker diffusion into the surrounding matrix that may lead to gelation failure [16]. Although initially comparable, the blocking capacity over time during chasefloods was consistently higher for pre-formed gels compared with gels with *in situ* gelation. This was explained by the presence of wormholes that collapsed and re-opened depending on the injection pressure.

2.4. Gel volume alterations

The blocking capacity of a gel placed in a fracture is also determined by the ability of the gel to maintain its volume relative to the fracture volume. After placement, the gel may undergo processes that change its volume and impact the success of a chaseflood. Several processes, such as *syneresis* [18, 19], *dehydration* [20–23] and *gel swelling* [24, 25], have been studied experimentally using bulk gel, core plugs and micromodels. During syneresis and dehydration, the gel volume is reduced due to loss of water caused by chemical reactions over time, changes in pressure gradients or matrix capillary forces adjacent to the gel network. Other conditions, such as temperature, solvent composition, ionic strength and external electric field, are the main causes of gel swelling, which impact the gel volume without the loss of water by influencing the osmotic pressure balance between the gel network and its surroundings [26]. The behaviour of a polymer gel during EOR chasefloods will, in summary, depend on both the properties of the gel itself and on the external conditions in the reservoir.

3. Foam flooding of fractured systems

EOR techniques in fractured reservoirs rely on maximizing the contact area between the injected EOR fluid and the rock surface, and therefore, the EOR fluid must transport effectively within the fracture network [27]. Most fracture networks, however, are heterogeneous themselves, with varying fracture aperture, orientation and connectivity.

3.1. Gas mobility reduction

Heterogeneous fracture networks may result in poor sweep of the injected EOR fluid, and mobility control should be implemented to maximize contact. Two-phase flow within rough-walled fractures has previously been investigated using Newtonian fluids [28–30] and non-Newtonian polymer solutions [31, 32]. Foam has the potential to increase oil recovery by better areal sweep, better vertical sweep (less gravity override), less viscous fingering and diversion of gas from higher permeable or previously swept layers [33]. Diversion of gas into lower permeable layers using foams may be important for fractured systems, where a very large permeability contrast exists and cross-flow between the zones occur [34].

3.2. Foam generation in fractures

Foam is generated in porous media by snap-off, lamella division or leave-behind mechanisms. Foam generation is affected by porous medium topological properties, wetting content, capillary suction pressure, surfactant formulation, gas fractional flow and flow rate. Snap-off and lamella division create "strong" foam in terms of separate gas bubbles above a critical capillary number [35], whereas leave-behind forms lamellae oriented parallel to the flow direction with only moderate effect on flow resistance, and the injected gas remains as a continuous phase. In porous media with permeability discontinuities, snap-off is an important mechanism for foam generation [36–38]. Foam generation within a fracture network was observed in a replica of a rough-walled fracture with variable aperture [39]. Foam was found to be generated by snap-off and the bubble size was four times larger during *in situ* generation in the fractured systems as a result of fewer snap-off sites in the fracture compared to the Berea sandstone used for bubble pre-generation. The resulting foam texture and the relationship of curvature with foam viscosity determined the flow resistance of the system. Similar snap-offs in idealized fractures at the transition from narrow to large aperture was reported [40], where the flow resistance increased with greater gas fractional flow and larger aperture. Similarly, flow in rough-walled fractures was previously characterized [39, 41], and may be favourable for mobility in fracture networks of varying aperture [42].

4. Experimental procedures

In this work, experiments providing insight to polymer gel behaviour during and after placement were performed using cylindrical outcrop core plugs with a 1 mm longitudinal fracture and aged to varying wetting states. *In situ* imaging by CT, MRI and PET was used to quantify and explain local saturation behaviour during polymer gel placement and chase-floods. Foam was investigated using a fractured marble tile model encased in Plexiglas that enabled us to visualize and describe foam flow in fractures (the marble itself is impermeable) at different gas fractions.

4.1. Establishing stable wettability preferences by dynamic ageing

Stable, predictable and uniformly distributed wettability preference is essential during core analysis to achieve reliable results [43–45]. The simplest wettability preference to achieve is the *strongly water-wet* condition, where the contact angle between oil and water on a smooth surface is between 0° and 30° [46]. All clean outcrop rocks are strongly water-wet before exposure to crude oil, and a strongly water-wet wettability preference may be achieved and maintained using mineral oils [47]. However, this wettability preference does not reflect the preference of most reservoirs [48], and it is therefore needed to change the wettability of outcrop cores to better reflect reservoir conditions. Because core plugs extracted from the subsurface are exposed to drilling muds and large changes in pressure and temperature conditions during extraction, wettability alteration is also needed for reservoir cores [49]. Based on a decade of wettability alteration studies in chalk [50–54], a dynamic wettability alteration method [55] is outlined below

1. Cylindrical core plugs are drilled from outcrop rock blocks and cut to length. The core plugs are thereafter washed in tap water and dried at 60°C for no less than a week. The core plugs are thereafter saturated by brine, and porosity, and permeability measured.

2. The crude oil is prepared for ageing by being heated to 90°C and thereafter injected through a chalk core at a constant injection rate to remove impurities. Before use, the chalk core filter is flooded with crude oil to low water saturation and aged by flushing crude oil through the core at 1 cm^3/h for 96 h, reversing the flow direction midways. The crude oil used for ageing the filter core plug is not re-used in the wettability alteration study. Due to its aged state, it was assumed that the adsorption of active wettability alteration components on the filter was significantly reduced. After filtration, the crude oil is stored in closed containers at 90°C with minimal interference and without air exposure until used to age the cores.
3. The fully water saturated core plugs are oilflooded to irreducible water saturation by crude oil injection at high differential pressures (2 bar/cm) at 90°C. When S_{wi} is reached, the injection rate is reduced to an ageing flow rate of 3 cm^3/h or 1.5 cm^3/h, for 2″ and 1.5″ diameter cores, respectively. Crude oil is continuously injected throughout the entire ageing process, and the direction of flow reversed midway. The ageing time is determined by the crude oil/rock/brine system and the desired wettability preference. After ageing, the crude oil is miscibly displaced from the core with 5PV of decaline (decahydronapthalene) followed by 5PV mineral oil (e.g. decane), all at 90°C.
4. Wettability is measured using the Amott-Harvey method: spontaneous and forced imbibition of water, followed by spontaneous and forced imbibition of the preferred mineral oil: using mineral oil to represent the oil phase ensures that the wettability of the core plugs is not further altered for the duration of experiments.
5. Experiments to investigate enhanced oil recovery (EOR) potential are commonly started at the irreducible water saturation, S_{wi}.

4.2. Imaging techniques applied in porous media

Several imaging techniques are currently applied to study flow in porous media, and most techniques originate from medical imaging. Here, we briefly review three imaging techniques used to study mobility control for EOR in fractured core plug systems.

4.2.1. Positron emission tomography (PET)

PET is based on positron-emitting radionuclides where a positron is emitted from the nucleus accompanied by an electron to balance atomic charge. Radioactivity is a spontaneous nuclear phenomenon insensitive to temperature and pressure [56]. The positron loses kinetic energy by interactions with the surroundings, and at near-zero momentum the positron combines with an electron and annihilates. The use of PET to study flow in porous media was recently reviewed and compared with CT [57]. Spatial fluid saturation is calculated based on the registered activity of the labelled phase, which in this work is water using the fluorine radioisotope ^{18}F.

4.2.2. X-ray computed tomography (CT)

CT measures the X-ray attenuation through gradual loss in flux intensity through the medium, and produces a time-averaged density distribution image of the rock [58, 59]. CT imaging relies on sufficient density contrasts which may often be fulfilled in low-porosity media. Because attenuation depends on both the electron density and the effective atomic number, the CT number will vary with the energy of the rays. Spatial fluid saturation is derived with sufficient fluid density difference.

4.2.3. Magnetic resonance imaging (MRI)

MRI provides high spatial resolution imaging and fast data acquisition necessary to study flow in porous media. When replacing hydrogen in the aqueous phase (H_2O) with deuterium (D_2O), the magnetic signal in the water phase is removed and one explicit fluid phase (oil) is imaged in an oil-water system. MRI has successfully been used to characterize flow behaviour and production mechanisms in fractured chalk and their dependency on wettability, injection rate, fracture aperture and configurations [56, 60].

Figure 1 shows the different views applied during *in situ* imaging of cylindrical core plugs in this study. The sagittal view was often used to capture the flow dynamics inside the open fracture—which was vertically aligned in all experiments.

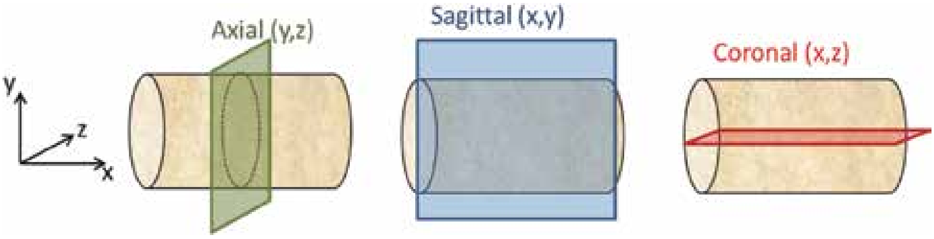


Figure 1. Schematic representation of the different views applied during *in situ* imaging of a core plug.

5. Recent advances in laboratory evaluation of polymer gel and foam for EOR

5.1. *In situ* imaging of polymer gel transport in fractured core plugs

Complementary *in situ* imaging techniques have been used to investigate different aspects of polymer gel treatments described in the following sections. For most experiments, artificially fractured core plugs with open, longitudinal fractures have been used and the matrix has been saturated by two immiscible phases: oil and water, to mimic the environment in an oil reservoir. The polymer gel used for all experiments was 0.5% HPAM (~5 million daltons molecular weight) cross-linked by 0.04% (417 ppm) Cr(III)-acetate and aged at 41°C for 24 h (five times the gelation time). After ageing, the gel was cooled to ambient temperature of ~23°C.

5.1.1. Gel shrinkage from spontaneous imbibition

Gel placement in fractured reservoirs and its behaviour during chasefloods have been widely studied [4, 15, 61], but gel interaction with the porous rock in which the fractures are embedded has been less discussed. The exchange of fluids between the gel and adjacent porous rock may be substantial, even without a viscous pressure gradient across the system, if spontaneous capillary imbibition of water occurs [23]. Spontaneous imbibition impact leakoff during gel placement and gel stability after placement, and the loss of water from the gel is influenced by relative permeability, capillary pressure and the wettability of the porous medium. A severe reduction in gel volume (up to 99%) was documented due to spontaneous imbibition into porous media from adjacent, non-flowing bulk gel [23], suggesting that gel treatments lose efficiency over time where a potential for spontaneous imbibition exists, because gel-treated fractures may be opened to flow. Polymer gel is often used to reduce water cut and is therefore placed in a well or zone of the reservoir that is watered-out, where spontaneous imbibition is reduced. During EOR operations, however, the local fluid saturations may change considerably, i.e. if an oil bank is generated, and spontaneous imbibition may again have impact on gel mobility control.

5.1.2. Leakoff dependency on wettability

In a strongly water-wet rock, a positive capillary force exists to attract water from the gel into the rock matrix. In an oil-wet rock, however, water will be repelled and must overcome a capillary threshold pressure to invade the pores. These two wettability conditions were directly compared using complementary imaging techniques during mature gel injection into open fractures. Cylindrical core plugs with longitudinal fractures of 1 mm aperture were used, and gel was injected with a constant volumetric injection rate into the fracture at ambient conditions.

In strongly water-wet, low-permeable chalk rock samples, where a strong positive capillary pressure exists, residual oil saturations were reached during gel placement due to water leakoff [25]. The chalk core was placed in a Bruker 4.7T MRI, and a spin-echo based sequence was used to produce images during D_2O-gel injection. MRI settings must be tuned for each experiments, and depend strongly on the core material used, the fluid saturation and type of experimental setup (e.g. if a core holder or epoxy layers were used as confinement vessel). Finding the right settings for each experiment requires expert knowledge of the imaging apparatus and is not the focus of this chapter. Readers are referred to [62]. **Figure 2** shows MRI images of water leakoff during gel placement in a low-permeable, strongly water-wet chalk core (permeability, K <10 mD, porosity, φ = 45%, d = 4.96 cm, L = 7.6 cm). The rock matrices adjacent to the fracture were initially fully saturated with mineral oil (*n*-decane) and appear light grey in the images. Bedding planes in the rock sample may be observed as darker features that are constant in the images. A strong positive capillary pressure exists due to the small pore sizes of this rock [63]. Water leaves the gel during leakoff and reduces the oil saturation in the rock matrix adjacent to the fracture first (darker grey regions due to loss of magnetic signal from the oil).

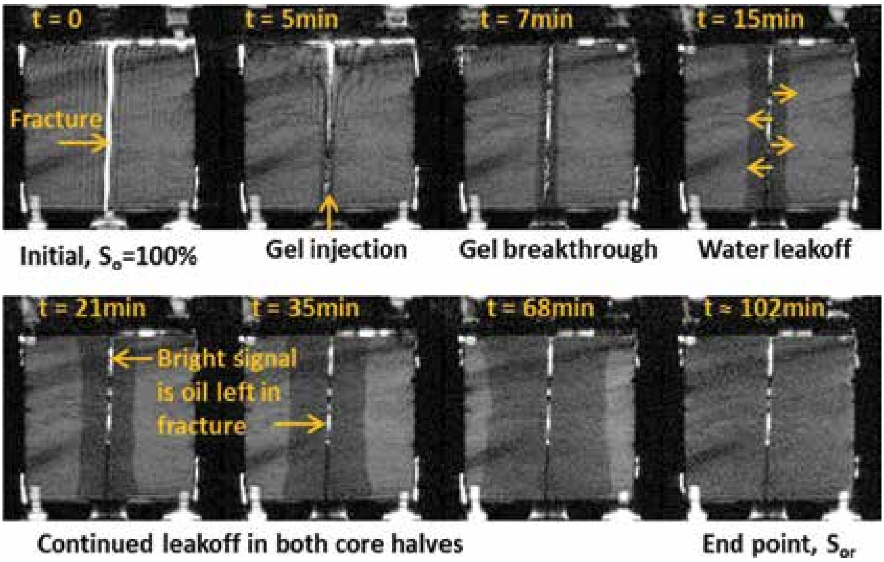


Figure 2. Coronal slices through a cylindrical, fractured core plug placed in an MRI during gel placement. As D_2O-gel (no signal) progress through the fracture, conventional material balance experiments suggest that the oil in the fracture is displaced; however, the MRI images shown here suggest that some oil remains in the fracture even after significant gel flooding.

The water leakoff from the gel in the fracture to the oil-saturated matrix was symmetric around the fracture and occurred by combined spontaneous and forced imbibition from the differential pressure generated. This combined displacement resulted in residual oil saturation in the matrix after gel placement, corresponding to 64% OOIP oil recovery during gel injection for the chalk core used. Although significant oil was produced in experiments at core plug scale, gel placement will not in itself contribute significantly to oil production at field scale because of the small fracture volume (1–2%) relative to matrix volume in most reservoirs. Hence, chasefloods are important to recover additional oil after a gel placement. The concept of gel placement is, however, important to study because it greatly affects the success of chaseflood oil recovery.

In oil-wet and low permeable rocks, a threshold pressure must be overcome to achieve water leakoff. Local water leakoff during mature gel placement in a fractured, oil-wet carbonate core plug ($K = 11.7$ mD, $\varphi = 17.6\%$, $d = 3.8$ cm, $L = 10.1$ cm) was investigated by CT [64]. The CT was a Picker PQ-6000 with 120 kV_P tube voltage. Scans were produced with 4 s scanning time, and the slice thickness was 2 mm. Using a low injection rate of 6 cm^3/h during gel injection reduced the differential pressure and no leakoff was observed. Gel progressed through the fracture without losing water and increasing its concentration—thus, rock saturation remained constant at the irreducible water saturation (**Figure 3**, top and middle). In fully water saturated rock, where capillary forces are not present, the differential pressure limit to achieve leakoff corresponds to the pressure needed to extrude gel through the fracture [3]. Improved sweep efficiency was observed during the subsequent chaseflood when the injected water displaced oil from the rock matrix, predominantly in the inlet part of the core (see **Figure 3**).

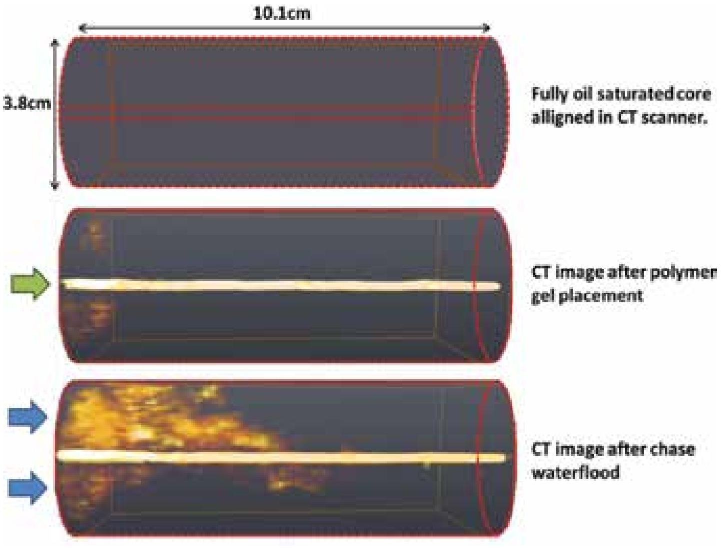


Figure 3. CT images of a fractured core plug. Top: the core is aligned in the CT at S_{wi}. Middle: CT image taken after gel placement. A strong signal from the gel is seen throughout the fracture. Matrix saturation changes were not observed during gel placement. Bottom: Chase waterflooding. A dispersed chase water front was clearly distinguishable by CT.

5.2. Visualization of EOR chaseflood behaviour

During gel placement in initially oil-filled fractured systems, it is assumed that the oil residing in the fracture is produced at gel breakthrough [25]. This assumption was based on the high differential pressure observed during chasefloods, comparable to conventional experiments using 100% water saturated cores.

5.2.1. Oil trapped in gel

Upon careful inspection of **Figure 2**, it is possible to observe oil remaining in the fracture (bright sections) during gel flooding, and also after significant gel throughput. A clear rupture pressure during water chaseflooding suggests that the oil did not impact the blocking capacity of the gel. By employing the MRI further to image the chaseflood (**Figure 4**), we determined that the water flow paths were narrow and presumably through wormholes in the dehydrated gel, and that the oil remaining in the fracture was trapped within the gel structure (light grey areas in **Figure 4**). **Figure 4** shows the water flow paths through the gel in the fracture (bright white). A thresholded image (**Figure 4B**) shows the wormhole flow pattern in more detail.

Wormhole size is known to change with injection rate due to the gel elasticity. Although the gel pressure resistance is stable at low injection rates (below 600 cm^3/h, corresponding to a maximum injection flux of 1100–1600 cm/h when all flow of water is through the fracture), the gel may erode in the vicinity of wormholes at higher injection rates over time (significant water throughput). In experiments where the purpose is to measure wormhole size, it is therefore advisable to use high flow rates within relatively short time intervals. Without imaging, the average wormhole size can be calculated indirectly by measuring the injection rate and average pressure drop across the core plug. With *in situ* imaging, such as applying PET, the wormhole size may be measured directly, and the wormhole dynamics with changes in injection rate directly observed. Wormholes within a gel-filled fracture were observed and quantified using PET, as shown in **Figure 5**. PET/CT sequences were acquired on a CT 80 W Nanoscan PC imager, featuring spatial resolutions of 800 and 30 μm of the respective PET- and CT-detector systems. The core used was of Edwards limestone material [65] and was fully saturated by brine with a composition equal to the gel solvent. The PET signal was not corrected for attenuation in the analysis because the low CT tube energy (70 kV_P) did not penetrate the core to produce spatial core plug density (needed for attenuation correction). The CT was thus only used for core plug positioning. In **Figure 5**, radioactively labelled water (^{18}FDG) was injected into the gel-filled fracture with a constant injection rate of 60 cm^3/h. When the pressure drop had stabilized across the core (at 1.6 kPa/cm for this injection rate), the wormhole flow pattern, visualized by PET, remained unchanged and covered 22.3% of the fracture volume. Dehydrated gel (no signal) covered the remaining fracture volume. *In situ* imaging by PET showed locally large variations in the wormhole width, from very narrow (almost invisible on images) in some sections of the fracture to spanning large parts of the fracture height in other sections.

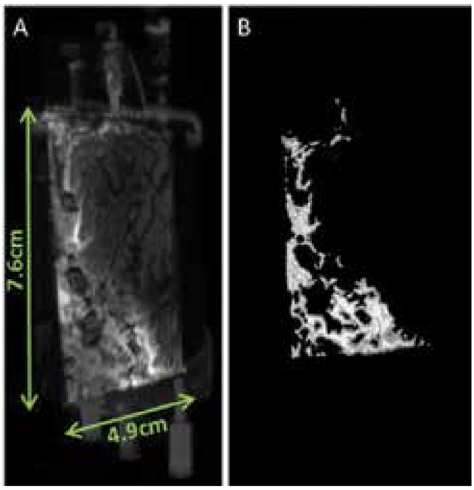


Figure 4. (A) Three-dimensional image of the core plug during water chaseflooding. All remaining signal is in the fracture. Grey areas represent *n*-decane, whereas white signal represent the intruding water phase. (B) With signal thresholding the water phase may be separated from the oil to exhibit the wormhole pattern.

Waterflooding after polymer gel placement may be efficient, and even if the gel has ruptured it provides significantly reduced fracture conductivity compared to open fractures. *In situ* imaging of core floods (**Figure 3**) have, however, shown that displacement fronts may be dispersed during water chasefloods. Enhanced oil recovery may be achieved by stabilizing the displacement front, e.g. using foam [64]. The gel treatment may also be strengthened after placement by injecting a water phase with lower salinity relative to the water in the gel [66]. Both injection pressures and matrix production rates during chasefloods increased with reduced salinity compared with chasefloods where the salinity was matched with the gel [25], presumably due to swelling of the polymer gel network. The improvement of the polymer gel treatment was reversible, and gel blocking efficiency immediately decreased during chasefloods with matched salinity. This shows that is possible to control the success of a chaseflood by influencing the gel properties. Combining polymer gel placement in fractures with low-salinity chasefloods is therefore a promising approach in iEOR. The new findings from PET imaging (**Figure 5**) may be helpful in explaining the mechanism for improved conformance control during low-salinity chase waterfloods and shed light on wormhole morphology when injected water salinity is varied.

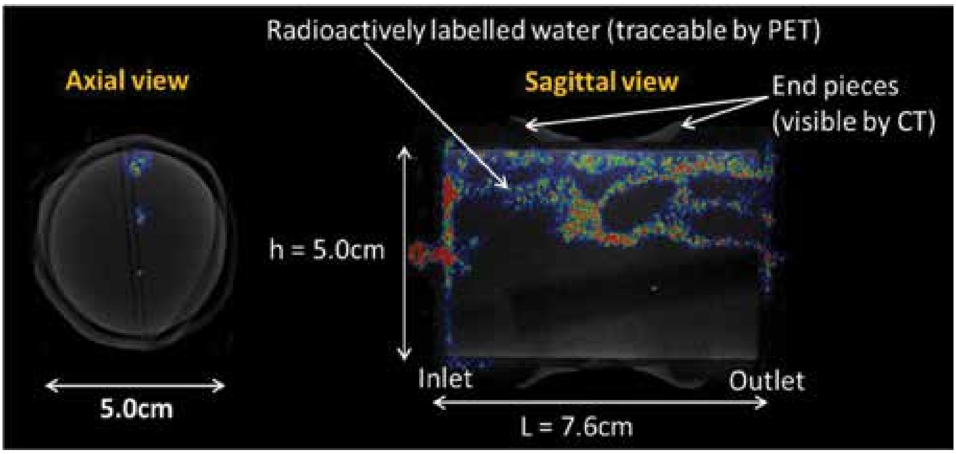


Figure 5. Positron emission tomography (PET) during radioactive chase waterflooding of a fractured core where gel has been placed in the fracture. The wormholes in the fracture are clearly seen and their development may be tracked as a function of flow rate and time. The colour pixels represent different spatial concentrations of brine in the fracture: the red signal corresponds to a high spatial concentration of radioactively labelled water, compared to e.g. blue colour (low spatial concentration). CT is applied to correctly position the PET signal in the core space.

5.3. Fractured tile model to investigate 2D foam flow in fractured systems

An experimental setup was built to visualize flow and to study mobility control by foam generation in fracture networks. A white marble tile was fractured using a ball-peen hammer and then carefully reassembled within a frame to create a fracture network with rough, calcite fracture surfaces. The (effective) porosity was assumed to be zero in the marble matrix blocks, and flow occurred through the fracture network only. The fracture network was characterized by injecting brine and gas separately into the model. Pure nitrogen (N_2) gas injection provided a baseline to which foam injection could be compared. **Figure 6** shows the marble tile model filled with red-dyed brine.

Aqueous surfactant solution (1 wt% alpha olefin sulfonate (AOS) surfactant in 5 wt% NaCl brine) and N_2-gas were co-injected into the fracture network at ambient conditions to form foam, using a range of gas fractions, to investigate the impact of the gas fraction on sweep efficiency. The fracture network was initially filled with aqueous solution, and the total flow rate for the co-injections was 60 cm^3/h.

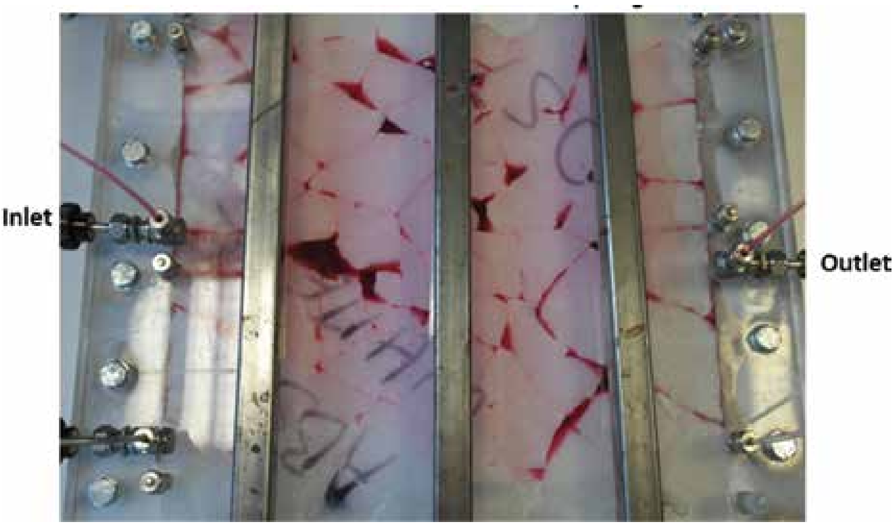


Figure 6. A square marble tile was fractured and reassembled within an aluminium frame sandwiched between two Plexiglas plates. The fracture network consisted mainly of narrow fractures with 12 large fractures. The vugular open fractures were larger bodies of open space varying between 0.4 and 2.2 cm aperture. These cavities were used to observe the advancing foam front during co-injection. In this figure, the marble tile model is filled with red-dyed brine to emphasize the fracture network.

5.3.1. Sweep efficiency

Areal sweep efficiency with changes in gas fraction was evaluated using the fracture network: a high-resolution camera was used to capture images at short time intervals throughput foam co-injection. From the images, total sweep was evaluated and it was possible to map flow patterns and calculate dynamic sweep efficiency as function of foam volume injected. Images could capture drainage of liquid from each fracture element, including vugs and narrow fractures. **Figure 7** compares total areal sweep efficiency for three N_2-gas fractions during foam co-injection: fg = 0.60, fg = 0.80 and fg = 0.90.

Figure 7 shows the development in sweep efficiency within the fracture network during co-injection with three different gas fractions. The sweep efficiency is compared at three time steps: after three fracture elements are filled; after five fracture elements and after seven fracture elements are filled. Only foam in the larger vugs could be visualized directly, but foam was also generated in, and flowed through, the smaller apertures. In general, we see that the sweep efficiency and spread of foam was higher with the increase of gas fractional flow. At higher gas fractions, breakthrough of gas was delayed, but in all cases delayed compared with pure gas injection. This demonstrated that foam reduced gas mobility and was formed within the fracture network itself.

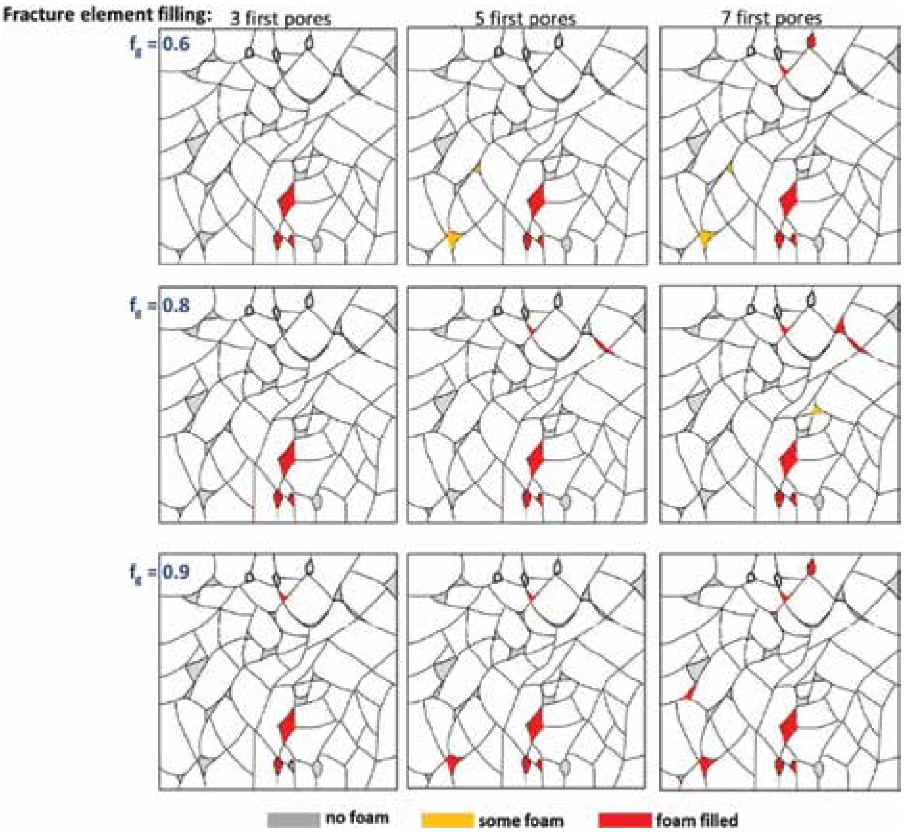


Figure 7. Foam propagation through a fractured marble tile system. Foam filling of the first three, five and seven fracture elements are shown for gas fractions of 60% (top), 80% (middle) and 90% (bottom), respectively. Co-injection was performed bottom to top in the images.

Unlike the foam bubble shape in a porous medium, where bubble shape is governed by pore configurations [35, 67], the bubbles in fractures are deformed according to interfacial tension, and the gas-liquid interfacial curvature varies according to gas fractional flow [41]. Foam coalescence in a porous medium is controlled by the 'limiting-capillary-pressure' [68] at moderate to high gas fractional flow. The limiting capillary pressure is determined by the pore size, surfactant formulation, local fluid saturation and the interstitial velocity. The capillary pressure in a fracture is much lower (generally set to zero in most simulations—although strictly not correct) at a given aqueous-phase saturation in comparison to permeable matrix. Capillary suction coalescence of foam lamellae appeared to become significant when the local aqueous phase saturation became very low. With increased gas fraction, the gas bubbles increased in size, on average. Large gas bubbles separated by thin lamellae occupied the majority of the fracture volume, especially at 0.95 gas fraction. This effect may be attributed to thinning of lamella at high gas fractional flow [69], resulting in foam coalescence and merging of smaller bubbles. Fewer and coarser bubbles related to the highest gas fraction are likely caused by thinning of lamellae (a larger fraction of the liquid is located in the Plateau border), followed by film rupture due to higher capillary-suction pressure compared to lower gas fractional flow. The observations are consistent with earlier results, where larger bubbles were observed with increased gas fractional flow in a fracture network [39, 70].

5.4. Combined polymer gel and foam chasefloods for iEOR

Using a low-field 8 MHz MRI (Oxford Instruments Maran DRX), we experimentally investigated an iEOR approach where the first step was polymer gel placement to reduce fracture conductivity and the second step was CO_2-foam injection to improve sweep efficiency compared to water chasefloods [64]. The experiments were performed at ambient conditions, thus the CO_2 was not miscible with the oil (*n*-decane). Pre-generated foam was injected into the core after gel placement, using a gas fraction of 0.8 and a surfactant solution containing 1 wt% AOS surfactant. The development in oil saturation during all experimental steps was compared to oil recovery during foam injection without mobility control, using magnetic resonance imaging. Two fractured carbonate core plugs were used ($K \approx 30$ mD, $\varphi = 23–24\%$, $d = 3.8$ cm, $L = 5.8$ cm), with a measured Amott-Harvey wettability index after dynamic ageing of $I_{AH} = -0.2$, which represents weakly oil-wet conditions. Waterfloods were not efficient due to the oil-wet conditions and only recovered 10–20% of the oil in place. *In situ* imaging showed that oil was primarily displaced from the inlet end of the core plugs, where water was injected directly into the matrix through specially designed end pieces [64]. Oil was displaced into the fracture, and no further oil recovery from the core matrix was detected after water breakthrough. Polymer gel placement was performed at 100 cm^3/h and yielded 20% oil recovery that was caused by the large fracture volume compared to the core pore volume at high injection pressure and low matrix threshold pressure due the weak oil-wet conditions. Chaseflooding by immiscible CO_2-foam was performed to mitigate fluid dispersion around the displacement front. **Figure 8** shows the *in situ* development of the oil saturation and displacement fronts during foam flooding in the twin cores, with and without polymer gel conformance control present in the fracture. Oil production was prevailing in the near-fracture area by direct foam injection (**Figure 8A**). Haugen et al. [71] showed, using CT imaging of oil-wet core plug systems, that oil was viscously displaced by surfactant solution, forced into the matrix by the increased pressure gradient provided by the foam. In **Figure 8B**, polymer gel was placed in the fracture prior to CO_2-foam flooding, and both foam constituents (gas and surfactant solution) entered the matrix during the foam flood. Immiscible foam injection after conformance control by polymer gel provided 28% OOIP (original oil in place) additional oil recovery during 12.7 PV foam injected. In comparison, recovery factors of 14% OOIP (**Figure 8A**) to 20% OOIP were obtained during injection of more than 30 PV foam in comparable core plugs. Improved sweep efficiency was visually observed by MRI during foam chasefloods (**Figure 8**); in which more stable displacement fronts and less tendency to viscous fingering were observed when compared to e.g. chase waterflooding. The combination of two established EOR methods to improve conformance in both the fracture and matrix has important implications for future work on the development of efficient integrated EOR schemes.

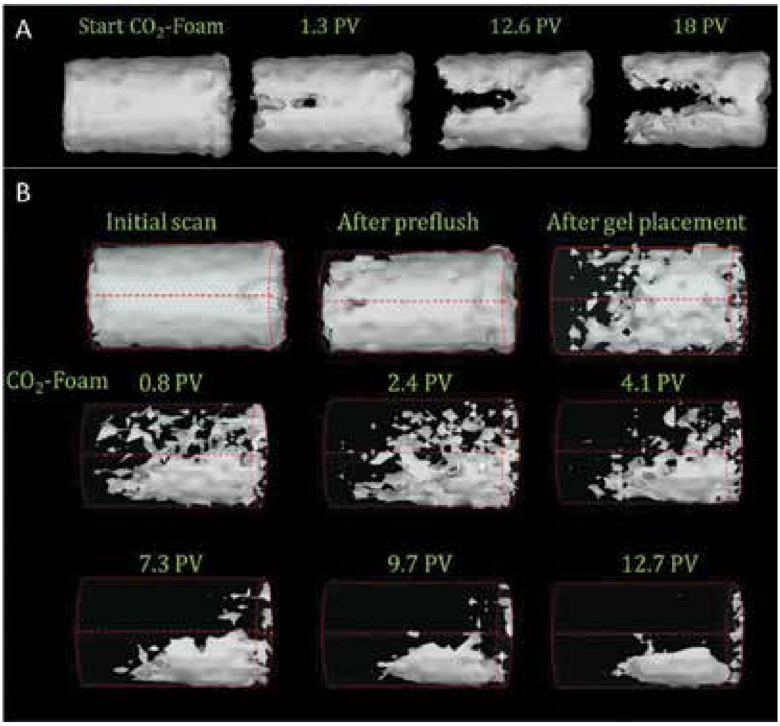


Figure 8. Development in *in situ* oil saturation (light grey areas) during foam flooding of fractured, oil-wet carbonate core plugs: (A) directly after waterflooding and (B) with polymer gel present in the fracture. Injections were performed left to right.

6. Conclusions

In situ imaging provides new insight and corroborates results from core analysis applying material balance or gravimetrical measurements, and several different imaging techniques may be used to closely investigate local changes in saturation, fluid flow and oil recovery mechanisms during EOR experiments. Using *in situ* imaging techniques in this work, we found that:

- Water leakoff during polymer gel propagation through a fractured, oil-saturated core plug could be captured using magnetic resonance imaging (MRI). Water leakoff was symmetric around the fracture and occurred by combined spontaneous and forced imbibition from the differential pressure generated by the gel injection.
- Residual oil within the gel structure was observed with MRI after gel injection into a fractured, oil-saturated core plug. The remaining oil did not impact the flow paths during water chasefloods, and it is likely that only a thin oil layer partly coated some region of the gel.

- Water flow paths known as wormholes were observed during chase waterfloods applying positron emission tomography (PET). We found large local variations in the wormhole shape and width that have not previously been observed during waterfloods. PET is able to catch rapid changes in fluid saturation during dynamic floods and may thus give valuable information about changes in wormhole morphology as a function of flow rate and pressure.
- *In situ* imaging by CT and MRI were used to investigate the shape of displacement fronts during chasefloods when polymer gel had been placed in a fracture. Imaging showed a dispersed displacement front during waterflooding of an oil-wet core plug. CO_2-foam injection stabilized the displacement front and improved sweep efficiency.

Advanced medical imaging is not always required or available, and important insight may be gained from relatively simple experimental setups, such as the study foam generation in fractures where Plexiglas models provide the visualization needed. We found that foam was generated in a fracture model during co-injection of surfactant and N_2-gas. A higher fractional flow of gas increased the sweep efficiency and spread of foam in vugs and fractures.

The crux of core plug scale experiments is proper design and planning of the experimental schedule using suitable equipment and imaging tools. When the core plug system is positioned within the imaging apparatus it cannot be moved. Hence, Testing the experimental setup without imaging, using simple material balance, is a good idea.

Author details

Bergit Brattekås[1] and Martin A. Fernø[2*]

*Address all correspondence to: martin.ferno@uib.no

1 National Improved Oil Recovery Centre, University of Stavanger, Stavanger, Norway

2 Department of Physics and Technology, University of Bergen, Bergen, Norway

References

[1] Liang, J.-T., R.L. Lee, and R.S. Seright, Gel Placement in Production Wells. SPE Production and Facilities, 1993. 8(November): p. 276–284.

[2] Seright, R.S., Gel Placement in Fractured Systems. SPE Production & Facilities, 1995. 10(4): p. 241–248.

[3] Seright, R.S., Gel Propagation Through Fractures. SPE Production & Facilities, 2001. 16(4): p. 225–231.

[4] Seright, R.S., Washout of Cr(III)-Acetate-HPAM Gels from Fractures, in International Symposium on Oilfield Chemistry. 2003, Society of Petroleum Engineers: Houston, TX.

[5] Ganguly, S., et al., The Effect of Fluid Leakoff on Gel Placement and Gel Stability in Fractures. SPE Journal, 2002. 7(03): p. 309–315.

[6] McCool, C.S., X. Li, and G.P. Wilhite, Flow of a Polyacrylamide/Chromium Acetate System in a Long Conduit. SPE Journal, 2009. 14(01): p. 54–66.

[7] Brattekås, B., et al., Washout of Cr(III)-Acetate-HPAM Gels From Fractures: Effect of Gel State During Placement. SPE Production & Operations, 2015. 30(02): p. 99–109.

[8] Seright, R.S., An Alternative View of Filter-Cake Formation in Fractures Inspired by Cr(III)-Acetate-HPAM Gel Extrusion. SPE Production & Facilities, 2003. 18(1): p. 65–72.

[9] Seright, R.S., et al., Improved Methods for Water Shutoff, in Final Technical Progress Report (US DOE Report No. DOE/PC/91008-14), US DOE Contract No. DE-AC22-94PC91008, BDM-Oklahoma Subcontract No. G4S660330. 1998. p. 21–54.

[10] Seright, R.S., R.H. Lane, and R.D. Sydansk, A Strategy for Attacking Excess Water Production. SPE Production and Facilities, 2003. 18(03): p. 158–169.

[11] Sydansk, R.D., A Newly Developed Chromium(III) Gel Technology. SPE Reservoir Engineering, 1990. 5(03): p. 346–352.

[12] Sydansk, R.D. and G.P. Southwell, More Than 12 Years Experience With a Successful Conformance-Control Polymer-Gel Technology. SPE Production & Operations, 2000. 15(4): p. 270–278.

[13] Portwood, J.T. Lessons Learned from Over 300 Producing Well Water Shut-Off Gel Treatments. in SPE Mid-Continent Operations Symposium. 1999. Oklahoma City, OK, USA.

[14] Portwood, J.T., The Kansas Arbuckle Formation: Performance Evaluation and Lessons Learned From More Than 200 Polymer-Gel Water-Shutoff Treatments, in SPE Productions and Operations Symposium. 2005: Oklahoma City, OK, USA.

[15] Willhite, G.P. and R.E. Pancake, Controlling Water Production Using Gelled Polymer Systems. SPE Reservoir Evaluation & Engineering, 2008. 11(3): p. 454–465.

[16] Wilton, R. and K. Asghari, Improving Gel Performance in Fractures: Chromium Pre-Flush and Overload. Journal of Canadian Petroleum Technology, 2007. 46(02).

[17] Zou, B., et al., Precipitation of Chromium Acetate Solutions. SPE Journal, 2000. 5(03): p. 324–330.

[18] Vossoughi, S., Profile Modification Using In Situ Gelation Technology—A Review. Journal of Petroleum Science and Engineering, 2000. 26(1–4): p. 199–209.

[19] Romero-Zeron, L.B., F.M. Hum, and A. Kantzas, Characterization of Crosslinked Gel Kinetics and Gel Strength by Use of NMR. SPE Reservoir Evaluation and Engineering, 2008. 11(03): p. 439–453.

[20] Dawe, R.A. and Y. Zhang, Mechanistic Study of the Selective Action of Oil and Water Penetrating into a Gel AMplced in a Porous Medium. Journal of Petroleum Science and Engineering, 1994. 12(2): p. 113–125.

[21] Al-Sharji, H.H., et al., Pore-Scale Study of the Flow of Oil and Water through Polymer Gels, in SPE Annual Technical Conference and Exhibition. 1999, Society of Petroleum Engineers: Houston, TX.

[22] Krishnan, P., et al., Dehydration and Permeability of Gels Used in In-Situ Permeability Modification Treatments, in SPE/DOE Improved Oil Recovery Symposium. 2000, Society of Petroleum Engineers: Tulsa, OK.

[23] Brattekås, B., et al., Gel Dehydration by Spontaneous Imbibition of Brine from Aged Polymer Gel. SPE Journal, 2014. 19(01): p. 122–134.

[24] Bai, B.J., et al., Preformed Particle Gel for Conformance Control: Factors Affecting its Properties and Applications. SPE Reservoir Evaluation & Engineering, 2007. 10(4): p. 415–422.

[25] Brattekås, B., A. Graue, and R.S. Seright, Low Salinity Chase Waterfloods Improve Performance of Cr(III)-Acetate HPAM Gel in Fractured Cores, in SPE International Symposium on Oilfield Chemistry. 2015, Society of Petroleum Engineers: The Woodlands, TX, USA.

[26] Horkay, F., I. Tasaki, and P.J. Basser, Osmotic Swelling of Polyacrylate Hydrogels in Physiological Salt Solutions. Biomacromolecules, 2000. 1: p. 84–90.

[27] Zuta, J. and I. Fjelde, Transport of CO_2-Foaming Agents During CO_2-Foam Processes in Fractured Chalk Rock. SPE Reservoir Evaluation & Engineering, 2010. 13(4): p. 710–719.

[28] Chen, C.-Y. and R.N. Horne, Two-phase Flow in Rough-walled Fractures: Experiments and a Flow Structure Model. Water Resources Research, 2006. 42(3): p. W03430.

[29] Fourar, M., et al., Two-phase Flow in Smooth and Rough Fractures: Measurement and Correlation by Porous-medium and Pipe Flow Models. Water Resources Research, 1993. 29(11): p. 3699–3708.

[30] Pruess, K. and Y.W. Tsang, On Two-phase Relative Permeability and Capillary Pressure of Rough-walled Rock Fractures. Water Resources Research, 1990. 26(9): p. 1915–1926.

[31] Auradou, H., et al., Enhancement of Velocity Contrasts by Shear-thinning Solutions Flowing in a Rough Fracture. Journal of Non-Newtonian Fluid Mechanics, 2008. 153(1): p. 53–61.

[32] Di Federico, V., Estimates of Equivalent Aperture for Non-Newtonian Flow in a Rough-walled Fracture. International Journal of Rock Mechanics and Mining Sciences, 1997. 34(7): p. 1133–1137.

[33] Rossen, W.R., Foams in Enhanced Oil Recovery, in Foams: Theory, Measurements, and Applications, R.K. Prud'homme and S.A. Khan, Editors. 1995, Marcel Dekker, Inc.: New York.

[34] Bertin, H.J., et al., Foam Flow in Heterogeneous Porous Media: Effect of Cross Flow. SPE Journal, 1999. 4(2).

[35] Ransohoff, T.C. and C.J. Radke, Mechanisms of Foam Generation in Glass-Bead Packs. SPE Reservoir Engineering, 1988. 3(2): p. 573–585.

[36] Tanzil, D., G.J. Hirasaki, and C.A. Miller, Mobility of Foam in Heterogeneous Media: Flow Parallel and Perpendicular to Stratification. SPE Journal, 2002. 7(2): p. 203–212.

[37] Falls, A.H., et al., Development of a Mechanistic Foam Simulator: The Population Balance and Generation by Snap-Off. SPE Reservoir Engineering, 1988. 3(03): p. 884–892.

[38] Rossen, W.R., Foam Generation at Layer Boundaries in Porous Media. SPE Journal, 1999. 4(4): p. 409–412.

[39] Kovscek, A.R., et al., Foam Flow Through a Transparent Rough-walled Fracture. Journal of Petroleum Science and Engineering, 1995. 17: p. 75–86.

[40] Buchgraber, M., L.M. Castanier, and A.R. Kovscek, Microvisual Investigation of Foam Flow in Ideal Fractures: Role of Fracture Aperture and Surface Roughness, in SPE Annual Technical Conference and Exhibition. 2012, Society of Petroleum Engineers: San Antonio, Texas, USA.

[41] Pancharoen, M., M.A. Ferno, and A.R. Kovscek, Modeling Foam Displacement in Fractures. Journal of Petroleum Science and Engineering, 2012. 100: p. 50–58.

[42] Yan, W., C.A. Miller, and G.J. Hirasaki, Foam Sweep in Fractures for Enhanced Oil Recovery. Colloids and Surfaces A: Physicochem. Eng. Aspects 2006(283–284): p. 348–359.

[43] Spinler, E.A., B.A. Baldwin, and A. Graue, Experimental Artifacts Caused by Wettability Variations in Chalk. Journal of Petroleum Science and Engineering, 2002. 33(1–3): p. 49–59.

[44] Graue, A., et al., Alteration of Wettability and Wettability Heterogeneity. Journal of Petroleum Science and Engineering, 2002. 33(1–3): p. 3–17.

[45] Aspenes, E., A. Graue, and J. Ramsdal, In Situ Wettability Distribution and Wetting Stability in Outcrop Chalk Aged in Crude Oil. Journal of Petroleum Science and Engineering, 2003. 39(3–4): p. 337–350.

[46] Anderson, W., Wettability Literature Survey—Part 2: Wettability Measurement. SPE Journal of Petroleum Technology, 1986. 38(11): p. 1246–1262.

[47] Graue, A., E. Tonheim, and B.A. Baldwin. Control and Alteration of Wettability in Low-Permeability Chalk. in Proc.: 3rd International Symposium on Evaluation of Reservoir Wettability and Its Effect on Oil Recovery. 1995. Laramie, WY, USA.

[48] Morrow, N.R., Wettability and Its Effect on Oil Recovery. Journal of Petroleum Technology, 1990. 42(12): p. 1476-1484.

[49] Anderson, W.G., Wettability Literature Survey—Part 1: Rock/Oil/Brine Interactions and the Effects of Core Handling on Wettability. SPE Journal of Petroleum Technology, 1986. 38(10): p. 1125–1144.

[50] Graue, A., B.G. Viksund, and B.A. Baldwin. Reproduce Wettability Alteration of Low-Permeable Outcrop Chalk. in SPE/DOE Improved Oil Recovery Symposium. 1998. Tulsa, Oklahoma: Society of Petroleum Engineers.

[51] Graue, A., et al., Systematic Wettability Alteration by Aging Sandstone and Carbonate Rock in Crude Oil. Journal of Petroleum Science and Engineering, 1999. 24(2–4): p. 85–97.

[52] Graue, A., et al. Impacts of Wettability on Capillary Pressure and Relative Permeability. in International Symposium of the Society of Core Analysts. 1999. Golden, CO, USA.

[53] Graue, A., B.G. Viksund, and B.A. Baldwin, Reproducible Wettability Alteration of Low-Permeable Outcrop Chalk. SPE Reservoir Evaluation & Engineering, 1999. 2(2): p. 134–140.

[54] Graue, A., et al., Wettability Effects on Oil-Recovery Mechanisms in Fractured Reservoirs. SPE Reservoir Evaluation & Engineering, 1999. 4(6).

[55] Fernø, M.A., et al., Dynamic Laboratory Wettability Alteration. Energy & Fuels, 2010. 24(7): p. 3950–3958.

[56] Ersland, G., et al., Complementary Imaging of Oil Recovery Mechanisms in Fractured Reservoirs. Chemical Engineering Journal, 2010. 158: p. 32–38.

[57] Fernø, M.A., et al., Combined Positron Emission Tomography and Computed Tomography to Visualize and Quantify Fluid Flow in Sedimentary Rocks. Water Resources Research, 2015.

[58] Heindel, T.J., A Review of X-Ray Flow Visualization With Applications to Multiphase Flows. Journal of Fluid Engineering-Transations of ASME, 2011. 133(7).

[59] Blunt, M.J., et al., Pore-scale Imaging and Modelling. Advances in Water Resources, 2013. 51(0): p. 197–216.

[60] Aspenes, E., et al., Wetting Phase Bridges Establish Capillary Continuity Across Open Fractures and Increase Oil Recovery in Mixed-Wet Fractured Chalk. Transport in Porous Media, 2008. 74(1): p. 35–47.

[61] Seright, R.S., R.H. Lane, and R.D. Sydansk, A Strategy for Attacking Excess Water Production, in SPE Permian Basin Oil and Gas Recovery Conference. 2001, Copyright 2001, Society of Petroleum Engineers Inc.: Midland, Texas.

[62] Oleg, P., G. Ersland, and A. Graue, T2-distribution Mapping Profiles with Phase-encode MRI. Journal of Magnetic Resonance, 2011. 209(1): p. 39–46.

[63] Johannesen, E.B., NMR Characterization of Wettability and How it Impacts Oil Recovery in Chalk, in Department of Physics and Technology. 2008, University of Bergen: Bergen. p. 71.

[64] Brattekås, B., et al., Fracture Mobility Control by Polymer Gel- Integrated EOR in Fractured, Oil-Wet Carbonate Rocks, in EAGE Annual Conference & Exhibition incorporating SPE Europec. 2013: London, UK.

[65] Tie, H., Oil Recovery by Spontaneous Imbibition and Viscous Displacement from Mixed-wet Carbonates, in Department of Chemical and Petroleum Engineering. 2006, The University of Wyoming: Laramie, Wyoming. p. 238.

[66] Tu, T.N. and B. Wisup, Investigating the Effect of Polymer Gels Swelling Phenomenon under Reservoir Conditions on Polymer Conformance Control Process, in International Petroleum Technology Conference. 2011, International Petroleum Technology Conference: Bangkok, Thailand.

[67] Mast, R.F., Microscopic Behavior of Foam in Porous Media, in Fall Meeting of the Society of Petroleum Engineers of AIME. 1972, Society of Petroleum Engineers: San Antonio, Texas.

[68] Khatib, Z.I., G.J. Hirasaki, and A.H. Falls, Effects of Capillary Pressure on Coalescence and Phase Mobilities in Foams Flowing Through Porous Media. SPE Reservoir Engineering, 1988. 3(3): p. 919–926.

[69] Gauteplass, J., et al., Pore-level Foam Generation and Flow for Mobility Control in Fractured Systems. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2015. 468(0): p. 184–192.

[70] Fernø, M.A., et al., Experimental Study of Foam Generation, Sweep Efficiency and Flow in a Fracture Network, in SPE Annual Technical Conference and Exhibition. 2014, Society of Petroleum Engineers: Amsterdam, The Netherlands.

[71] Haugen, Å., et al., Miscible and Immiscible Foam Injection for Mobility Control and EOR in Fractured Oil-wet Carbonate Rocks. Transport in Porous Media, 2014(104): p. 109–131.

Chapter 4

Application of Multifunctional Agents During Enhanced Oil Recovery

Luis A. Alcázar-Vara, Luis S. Zamudio-Rivera and
Eduardo Buenrostro-González

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/64792

Abstract

During the application of enhanced oil recovery (EOR) processes, complex operational issues, such as the deposition of organic compounds (i.e., wax, resins, and asphaltenes, among others), reservoir formation damage, rock wettability alteration, and high fluids viscosity negatively affect oil recovery. This chapter presents the experimental evaluation of the multifunctional properties of two novel chemical agents recently developed: a zwitterionic surfactant (ZS) and a supramolecular complex (named here as AMESUS) for chemical EOR applications. The performance of the new multifunctional agents and the mechanisms in play on the removal/control of organic compounds deposition oil recovery, asphaltenes inhibition-dispersion activity, reduction in heavy crude oil viscosity, rock wettability modification, and relative permeability are discussed in this chapter.

Keywords: chemical enhanced oil recovery, multifunctional surfactants, asphaltenes, formation damage, viscosity reduction

1. Introduction

On average, only one-third of the original oil in place (OOIP) is economically recoverable after the application of primary and secondary oil recovery (SOR) methods. The implementation of enhanced oil recovery (EOR) processes is increasing due to the decline in the discovery of new oil fields during the last decades [1–3]. EOR is defined as a process to reduce oil saturation below the residual oil saturation [4], and it refers to the injection of any fluid (i.e., steam, polymer solution, solvents, etc.) into the reservoir to change and/or to modify the existing rock/oil/brine interactions. It has been reported that for light and medium oil reservoirs, the residual oil saturation ranges from 50 to 60% of the OOIP, whereas for heavy crude oil reservoirs, it could range from 80 to 95% [1, 5]. Several EOR methods have been reported such as the use of chemical products (polymers and surfactants), thermal methods (steam stimulation, in-situ combustion, electrical heating, vibrational methods etc.), miscible gas injection, and microbial EOR, among others [4]. However, the application of EOR technologies can modify in an adverse way the flow and phase behavior of the reservoir fluids as well as the formation rock (FR) properties that can promote oil productivity decline. Some of these issues include organic compounds deposition leading to formation damage, plugging of the formation rock (within the reservoir and at the wellbore), as well as flow restrictions in tubing, flow lines, and production facilities [2, 3].

Deposition of heavy organics such as asphaltenes can take place at the oil producing slots and at the rock formation face, while the deposition of solid phases (i.e., asphaltenes) over pore surface and/or across pore throats within the oil formation can reduce significantly the effective permeability of the reservoir and severely impair the flow of crude oil through the porous medium (formation damage). The deposition of organic components also renders rock wettability changes from water-wet to oil-wet. Another issue could be the increase in the viscosity of the oil phase due to the formation of water in oil emulsions [6, 7].

This complicated association of problems can occur simultaneously during oil recovery processes. Several methods to remediate these operational problems are available such as the use of chemical additives, which have been used in the field without testing their actual effectiveness in remediating the situation [7, 8]. The removal and control of formation damage caused by asphaltenes deposition are usually achieved by the application of chemical treatments based on aromatic solvents that are applied in both at the wellbore and deeper within the formation. However, there is an economical limitation due to the transient effect of such cleanup methods. Moreover, aromatic solvents do not efficiently dissolve the heavy organic deposits or extract the asphaltenes fractions that remain fixed onto carbonated and clay minerals surfaces [7, 9, 10]. In the case of heavy crude oils, some of the methods that have been reported for viscosity reduction include dilution with lighter crudes or alcohols, the use of chemical additives such as polymers, or nanoparticles, and the use of surfactants to stabilize emulsions [11].

Chemical flooding using surfactants is a method that has been widely studied over several decades; it is considered an efficient process to achieve incremental recovery of residual oil with great potential as an EOR process for the petroleum industry. Although the mechanisms involved in the interactions of the surfactants with oil and brine within the porous media are complex, interfacial-tension reduction and formation rock wettability alteration are the most accepted mechanisms responsible for recovering residual oil saturation [4, 7, 12, 13].

This chapter presents the experimental evaluation of the multifunctional properties of two novel chemical agents recently developed: a zwitterionic surfactant (ZS) and a supramolecular complex (named here as AMESUS) for chemical EOR applications. The performance of the new multifunctional agents and the mechanisms in play on the removal/control of organic compounds deposition oil recovery, asphaltenes inhibition-dispersion activity, reduction in the viscosity of the heavy crude oil, rock wettability modification, and relative permeability are presented and discussed in this chapter.

2. Multifunctional agents

2.1. Zwitterionic surfactant (ZS)

Surfactants that are composed of two hydrophilic and two hydrophobic groups have been the subject of significant research interest since the early 1990s. These surfactants are called "Gemini" because their chemical structures can be perceived as two classic surfactant molecules chemically connected at or near the head groups. Their chemical arrangement provides a rich array of aggregate morphologies and solution properties that are dependent upon the nature and size of the linking group and/or head groups. These types of surfactants with unsymmetrical geometry have interesting characteristics in terms of self-assembly into aggregates and packing at interfaces [14].

Zwitterionic surfactants (ZSs) are considered among the surfactant molecules that can be applied in EOR with molecular structures made up by two hydrocarbon chains, a bridge, and two polar groups of zwitterionic type that can be a cation and an anion in different atoms of the same molecule. ZSs are electrically neutral, and they can behave as bases or acids (acceptor or donor) according to the properties of the medium where they are found. Therefore, zwitterionic surfactants can play a role as smart wettability modifiers that react efficiently according to the characteristics and properties of the specific medium [8, 15–17].

Figure 1 displays the general chemical structure of zwitterionic surfactants (ZSs), which corresponds to a recently developed alkyl betaine zwitterionic gemini surfactant with polyethylene spacers [17]. This molecule was designed as a wettability modifier of rock surfaces such as limestone, dolomite, sand, quartz or heterogeneous lithology in the presence of brines with high content of divalent ions (i.e., calcium, magnesium, barium, and strontium), high temperature, and high pressure for EOR applications.

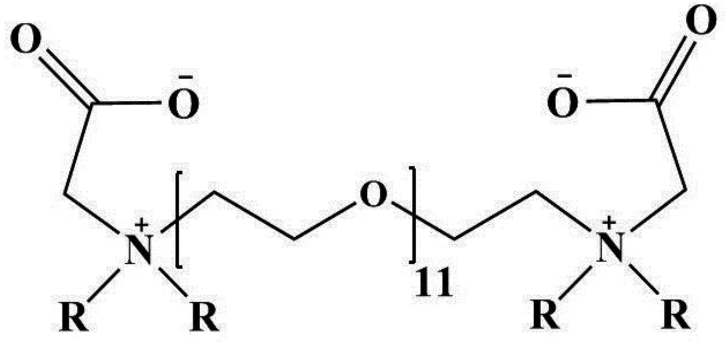


Figure 1. General chemical structure of the geminal zwitterionic surfactant. R is dodecyl radical [17].

2.2. Supramolecular complex

Supramolecular chemistry is based on the phenomenon of molecular recognition through weak forces between molecules, which promotes self-assembly [18]. This is a promising technology that has impacted the design of new materials with interesting applications in the chemical industry including the petroleum industry [7, 19, 20].

Supramolecular technology has been used for EOR applications. For instance, supramolecular assemblies, such as micellar structures, have been developed for applications in wettability alteration where it is beneficial to modify the rock formation wettability from oil-wet to preferentially water-wet to enhance oil recovery [19, 20]. It has also been reported that supramolecular agents can interact with crude oil fractions within the reservoir to reduce their viscosity promoting additional recovery of residual oil [7, 19, 20].

The supramolecular complex, AMESUS, is a surfactant developed from the interactions among cocamidopropyl hydroxysultaine (CAHS), sodium dodecyl alpha-olefin sulfonate, and sodium dodecyl hydroxyl sulfonate. AMESUS offers multifunctional features including foaming, corrosion-inhibition, and wettability-alteration properties. AMESUS can be used in high salinity brines at reservoir conditions without alteration of its molecular structure [19]. **Figure 2** shows the characteristic chemical structure of a supramolecular structure.

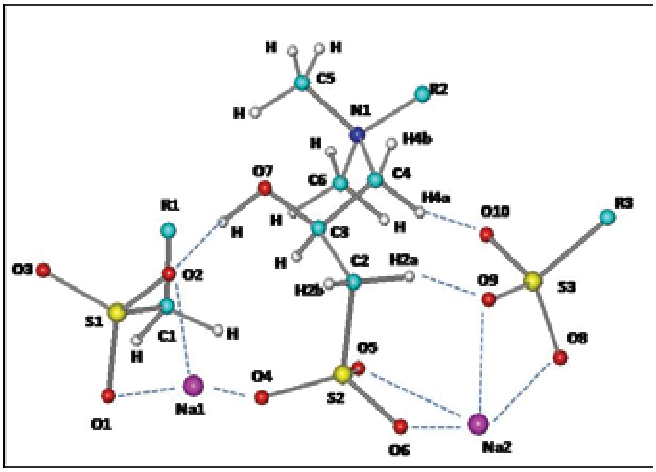


Figure 2. Characteristic chemical structure of the supramolecular complex, wherein R1, R2, and R3 are alkyl, alkenyl linear, or branched chains, whose length ranges from 1 to 30 carbon atoms [19].

3. Evaluation of the multifunctional properties

3.1. Interfacial tension (IFT) and contact angle

The dominant oil recovery mechanisms during surfactant flooding are interfacial tension (IFT) reduction and wettability alteration [12, 13]. The mobilization of residual oil requires the reduction in the interfacial tension at the oil-brine interfaces to ultralow values to overcome the capillary forces responsible for trapping residual oil at the pore scale [8]. Therefore, IFT reduction mechanism depends on the surfactant effectiveness in reducing the oil-water IFT by four to six orders of magnitude. **Figure 3** shows the interfacial tension as a function of surfactant concentration and surfactant type (AMESUS and a ZS) obtained from a light crude oil (31° API)—high-salinity brine (2.6 wt.% NaCl) system.

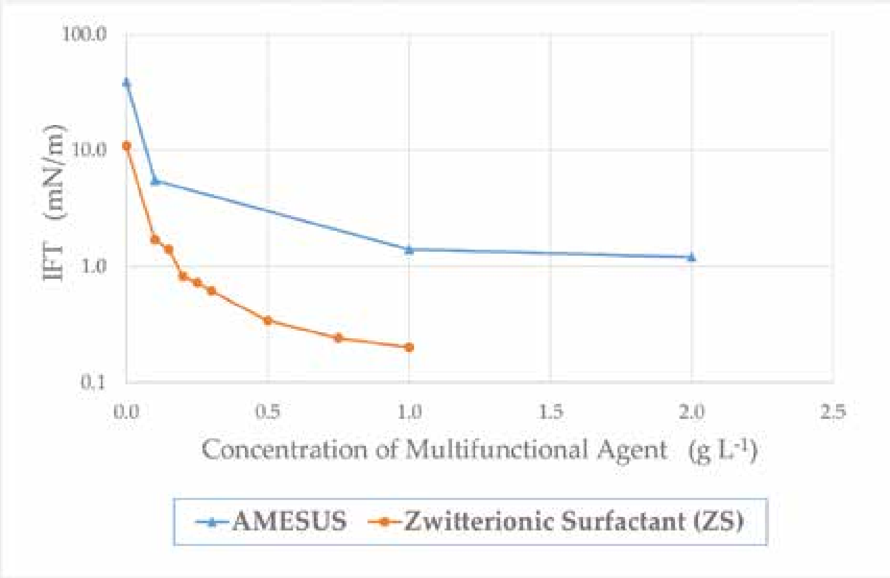


Figure 3. Interfacial tension (mN/m) as a function of surfactant concentration and surfactant type.

As expected, multifunctional agents (surfactants) decrease the interfacial tension as the concentration of surfactant increases until the critical micelle concentration is reached. According to the data presented in **Figure 3**, "ultra-low" IFT values were not obtained for this system with these surfactants. However, it is important to realize that oil recovery is not only influenced by IFT reduction, there are other several factors affecting the mobilization of oil at pore scale such as rock wettability (contact angle), capillary and viscous forces, and fluid properties, among others [4, 8, 12, 13]. Wettability determines the adhering tendency of a fluid toward a solid surface in the presence of other immiscible fluids, and it is a function of the interfacial chemistry of the phases present in the system. Contact angle is the point at which the oil or water interface meet at the solid (i.e., rock) surface; therefore, it indicates the affinity of the solid surface for any of the fluids present in the system. Contact angle determination is commonly used to establish wettability changes of solid surfaces [21]. In this regard, reliable wettability alteration measurement tools are necessary for the accurate evaluation and monitoring of wettability alteration treatments.

Figure 4 shows the effect of multifunctional agents (i.e., surfactant) addition on the contact angle for each system as a function of time. The solid surfaces used were carbonate minerals (dolomite), and the concentration of multifunctional agents was 0.1 g/L in high salinity brine concentrations (3.2 wt.% NaCl). As observed in **Figure 4**, both multifunctional agents changed the contact angle between oil and the solid surface. In the AMESUS system, the contact angle was changed from 0 to 51°, while for the ZS system the contact angle changed from 0 to 30°. These results demonstrate the effectiveness of these additives as wettability modifiers. Therefore, these results show that despite the slow decrease in interfacial tension, these multifunctional agents are efficient in altering the rock wettability.

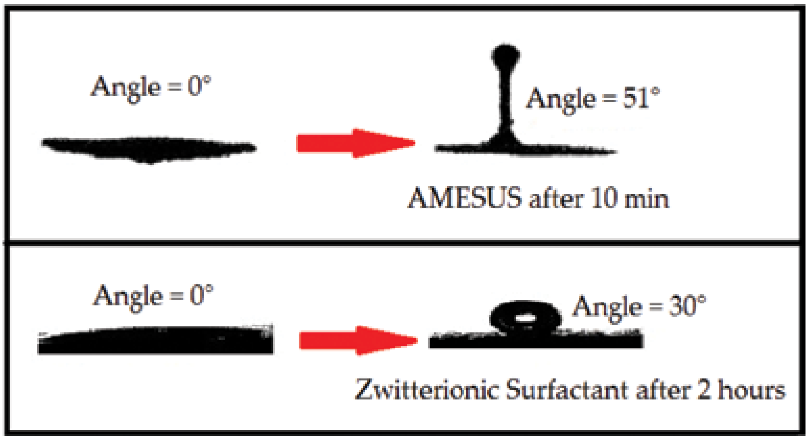


Figure 4. Effect of multifunctional agents on contact angle between oil and the solid surface.

3.2. Asphaltenes aggregation inhibition and dispersion activity

Asphaltenes can be defined according to their solubility as the fraction of oil that is insoluble in low-molecular-weight alkanes, specifically n-pentane and n-heptane, but completely soluble in aromatic hydrocarbons, such as benzene and toluene. Asphaltenes fraction is formed of associated systems of polynuclear aromatics bearing alkyl side chains and organic molecules containing oxygen, nitrogen, sulfur, vanadium, and nickel porphyrins [22]. Asphaltenes are known to aggregate due to the propensity of their fused aromatic ring systems to stack via π-bonding [23].

Oil production operations can induce asphaltenes precipitation because of pressure and temperature decrease and oil-phase compositional changes. The disruption of the initial reservoir conditions could induce undesirable phase separation that negatively impacts every stage of the oil production process. As mentioned earlier, deposition of asphaltenes aggregates onto the rock surface can modify the wettability of the reservoir from water-wet to oil-wet, affecting significantly the oil displacement efficiency during the oil recovery processes. Thus, surfactants agents designed for chemical enhanced oil recovery must effectively interact with the heavy fractions of the crude oil such as asphaltenes and resins. Surfactants must inhibit their aggregation and/or disperse their aggregates to prevent their deposition or accumulation onto the rock surface, which would alter the wettability and the effective permeability of the formation rock affecting oil sweep efficiency.

Multifunctional agents used as asphaltenes aggregation inhibitors have been evaluated through ultraviolet-visible (UV-vis) spectroscopy by determining the concentration of asphaltenes remaining in solution after induced precipitation with n-heptane [8]. This study was carried out taking advantage of the insolubility of the asphaltenes fraction in low-molecular-weight alkanes such as n-heptane. However, under these conditions, the addition of the chemical agents promotes a colloidal stability to the asphaltenes particles in the liquid phase by preventing their aggregation through steric hindering or by modifying the electrostatic forces involved in the system [8].

The asphaltenes used in this experimental study were extracted from a Mexican heavy crude oil sample (18°API) using n-heptane. The solvent (volume) to heavy oil (mass) ratio was 40:1 (cm^3/g of oil). The solution was mixed for 8 h, filtered (1 μm porous size membrane), and dried under vacuum at 60°C. The obtained fraction of asphaltenes was redissolved at a concentration of 10 wt.% in methylene chloride, reprecipitated using n-heptane, and refiltered.

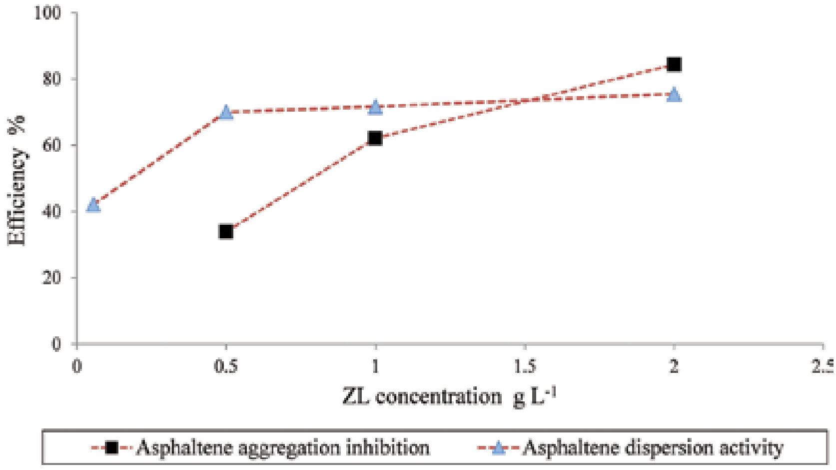


Figure 5. Performance of zwitterionic surfactant on asphaltenes aggregation inhibition and dispersion activity.

Figure 5 shows the effect of the zwitterionic surfactant (ZS) on asphaltenes aggregation inhibition and dispersion activity. The evaluations of the inhibition properties were carried out using solutions (1000 μL) of 5.0 g/L of asphaltenes in toluene mixed with *n*-heptane solutions (9000 μL) at different concentrations (0.5, 1, and 2 g/L) of ZS according to experimental techniques described elsewhere [8]. The dispersion activity experiment was performed using a sample of sediment extracted from a light crude oil (35° API) by centrifugation and with a composition of 59.99 wt.% saturates, 20.82 wt.% aromatics, 17.47 wt.% resins, and 1.45 wt.% asphaltenes [8]. **Figure 5** shows that the efficiency of asphaltenes aggregation inhibition increases as the concentration of ZS increases, while the dispersion activity efficiency increases initially as the concentration of ZS increases but it levels off at a concentration of ZS of 0.5 g/L.

The mechanism by which ZS inhibits asphaltenes aggregation can be elucidated through interactions between asphaltenes and ZS resulting in the formation of ion-dipole pairs that generate disorder in the system by steric effects [8]. This multifunctional agent (ZS) not only inhibits asphaltenes aggregation but also exhibits suitable asphaltenes dispersion performance (**Figure 5**).

3.3. Formation damage

The assessment, control, and remediation of formation damage are among the most important issues to be resolved to ensure the efficient exploitation of hydrocarbon reservoirs. Formation damage is a detrimental operational and costly problem that could arouse during several stages of oil and gas production. Formation damage can occur during drilling, production, hydraulic fracturing, workover operations, and EOR [24].

Organic deposition is one of the main factors that can induce formation damage due to permeability impairment. For instance, asphaltenes deposition is a common cause of formation damage [24, 25]. It has been reported that asphaltenes induced formation damage can be explained by three mechanisms: (1) increase in the reservoir fluid viscosity due to the formation of water-in-oil emulsions and/or due to the increased concentration of asphaltenes particles in the bulk of the oil phase, especially in the near wellbore region as the oil converges radially toward the wellbore; (2) change in the wettability of the reservoir formation from water-wet to oil-wet by the adsorption of asphaltenes onto the rock surface; and (3) reduction in the reservoir formation permeability by plugging of pore throats and/or constrictions by asphaltenes particles [24].

This section summarizes the experimental evaluation of the effectiveness of multifunctional agent AMESUS in removing and inhibiting the deposition of heavy organics components onto the porous media. As heavy crude oil flows through porous media, the interactions between the asphaltenes aggregates contain in the heavy oil and some of the mineral compounds present in the rock surface induce the adsorption of asphaltenes onto the rock surfaces, which results in the gradual decrease in the effective permeability of the rock [7, 25].

This experimental work was performed by conducting coreflooding tests at reservoir conditions: temperature of 150°C, average pore pressure of 2400 psi, and overburden pressure of 3500 psi.

The experimental procedure was carried out as follows: (1) core damage was generated by flowing a sample of crude oil (1 ml/min) with high propensity for asphaltenes precipitation, through the porous medium (at least 50 pore volumes, PV). It was assumed that core impairment was caused by asphaltenes deposition. The degree of core damage was evaluated through the determination of permeability reduction; (2) application of the corresponding chemical treatment either xylene or AMESUS solutions dissolved in brine at a concentration of 2.0 g/L to the damaged core. The volume of treatment applied was five PV injected at a flow rate of 1 ml/min that was followed by a soaking period of 6 h; (3) injection of crude oil through the treated core plug in order to evaluate the effectiveness of the applied chemical treatment in removing the damage previously caused to the core [7]. **Table 1** summarizes the composition and other properties of the crude oil sample, and **Table 2** lists some petrophysical properties of the core plug used (Bedford limestone).

API° gravity		**36.7°**
SARA analysis (wt.%)	Saturates	63.65
	Aromatics	24.11
	Resins	11.68
	Asphaltenes	0.56
Colloidal instability index		1.79
Acidity (mg KOH/g)		0.1

Table 1. Composition and other physical properties of the crude oil.

Mineralogy	**Length (cm)**	**Diameter (cm)**	**Porosity (%)**	**Pore volume (cm^3)**	**K_{absgas} (mD)**
Calcite (~100%)	6.9	3.8	20	14.4	104

Table 2. Some petrophysical properties of the core plug sample.

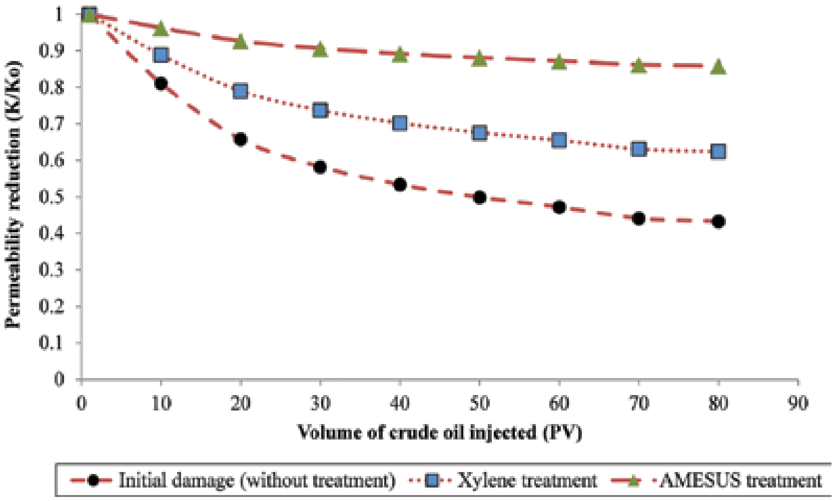


Figure 6. Performance of chemical treatments in removing and inhibiting the deposition of asphaltenes.

Figure 6 plots the experimental results obtained during the application of different remediation treatments. The reference case (black solid circles in **Figure 6**), in which the core plug was flooded with 80 pore volumes (PV) of crude oil without a previous chemical treatment, shows a severe permeability reduction due to the retention and adsorption of asphaltenes and resins within the porous medium sample [7]. The application of the xylene treatment to the damaged core (blue solid square symbols in **Figure 6**) shows that permeability is recovered to some extent, while the application of AMESUS (green solid triangles in **Figure 6**) revealed a significant recovery of the core plug permeability. These results demonstrate the effectiveness of the supramolecular complex (AMESUS) in simultaneously removing the organic deposits and inhibiting the further adsorption of asphaltenes onto the core plug during the second stage of crude oil injection. It seems that the application of AMESUS changes the surface properties of the core by adhesion to the mineral surface forming a film that alters its wettability and thus inhibits the adsorption of asphaltenes and prevents further formation damage [7].

3.4. Effect of the multifunctional agents on crude oil viscosity

Residual oil saturation in heavy crude oil reservoirs has been reported to range from 80 to 95% of the OOIP, after primary and secondary oil recovery [1, 5]. The most practical approach to enhance the recovery of heavy oil is viscosity reduction through thermal EOR.

This section of the chapter describes the effectiveness of the multifunctional agents in reducing the viscosity of heavy oil. An Anton-Paar Physica MCR-301 rheometer equipped with a 50 mm PP50 plate-plate configuration and a gap of 1 mm was used to determine the viscosity of the oil samples. **Figure 7** summarizes the composition, API°, and viscosity behavior of the heavy oil as a function of temperature and shear rate.

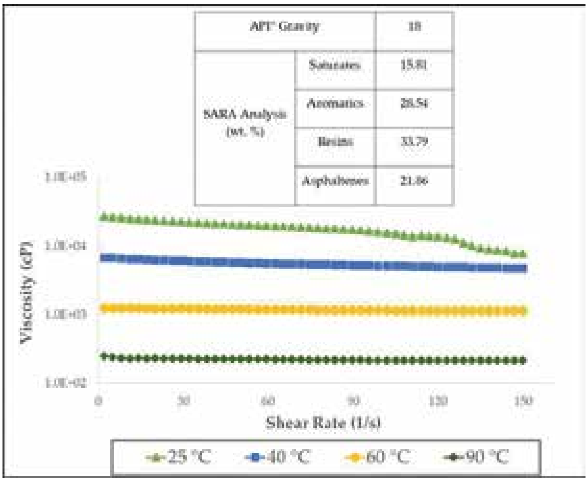


Figure 7. Heavy crude oil: composition and viscosity as a function of temperature and shear rate.

The high viscosity of this heavy oil can be attributed to its high content of resins and asphaltenes (33.79 and 21.86%, respectively). In addition, this heavy oil exhibits a non-Newtonian rheological behavior at 25°C (**Figure 7**), most likely due to the formation of wax-resin aggregates within the bulk of the oil phase at this temperature.

The multifunctional agents—AMESUS and the zwitterionic surfactant—were diluted in a fixed volume of n-heptane (1 ml) at preestablished concentrations to achieve a final concentration of the chemicals in the crude oil sample of 0.5 g/L. For comparative purposes, a reference system was prepared by dosing the heavy oil sample with the equivalent fixed volume of n-heptane that was used for dilution of the chemical agents. **Figure 8** plots the apparent viscosity of the crude oil as a function of shear rate and chemical treatment. The experiments were conducted at 25°C, and the range of shear rate evaluated was 0.1/s to 100.0/s.

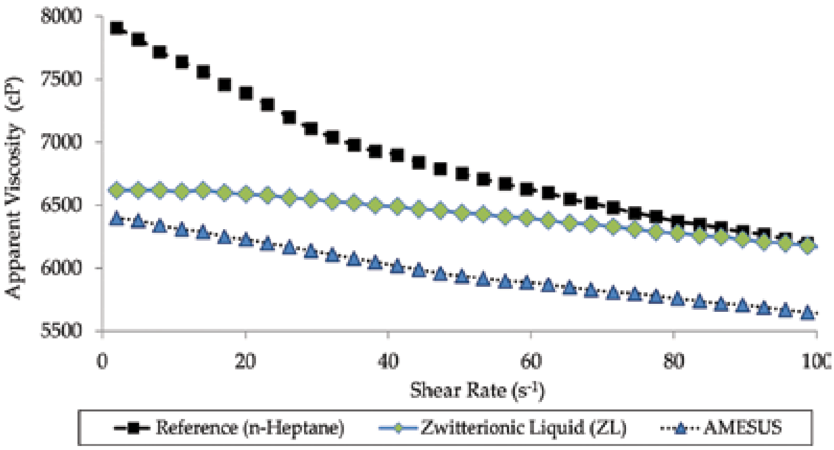


Figure 8. Apparent viscosity as a function of shear rate and chemical treatment.

Figure 8 indicates that the viscosity of the samples (baseline and chemical treated oil) decreases as the shear rate increases following a shear thinning behavior. The chemical-treated oil samples show lower viscosities when compared with the viscosity of the reference sample. Therefore, both multifunctional agents are effective in decreasing the viscosity. Nevertheless, AMESUS offers a better performance in reducing the viscosity of the heavy oil than the ZS agent. Moreover, the performance of the ZS agent is hindered as the shear rate increases.

These experimental observations demonstrate that the multifunctional agents interact with the asphaltenes and resins contained in the heavy oil sample providing a significant viscosity reduction. The AMESUS supramolecular complex exhibits a suitable performance in preventing the aggregation of asphaltenes and resins which allows reducing the viscosity of the heavy crude oil evaluated [7].

3.5. Oil recovery

This section describes the experimental evaluation of the multifunctional agents as chemical additives for enhanced oil recovery (EOR) through coreflooding displacement tests at reservoir conditions. **Figure 9** displays the experimental setup of the coreflooding apparatus [7, 8]. The dead volumes of the flow lines were measured and accounted for in all material balance calculations. The performance of the corresponding chemical EOR applications was estimated in terms of incremental oil recovery [7, 8].

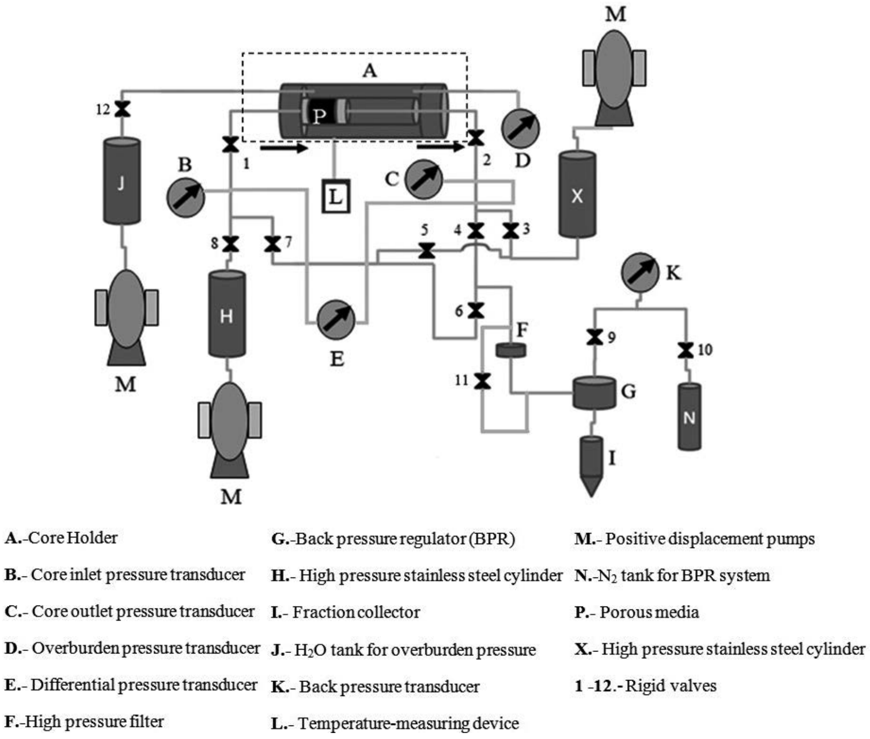


Figure 9. Experimental setup for coreflooding displacement tests.

The protocol used during coreflooding testing was as follows:

1. *Core plug preparation*. First, the core was cleaned using solvents such as toluene/methanol; afterward, the core was dried at 120°C for 24 h. The clean core plug was positioned into a standard core holder (manufactured by Core Laboratories). Flooding conditions were set at: temperature, 90°C; average core pressure, 2400 psi;, and overburden pressure, 3500 psi. A Bedford limestone (BL), core plug was used, which consists of 100 wt.% $CaCO_3$. The dimensions of the core plug were 6.7 cm in length and 3.8 cm in diameter. The absolute permeability of the core plug was 139 mD and the porosity 20%.

2. *Brine injection*. Brine with a concentration of 2.6 wt.% in NaCl was used. In this step, the core plug was saturated with brine at a flow rate of 1 ml/min.

3. *Crude oil injection*. **Table 1** displays the composition and some physical characteristics of the crude oil used in this experimental section. The core plug was flooded with crude oil at a constant flow rate of 1 ml/min. In this stage, the irreducible water saturation (S_{wi}) and initial oil saturation (S_{oi}) were determined.

4. *Waterflooding* (*WF*) *stage*. Waterflooding as a secondary oil recovery (SOR) process was carried out by injecting brine at a constant flow rate of 1 ml/min. The produced fluids were collected using graduated centrifuge flasks. Pressure profile data along the core plug were recorded. The residual oil saturation (S_{or}) was established when the production of crude oil became negligible. Oil recovery (% OOIP) was calculated by material balance as a function of time.

5. *Surfactant flooding* (*SF*) *stage*. This stage was carried out injecting the corresponding multifunctional agent dissolved in brine at a fixed concentration of 1.0 g/L at a flow rate of 1 ml/min [7, 8].

Figure 10 shows the experimental results of oil recovery (OOIP %) as a function of the volume of fluid injected, recovery stage, and type of surfactant treatment (AMESUS or ZS).

An incremental oil recovery of 12.9% was obtained for the AMESUS chemical flooding, whereas an incremental oil recovery of 10.2% was achieved for the ZS chemical flooding. Therefore, the multifunctional agents evaluated are effective in mobilizing and displacing residual oil. This indicates that the proper physicochemical interactions among the chemical solutions, rock, and crude oil were established during surfactant flooding.

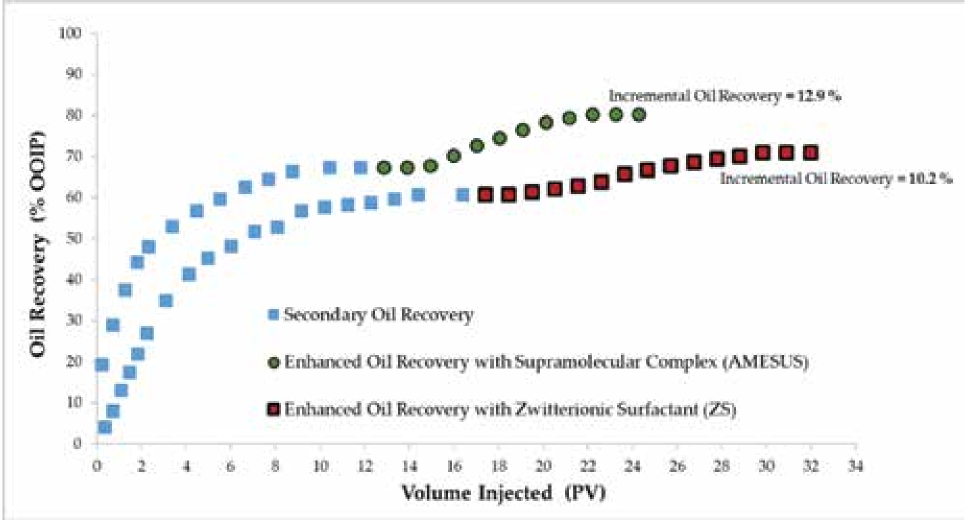


Figure 10. Oil recovery (OOIP %) versus volume of fluid injected (PV), recovery stage, and surfactant type.

Rock permeability, porosity, and the spatial distribution of these parameters within the porous media influence oil recovery [26]. Thus, in order to evaluate the effect of permeability on oil recovery during surfactant flooding, coreflooding displacement tests were conducted using two different core plugs. A formation rock (FR), which consists of 92% calcite and 8% clays (kaolinite and sodium montmorillonite), having an absolute permeability of 9 mD, a porosity of 19%, a length of 8.3 cm, and a diameter of 3.8 cm. The second core plug was a Bedford limestone (BL), containing 100 wt.% $CaCO_3$, an absolute permeability of 139 mD, 20% porosity, a length of 6.7 cm, and a diameter of 3.8 cm. In terms of rock wettability and as shown below in section 3.6 by using oil-water relative permeability curves, the FR rock is more oil-wet than the BL core [8].

API° gravity		31°
SARA analysis (wt.%)	Saturates	41.05
	Aromatics	36.66
	Resins	20.32
	Asphaltenes	1.97
Colloidal instability index		0.75
Acidity (mg KOH/g)		0.13

Table 3. Composition and some physical characteristics of the crude oil.

A sample of crude oil with the properties presented in **Table 3** and brine (2.6 wt.% NaCl) were used in these experimental runs. The displacement tests were conducted following the injection protocol previously described. During the surfactant flooding stage, the ZS chemical was used at a concentration of 1.0 g/L. **Figure 11** summarizes these experimental observations, which indicate that the secondary oil recovery stage is significantly affected by the core permeability and mineralogy: the heterogeneous FR core with lower permeability (K_{absgas} = 9 mD) had the higher residual oil saturation (S_{or} = 56.4%) after waterflooding, whereas a lower residual oil saturation of 39.3% was obtained for the homogeneous BL core sample (K_{absgas} = 139 mD). As expected, the higher the permeability of the rock, the higher the oil recovery. Furthermore, a higher oil recovery by waterflooding was obtained from the more water-wet or BL core, as previously reported [7].

As **Figure 11** shows, after the waterflooding stage, surfactant EOR flooding was carried out. An incremental oil recovery of 10.2% of the OOIP was obtained from the BL core plug, while only an incremental oil recovery of 4.9% was obtained from the FR core plug.

The higher incremental EOR obtained from the BL core sample might be explained by the higher permeability and wettability conditions (more water-wet) of this core as has been previously reported [8]. Nonetheless, the ZS multifunctional agent is effective in rendering incremental EOR from both porous media that otherwise would not be recovered.

Figure 11 also shows the pressure drop profiles as a function of volume injected. Both porous media show similar behavior. At the beginning of waterflooding, the pressure drop rises slightly as oil production increases; however, as soon as brine breakthrough at the production end, pressure drop declines progressively, as well as oil production. During surfactant flooding, the pressure drop rapidly decreases, whereas oil production increases slowly. The pressure drop profiles exhibited in **Figure 11** also show that despite the high salinity characteristics of the brine used (2.6 wt.% NaCl), surfactant precipitation and/or blockage of the core plug was not observed during the flooding processes [8].

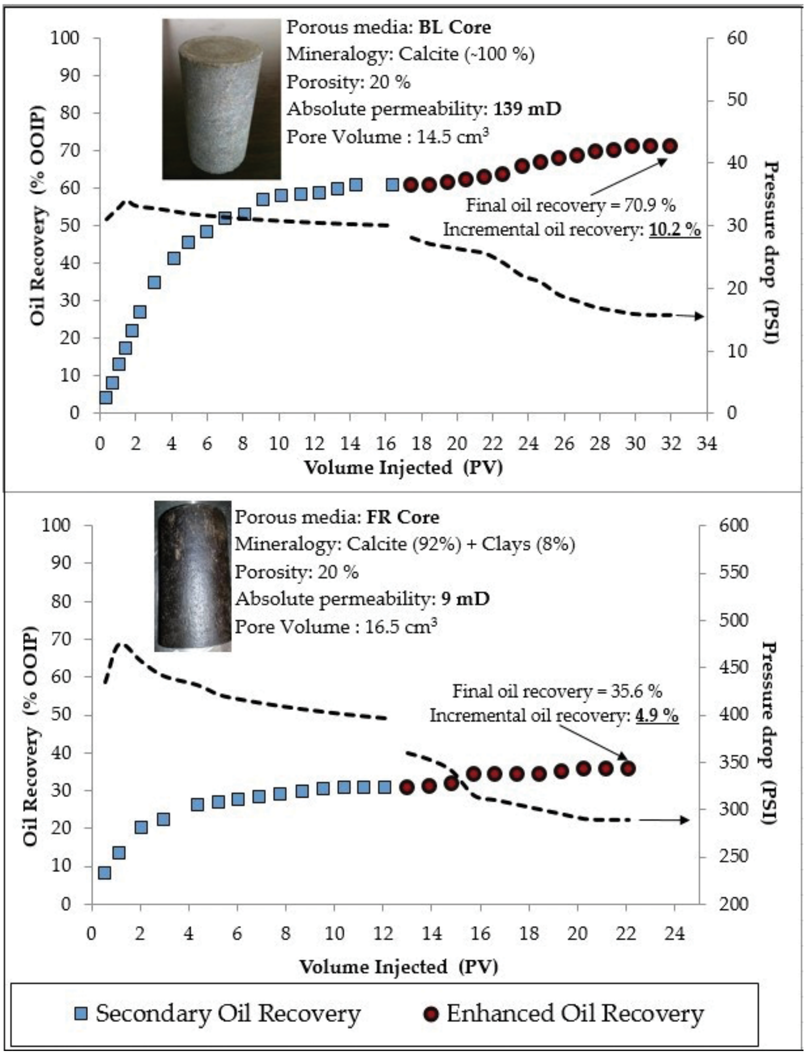


Figure 11. Influence of porous media on oil recovery performance of zwitterionic surfactant (ZS).

The effectiveness of AMESUS during surfactant flooding was also evaluated. In these experiments, the rock sample used was a Bedford limestone (BL) (100 wt.% $CaCO_3$), with absolute permeability of 139 mD, a porosity of 20% porosity, a length of 6.7 cm, and a diameter of 3.8 cm. Samples of crude oil (31° API) and brine (2.6 wt.% NaCl) were used following the injection sequence previously described. Furthermore, in these coreflooding tests, different concentrations of AMESUS (0.5 g/L, 1 g/L, and 2 g/L) were evaluated to establish the effect of surfactant concentration on oil recovery. **Figure 12** presents oil recovery as a function of pore volume of fluid injected and surfactant concentration. These experimental results indicate that as the concentration of AMESUS increases, oil recovery increases.

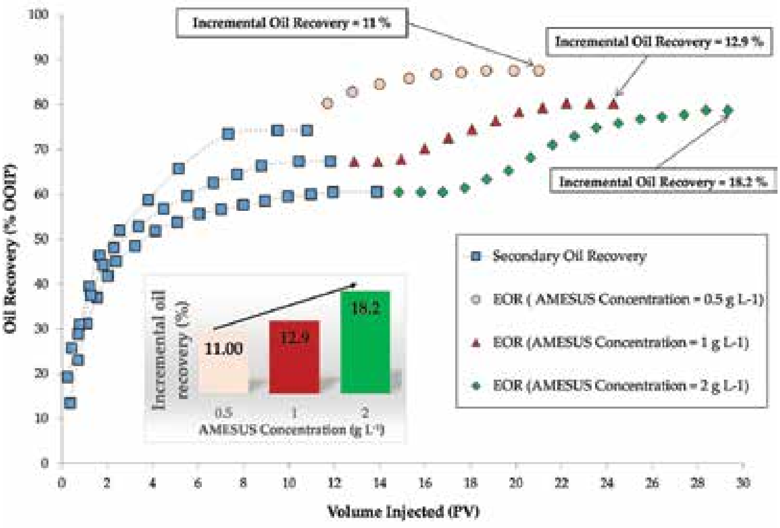


Figure 12. Effect of AMESUS concentration on oil recovery performance.

3.6. Relative permeability

Oil-water relative permeability data offer relevant insights into the simultaneous flow of crude oil and brine that allows predicting the performance of waterflooding processes. Oil-water relative permeability is influenced by several variables such as fluids saturation, fluids saturation history, interfacial tension, fluids viscosity, overburden pressure, temperature, flow rate, wettability, and capillary end effects [27]. In addition, relative permeability curves provide information on the wettability of the porous media, which significantly affect oil recovery processes [7, 8].

In this study, the oil-water relative permeability curves were obtained following the Johnson-Bossler-Neumann (JBN) method and the data were fitted using a Corey-type correlation [7, 8, 28–30].

The effect of the multifunctional agent ZS on the oil-water relative permeability curves was evaluated to establish their efficiency in altering rock wettability.

In this experimental work, the wettability of the core plugs was determined after waterflooding. **Figure 13** presents the oil-water relative permeability curves after waterflooding. The crossover point (equal relative permeabilities) of the oil and water relative permeability curves shown in **Figure 13** indicates that both porous media (BL and FR rocks) are predominantly oil-wet, which is expected for calcite rock formations [31]. However, the FR core plug is more oil-wet (crossover point more shifted toward the left side of the relative permeability curves) than the crossover point of the BL core, which also explains the waterflooding oil recovery behavior presented in **Figure 11**, where a higher secondary oil recovery was obtained from the rock sample showing less oil-wetting tendency (i.e., BL core plug).

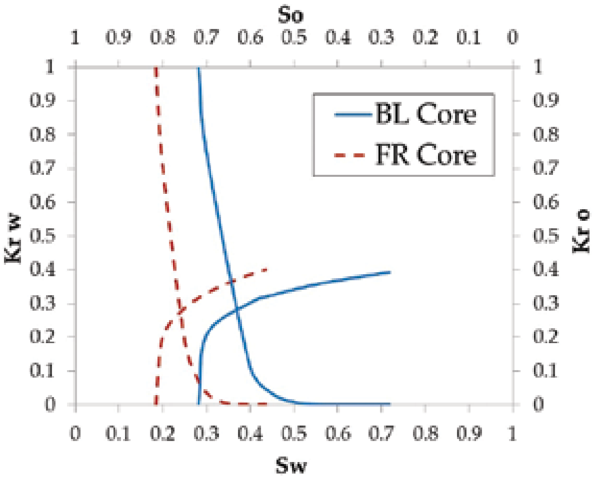


Figure 13. Relative permeability curves after waterflooding.

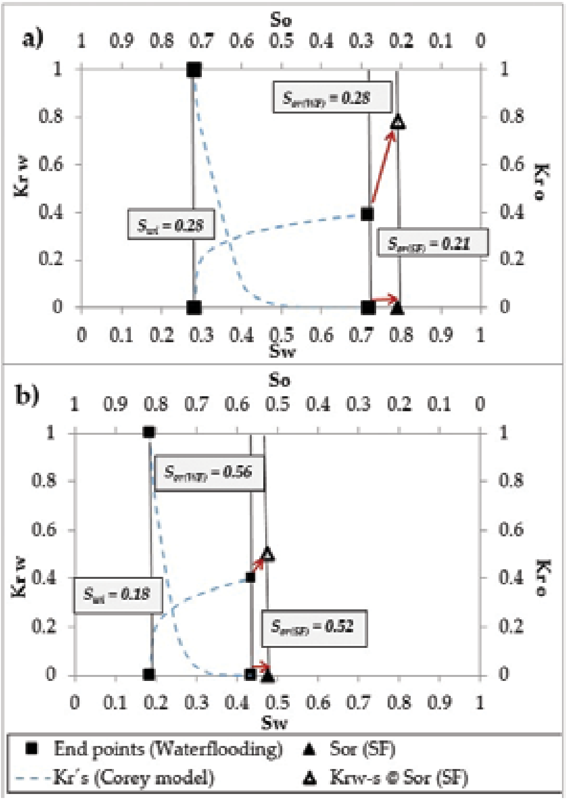


Figure 14. Effect of ZS chemical agent on the relative permeability curves. (a) BL core and (b) FR core.

The effect of rock wettability on oil recovery has been reported in the literature [32, 33]. **Figure 14** displays the effect of surfactant flooding (SF) using the ZS agent on the oil-water relative permeability curves corresponding to the oil-recovery coreflooding results previously discussed (**Figure 11**). **Figure 14** shows the end points of the relative permeability curves of both waterflooding (WF) and surfactant flooding (SF) processes. For the WF process, the initial water saturation (S_{Wi}) and the residual oil saturation (S_{or}) are presented, whereas for the SF process, the final residual oil saturation ($S_{or(SF)}$) and the final relative permeability ($K_{rw\text{-}s}$ at $S_{or(SF)}$) obtained for both the BL and the FR core plugs are presented.

These results demonstrate that the injection of ZS alters the wettability of both core plugs toward more water-wet conditions, which is in agreement with the incremental oil recovery previously presented [8].

4. Mechanisms

Key mechanisms involved in the multifunctional activity of the chemical agents evaluated in this work are proposed and discussed in this section.

In the context of this study, formation damage is caused by the deposition of polar heavy organic fractions present in the crude oil, such as asphaltenes and resins, which could form a hydrophobic layer on the rock surface altering its wettability toward more oil-wet [**Figure 15(a)**]. Remediation of this type of formation damage by chemical treatment using the multifunctional agents AMESUS and ZS takes place due to the strong interactions established between the chemicals and the deposited layer of asphaltenes and resins, as sketched in **Figure 15(a)** and **(b)**. The interactions between the chemical agents and asphaltenes are different for each of the multifunctional agents. For instance, the ZS-asphaltenes interactions are of the ion-dipole pair types [16], whereas the asphaltenes-AMESUS interactions are of the dipole-dipole pair types [7]. As a result, the deposited asphaltenes are desorbed, disaggregated, and dispersed within the crude oil phase by the multifunctional agents, while simultaneously part of the chemical agents is adsorbed onto the rock surface replacing the previously deposited asphaltenes molecules [**Figure 15(d)**]. Moreover, the adsorption of the multifunctional agents onto the mineral surface modifies the wettability of the rock toward more water-wet condition and inhibits the further adsorption of asphaltenes, which prevents formation damage. Furthermore, the interactions of the multifunctional agents with the crude (bulk) oil indicate their effectiveness in inhibiting the formation of asphaltenes aggregates. Therefore, these surfactants are efficient in dispersing these heavy oil fractions within the crude oil reducing its viscosity [7, 8, 16].

It is important to emphasize that the mechanisms proposed here might be dependent on the characteristics of the brine/rock/crude oil system including resins and asphaltenes content, rheological properties of crude oil, brine composition, and the mineralogy of the porous media [7, 8]. Therefore, wettability alteration and reduction in crude oil viscosities are considered the key mechanisms that allow the multifunctional agents to increase oil recovery.

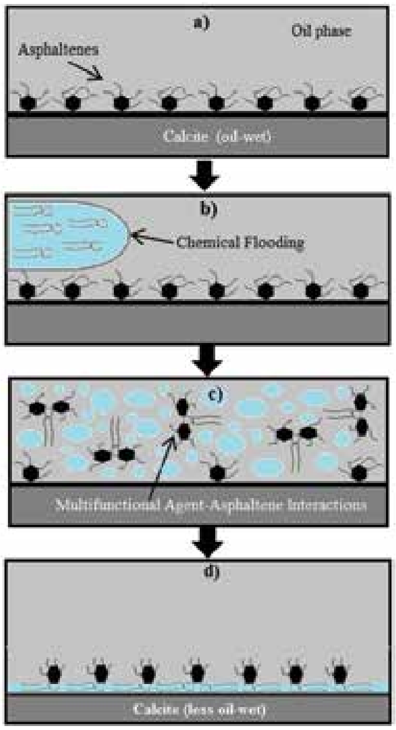


Figure 15. Sketch of the suggested mechanisms: (a) initial conditions, asphaltenes adsorbed onto the rock surface (oil-wet core condition), (b) chemical flooding, (c) multifunctional agent-asphaltene interactions promoting asphaltenes desorption, and (d) wettability alteration to less oil-wet conditions due to the adsorption of the chemical agents onto the rock surface.

5. Conclusions

This chapter summarizes the evaluation of the multifunctional properties of two novel chemical agents applied for enhanced oil recovery (EOR). These chemical agents demonstrate suitable performance during surfactant flooding at reservoir conditions (i.e., temperature and pressure) and high salinity brine concentration. These chemical agents are effective as asphaltenes aggregation inhibitors. Similarly, they are suitable asphaltenes dispersants. Therefore, these agents are applicable for the removal and prevention of asphaltenes deposition and/or adsorption onto the rock surface. Furthermore, these multifunctional agents can significantly decrease the viscosity of heavy oil through the breaking and dispersion of asphaltenes and resin aggregates within the bulk oil phase.

The dominant mechanisms responsible for the multifunctional activity of these chemical agents are the reduction in the viscosity of the heavy oil and the modification of the rock wettability. Finally, the novel multifunctional chemical agents have the potential of providing a feasible technological solution to the complex problems related to the heavy crude oil viscosity reduction and formation damage commonly found in the petroleum industry.

Acknowledgements

The authors express gratitude to the Instituto Mexicano del Petróleo (IMP) for both providing the research facilities and granting permission to publish these results. L.A.A.-V. thanks both the IMP for the postdoctoral fellowship granted to conduct the research presented in this work and the Dirección de Cátedras CONACYT for the financial support provided during the writing of this chapter. This work was supported by the IMP Projects D.00509, H.61003 and Y. 00123 and CONACYT-SENER-HIDROCARBUROS Fund (Project 146735).

Author details

Luis A. Alcázar-Vara[1*], Luis S. Zamudio-Rivera[2] and Eduardo Buenrostro-González[2]

*Address all correspondence to: luis.alcazar.v@gmail.com

1 CONACYT—Mexican Institute of Petroleum (IMP), Mexico, Mexico

2 Mexican Institute of Petroleum (IMP), Mexico, Mexico

References

[1] Moritis G. Special Report: EOR/Heavy Oil Survey. *Oil and Gas Journal*. 2006; 104(17): 37-57.

[2] Alvarado V, Manrique E. Enhanced Oil Recovery: An Update Review. *Energies*. 2010; 3(9): 1529-1575.

[3] Farouq Ali SM, Thomas S. The Promise and Problems of Enhanced Oil Recovery Methods. *Journal of Canadian Petroleum Technology*. 1996; 35(7): 57-63.

[4] Sheng JJ. Modern Chemical Enhanced Oil Recovery – Theory and Practice. Burlington, MA, USA: Gulf Professional Publishing, 2011.

[5] Tang M, Zhang G, Ge J, Jiang P, Liu Q, Pei H, Chen L. Investigation into the Mechanisms of Heavy Oil Recovery by Novel Alkaline Flooding. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2013; 421: 91-100.

[6] Leontaritis KJ, Mansoori GA. Asphaltene Deposition: A Survey of Field Experiences and Research Approaches. *Journal of Petroleum Science and Engineering* .1988; 1(3): 229-239.

[7] Alcazar-Vara LA, Zamudio-Rivera LS, Buenrostro-González E. Multifunctional Evaluation of a New Supramolecular Complex in Enhanced Oil Recovery, Removal/ Control of Organic Damage, and Heavy Crude Oil Viscosity Reduction. *Industrial & Engineering Chemistry Research*. 2015; 54(32): 7766-7776.

[8] Alcazar-Vara LA, Zamudio-Rivera LS, Buenrostro-González E, Hernández-Altamirano R, Mena-Cervantes VY, Ramírez-Pérez JF. Multifunctional Properties of Zwitterionic Liquids. Application in Enhanced Oil Recovery and Asphaltene Aggregation Phenomena. *Industrial & Engineering Chemistry Research*. 2015; 54(11): 2868-2878.

[9] Minssieux L. Removal of Asphalt Deposits by Cosolvent Squeeze: Mechanisms and Screening. *SPE Journal*. 2001; 6(1): 39-46.

[10] Dubey ST, Waxman MH. Asphaltene Adsorption and Desorption From Mineral Surfaces. *SPE Reservoir Engineering*. 1991; 6(3): 389-395.

[11] Martínez-Palou R, de Lourdes-Mosqueira M, Zapata-Rendón B, Mar-Juárez E, Bernal-Huicochea C, de la Cruz Clavel-López J, Aburto J. Transportation of Heavy and Extra-Heavy Crude Oil by Pipeline: A Review. *Journal of Petroleum Science and Engineering*. 2011; 75(3): 274-282.

[12] Hirasaki G, Zhang DL. Surface Chemistry of Oil Recovery from Fractured, Oil-Wet, Carbonate Formations. *SPE Journal*. 2004; 9(2): 151-162.

[13] Austad T, Matre B, Milter J, Saevareid A, Øyno L. Chemical Flooding of Oil Reservoirs 8. Spontaneous Oil Expulsion from Oil- and Water-Wet Low Permeable Chalk Material by Imbibition of Aqueous Surfactant Solutions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 1998; 137(1): 117-129.

[14] Kumar A, Alami E, Holmberg K, Seredyuk V, Menger FM. Branched Zwitterionic Gemini Surfactants Micellization and Interaction with Ionic Surfactants. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2003; 228(1): 197-207.

[15] Hernandez-Altamirano R, Mena-Cervantes VY, Zamudio-Rivera LS, Beltran-Conde HI, Lopez- Ramirez S. Gemini Surfactants, Process of Manufacture and Use as Multifunctional Corrosion Inhibitors, US Patent 8,518,868; 2010.

[16] López-Chávez E, García-Quiroz A, Muñoz-Vega R, Benítez-Puebla JI, Zamudio-Rivera LS, Martínez-Magadán JM, Buenrostro-González E, Hernández-Altamirano R. Density Functional Theoretical Study of the Interaction of Geminal Zwitterionic Liquids with Limestone, Regarding the Behavior of the Wettability Parameter. *Journal of Chemical & Engineering Data*. 2012; 57(12): 3538-3542.

[17] Ramírez-Pérez JF, Hernández-Altamirano R, Mena-Cervantes VY, Zamudio-Rivera LS, Cisneros-Dévora R, Oviedo-Roa R, Cartas-Rosado AR, Ramírez-Estrada A. Branched

geminal zwitterionic liquids, method for obtaining same and use thereof as wettability modifiers having viscosity reducing properties, Mexican patent application MX/E/2014/006223, 2014.

[18] Reinhoudt DN. Supramolecular Materials and Technologies, Perspectives in Supramolecular Chemistry, Vol. 4. New York: John Wiley & Sons, 1999.

[19] Hernandez-Altamirano R, Zamudio-Rivera LS, Mena-Cervantes VY, Luna-Rojero E, Serrano-Saldaña E, Martinez-Magadán JM et al. Foaming Composition with Wettability Modifying and Corrosion Inhibitory Properties for High Temperature and Ultra-High Salinity. Patent Application US 2014/0151041.

[20] Pons-Jiménez M, Cisneros-Dévora R, Gómez-Balderas R, Cartas-Rosado R, Oviedo-Roa R, Beltrán HI, Martínez-Magadán JM. Supramolecular Pairing among Heteroaromatic Compounds and the Cationic Surfactant C 12 TAC. *Fuel*. 2015; 149: 174-183.

[21] Mohammed M, Babadagli T. Wettability Alteration: A Comprehensive Review of Materials/Methods and Testing the Selected Ones on Heavy-Oil Containing Oil-Wet Systems. *Advances in Colloid and Interface Science*. 2015; 220: 54-77.

[22] Speight JG. The Chemistry and Technology of Petroleum, 3rd Ed. New York: Marcel Decker, 1999.

[23] Buenrostro-Gonzalez E, Groenzin H, Lira-Galeana C, Mullins OC. The Overriding Chemical Principles that Define Asphaltenes. *Energy Fuels*. 2001; 15(4): 972-978.

[24] Civan F. Reservoir Formation Damage-Fundamentals, Modeling, Assessment, and Mitigation. Houston: Gulf Publish Company, 2000.

[25] Minssieux L, Nabzar L, Chauveteau G, Longeron D. Permeability Damage due to Asphaltene Deposition: Experimental and Modeling Aspects. *Oil & Gas Science and Technology*.1998; 53(3): 313-327.

[26] Muggeridge A, Cockin A, Webb K, Frampton H, Collins I, Moulds T, Salino P. Recovery Rates, Enhanced Oil Recovery and Technological Limits. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*. 2014; 372: 20120320.

[27] Torabi F, Mosavat N, Zarivnyy O. Predicting Heavy Oil/Water Relative Permeability using Modified Corey-Based Correlations. *Fuel*. 2016; 163: 196-204.

[28] Buckley SE, Leverett M. Mechanism of Fluid Displacement in Sands. *Transactions of the AIME*. 1942; 146(01): 107-116.

[29] Johnson EF, Bossler DP, Bossler VO. Calculation of Relative Permeability from Displacement Experiments. *Transactions of the AIME*. 1959; 216: 370-372.

[30] Corey AT. The Interrelation Between Gas and Oil Relative Permeabilities. *Producers monthly*. 1954; 19(01): 38-41.

[31] Anderson WG. Wettability Literature Survey – Part 5: Effects of Wettability on Relative Permeability. *Journal of Petroleum Technology*. 1987; 39(10): 1283-1300.

[32] Abeysinghe KP, Fjelde I, Lohne A. Acceleration of Oil Production in Mixed-Wet Reservoirs by Alteration of Relative Permeability Curves Using Surfactants. *Society of Petroleum Engineers EOR Conference at Oil and Gas West Asia*, Muscat, Oman, April 16–18, 2012; Paper SPE 155626.

[33] Ayirala SC, Rao DN. Multiphase Flow and Wettability Effects of Surfactants in Porous Media. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2004; 241(1): 313-322.

Chapter 5

Microbial Enhanced Oil Recovery

Aliya Yernazarova, Gulzhan Kayirmanova,
Almagul Baubekova and Azhar Zhubanova

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/64805

Abstract

The ever-rising global demand for energy and the issue of large volumes of unrecovered oil after primary and secondary oil production operations are driving the development and/or advancement of enhanced oil recovery (EOR) techniques. Conventional EOR processes include thermal, immiscible and miscible gas injection, chemical, and microbial enhanced oil recovery (MEOR), among others. This chapter provides an overview of MEOR including its history, strata microflora, mechanisms of MEOR for oil recovery, and a brief recount of field MEOR applications.

Keywords: microbial enhanced oil recovery, MEOR, microorganisms, strata microflora, biosurfactants, oil reservoirs

1. Introduction

The necessity of improving and/or advancing the current enhanced oil recovery (EOR) processes to make them more efficient has attracted the attention of researchers and oil field operators. Thus, over the last few decades, this problem has received constant attention resulting in slow but steady growth of the average oil recovery factors. For instance, at present the worldwide average recovery rate is about 30%, whereas in the USA, the average oil recovery factor is 39%. However, many experts believe that in the foreseeable future the recovery factor may well reach 50–60% and even 70–80% [1].

The development of an oilfield refers to the process of displacing the accumulated liquid and gas hydrocarbons in the reservoir towards production wells. Oil is produced initially using the natural driving energy of the reservoir (i.e., primary recovery operations), or by introducing energy into the reservoir during secondary oil recovery (i.e., waterflooding or gas flooding), as soon as the natural reservoir energy is depleted.

Particularly, in Kazakhstan most of the hydrocarbon deposits have already been discovered and commercially produced. Currently, fewer and fewer drilling sites in those mature reservoirs are of interest from the commercial standpoint. In this regard, the residual oil left behind in these mature hydrocarbon deposits after primary and secondary oil recovery offers an opportunity for the implementation of EOR processes, including the application of microbial enhanced oil recovery (MEOR) technology.

2. Review on MEOR

2.1. History of MEOR

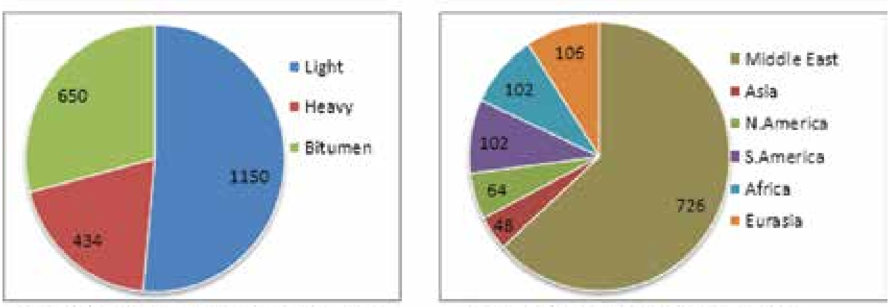
In 1926, J. W. Beckman [2] came to the conclusion that it was necessary to develop additional methods to augment oil recovery beyond primary and secondary oil recovery processes. Therefore, he proposed the utilization of microorganisms as one of the solutions to the oil recovery issue. Later on, the use of microorganisms for oil recovery enhancement was patented by C. E. ZoBell in 1946 [3], since then, the MEOR process has been validated by numerous studies and successful fields tests, the first of them carried out in Arkansas, USA, in 1954 [4].

Since the 1970s, intense research efforts on MEOR have been made in the USA, USSR, Czechoslovakia, Hungary, and Poland. The oil crisis in the 1970s further aroused the interest in MEOR research in more than 15 countries. For instance, in 1976, the Soviet Government enacted a special regulation "…concerning measures on achieving the most efficient oil recovery processes." This regulation defined the target volumes of additional oil recovery that were required using tertiary enhancement methods and provided economic incentives to encourage oil-production enterprises [5].

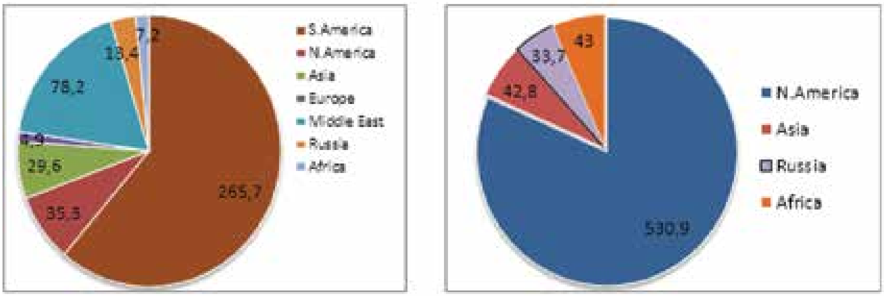
Since year 1970 until the 2000s, microbial ecology and deposit characterization were the focus of MEOR research. By 1990, MEOR reached interdisciplinary technological status. In 2007, a review of 322 MEOR projects in USA showed that 78% of the total number of projects were successful in enhancing oil recovery; while no cases of lowered oil recovery were revealed [6]. At present, there is a grown interest in the application of MEOR to enhance oil production from depleted reservoirs, because its low capital cost and environmental friendliness.

MEOR mechanisms are the same mechanisms obtained from other chemical enhanced oil recovery (EOR) methods; however, MEOR presents the advantage that microbial metabolites are directly produced in the reservoir rock formation, which makes them more effective. Furthermore, microorganisms metabolize different hydrocarbons at different rates [6].

Figure 1 presents a breakdown of the worldwide recoverable petroleum reserves by type and region prepared by Meyer and Attanasi [7] and Schmitt [8].



Recoverable petroleum reserves by type **Conventional reserves by region**



Heavy oil reserves by region **Bitumen reserves by region**

Figure 1. World's current recoverable petroleum reserves by oil type and region in billions of barrels. From Meyer and Attanasi [7] and Schmitt [8].

Worldwide accumulations of heavy oil and bitumen are about five times higher than the reserves of light conventional oils. For instance, heavy oil resources are an essential part of the oil industry in Kazakhstan as well as in a number of other oil-producing countries.

The largest reserves of bitumen and heavy oil are located in Canada and Venezuela; while significant reserves are also found in Mexico, the United States, Russia, Kuwait, and China [9].

Kazakhstan is currently experiencing a period of late-stage development. Oil fields under waterflooding have reached a high water cut ranging from 80 to 90%, while a large volume of undeveloped oil reserves (up to 60–-70%) are located in deep oil reservoir formations. In addition, most deposits of Kazakhstan are characterized by high viscosity oils and complex geological structures [10].

2.2. MEOR: Challenges and Opportunities

Primary and secondary oil recovery processes achieve on a worldwide basis an average recovery of 33% of the original oil in place (OOIP); while the unrecovered oil (67%) might be retained in the reservoir by viscous and/or capillary forces. Conventional chemicals, such as solvents and surface-active compounds (surfactants) are used during chemical EOR applications. Solvents reduce the oil viscosity to improve the oil mobility by overcoming viscous forces; while surfactants reduce the interfacial tension between oil and rock or oil and water overcoming capillary forces. These chemicals are added to the injection water and transported within the reservoir during water flooding, however, the chemicals reach only the places where oil has already been displaced by water; furthermore, the chemicals could be partially consumed and/or retained within the rock formation before they reach the target area in the reservoir for their intended use [6].

The injection of solvents and surfactants into some reservoirs have yield unsatisfactory results because the chemicals failed to contact the residual oil for the required time period, which is needed to achieve a long-term effect. Another problem is the natural heterogeneity of the reservoirs; therefore, the injected chemicals inevitably flow along the paths of least resistance (i.e., high permeability zones, natural fractures, etc.) where the saturation of residual oil is usually the lowest.

It has been known for decades that specifically selected microorganisms are capable of metabolizing hydrocarbons producing organic solvents, such as alcohols, aldehydes, surface-active fatty acids, and other metabolites which can interact with the crude oil improving its fluidity. Other oil production issues such as the presence of paraffin, emulsions, and corrosion problems can also be controlled using microorganisms. For instance, extensive research has been conducted on the use of biosurfactants (BS) for enhanced oil recovery applications [11–14].

Prior to the application of MEOR technologies, the projects are assessed to determine the compatibility of the crude oil and reservoir properties with MEOR taking into account the physicochemical properties of the crude oil, reservoir production performance, and reservoir properties (i.e., temperature). At the preliminary stage, reservoir fluid samples are collected and tested for compatibility with the MEOR systems. The first stage is the identification of the indigenous hydrocarbon-consuming bacteria, which is already adapted to the in situ reservoir conditions; after which the best action strategy for each project is designed and developed [4, 6].

MEOR can be applied on individual wells as follows: (1) from the well being treated or (2) from the target well and adjacent wells of the same reservoir. The MEOR solution is injected into adjacent wells in the same way as water is injected into the reservoir. The volume of the MEOR biomaterial to be injected is calculated based on the pore volume of the target reservoir. The solution is mixed and pumped through the injection well followed by the injection of water to drive the biological solution into the oil saturated zones. Then, the treated well is shut in for the required period of time (normally 24 h to 7 days) after which oil production is resumed. This procedure is repeated every 3–6 months to enable microorganisms to move deeper into the deposit to oil saturated zones [6].

Some of the general advantages of MEOR are outlined as follows:

- Increase of the productivity of the oil fields [9];
- Increase in the total oil produced and more efficient operation of wells and oil fields;

- Increase of the viscosity of the formation water due to the upsurge of biomass concentration and the microorganisms' metabolic products, such as soluble biopolymers, which reduces the mobility of the formation water within the formation rock [9];
- The MEOR set up is less expensive, because the injected bacteria and nutrients are inexpensive [15, 16];
- Low energy input requirement for microbes to produce MEOR agents [16];
- Reduced of the operations downtime [9];
- MEOR is environmentally friendly, because microbial products are biodegradable [15, 16].

In terms of the quality of the oil produced, some benefits are [9]:

- An increase of light alkanes <C20;
- Reduction of the average content of C20–C40 alkanes;
- Biodegradation of high molecular heavy hydrocarbon components;
- Splitting of aromatic ring structures;
- Splitting of phenolic ring chemical structures;
- Transformation of sulfur-containing organic compounds;
- Emulsification of crude oil that can be easily mobilized to the production well.

MEOR methods can be divided into two main groups:

1. *Ex-situ* production of the MEOR metabolites such as biosurfactants, biopolymers, and emulsifiers using exogenous or indigenous bacteria. In this case, microorganisms are grown using industrial fermenters or mobile plants and then injected into the oil formation as aqueous solutions.
2. *In-situ* production of the MEOR metabolites. In this case, the formation of metabolites is the result of the microbiological activity that takes place directly in the reservoir. The MEOR metabolites are produced by indigenous bacteria or by exogenous bacteria that are injected into the reservoir.

In-situ MEOR can be divided into two categories depending upon the method of injection of microorganisms and nutritional media (e.g., molasses, whey, and other waste food or chemical products) into the reservoir [17]. The first category consists in the *in-situ* stimulation of the natural indigenous microflora of the reservoir by means of injecting nutrients into the reservoir. The alternative (second category) is the injection of microbial cultures (exogenous or indigenous) along with nutrients; which is the preferred mode of application in the field. In any case, the development of these methods is impossible without the knowledge of the physicochemical and microbiological conditions in the oil bed. Oil recovery by water flooding is characterized at later stages by the formation of a mature biocenosis. The growth of this integrated microorganism community depends on the availability of nutrients.

The *in-situ* production of metabolites is carried out in two stages. First, water and oxygen are pumped into the formation as a water-air mixture containing mineral salts, nitrogen, and phosphorous to activate the indigenous microflora. In the presence of water and air, aerobic bacteria oxidize hydrocarbons producing low molecular weight organic acids (acetic, propionic, butyric, etc.), alcohols (methanol and ethanol), biosurfactants, and carbon dioxide, which increase the pressure in the reservoir [18–20].

In the second step, oxygen-free water is injected into the reservoir to activate anaerobic indigenous bacteria that metabolize crude oil to acids, and gas (i.e., methane, carbon dioxide). The accumulation of these biogases increases the reservoir pressure. If the pressure in the reservoir is high enough, methane could be dissolved into the liquid hydrocarbon phase reducing its viscosity. Similarly, carbon dioxide could also reduce the oil viscosity if the pressure in the formation allows the miscibility of CO_2 into the bulk oil phase. A reduction of the oil viscosity improves the oil-displacing properties through the reservoir increasing oil production [14]. Furthermore, CO_2 could react with the minerals in the rock and dissolve carbonate increasing the permeability of the formation rock.

In the oil industry, MEOR has been applied for several uses besides enhanced oil recovery, such as well stimulation; remediation of oil spills in soil and ground water; and to clean borehole, down hole equipment, and piping, among others.

2.3. MEOR process components

The MEOR process consists of two essential components: hydrocarbon-consuming microorganisms and a nutritional medium as the source of nitrogen and phosphorus. Hydrocarbon-consuming microorganisms can be exogenous or indigenous. Indigenous are isolated for characterization from the hydrocarbon deposit where they will be employed.

The use of industrial byproducts as nutritional media such as molasses [21–24], corn steep liquor [25], and cheese whey [24] has been documented. The injection of nitrate aqueous solution at a concentration of 1.5 g/l of injected water has been recommended to suppress the activity of sulfate-reducing bacteria [22]. Reduction of the cost of nutrients during the application of MEOR processes can be achieved by injecting only nitrogen and phosphorous sources. Nitrogen is an essential nutrient for bacterial growth. Likewise, phosphorous is another key nutrient. If phosphorous nutrients are lacking, microbial cells cannot synthesize enough ATP for their metabolic activity [26].

2.4. Reservoir microflora

Microbial communities in oil rock formations are dated as the Earth's most ancient biocenoses, which sank to great depths along with organic residues and biogenic sludge.

Numerous varieties of microorganisms have been isolated and detected from different oil reservoirs such as sulfate and sulfur reducers hydrogenotrophic and heterotrophic methanogens [27–30], fermentative bacteria [31, 32], hydrocarbon and oil-oxidizing bacteria [19, 33], iron and manganese reducing microbes [34].

The presence of indigenous microflora and exogenous microorganisms in water and oil-bearing deposits has been demonstrated [3]. Exogenous microorganisms have been introduced into the reservoirs during drilling and flooding (i.e., secondary and tertiary oil recovery) operations. In the absence of molecular oxygen (i.e., absence of a terminal electron acceptor), microbial hydrocarbon decomposition is possible through anaerobic respiration using nitrate, iron oxide, carbon dioxide, or sulfate. Interspecific electron transfer is also possible with methanogenic or sulfate reducing bacteria as biological acceptors. In oil strata with temperatures between 20 and 80°C, there are complex microbial communities made up by fermentative bacteria and methanogens that can oxidize hydrocarbons and reduce sulfur, sulfate, and iron. The microbial count in high temperature oil reservoirs is low.

The studies of microbial communities conducted on samples of formation water from the Zhetybay and Kulsary oil fields located in Western Kazakhstan gave total aerobic counts of 1.8 10^6 and 25.1 10^6 cells/ml, respectively. The number of aerobic microorganisms present in the water samples from the Zhetybay field is lower than the bacterial count from the Kulsary field by an order of magnitude. While the count of anaerobes is 0.38 10^5 cells/ml for the Zhetybay field sample and 0.5 10^2 cells/ml for the Kulsary field. These observations correlate well with the respective depth of each reservoir; the water samples from the Kulsary field were collected at a depth of 250 m; while the water samples of the Zhetybay field were collected at a depth of 1900 m, therefore it is expected that at deeper reservoirs conditions (i.e., Zhetybay field) anaerobic microorganism would adjust better. It has been reported that in deep water and oil-bearing strata the total bacterial count is as high as 10 million cells/ml [35].

The effect of microorganisms is significant if they are numerous and physiologically active. An arbitrary threshold for bacteria is estimated at 1 million/1 g substrate since it is only in such quantities that they can have significant ecological impact. For each ecological factor (temperature, amount of nutrients, concentration of microcells, and trace elements), there are optimum values which favor the growth of an organism and the extreme values at which growth is suppressed. At values close to the extremes of the preferred range for a given organism, its survival is still possible though its growth is limited because the organism is under physical stress conditions. Microbiological studies on bacteria obtained from the Zhetybay and Kulsary hydrocarbon deposits show that aerobes play an important ecological role since they are found in large numbers and in physiologically active states [35].

Exogenous bacteria such as allochthonic bacteria are present in oil reservoirs, which were introduced during water injection creating a mixture of exogenous and indigenous microflora. At reservoir depths of 1–3 km, thermophilic microbial communities are found. These microbial communities are made up of microorganisms commonly found in deep reservoirs and bacteria normally encountered in shallow areas of the reservoirs (i.e., <1 km) but in lower numbers.

For instance, the Zhetybay and Kulsary oil reservoirs contain several groups of microorganisms including spore-forming bacteria, *Micromyce*tes, *Pseudomo*nas, *Bacil*lus, *Enterobacteriac*eae, with the most prevalent being the spore-forming bacteria whose counts reach 0.12 10^5 cells/ml [35].

Total bacterial counts and the abundance of certain groups of aerobic and anaerobic bacteria are remarkably lower in oil reservoirs than the count of bacteria determined in the water used during waterflooding. The reason is that not all microorganisms survive extreme reservoir oil conditions. Some bacteria may be immobilized on the surface of the rocks lowering the number of bacteria in the liquid phase. Viable cells of methanogenic microorganisms have been found in reservoir fluids (i.e., formation brine) with salinity as high as 200 g/l, however, these and other microorganisms were also present in large numbers in substantially desalinated fluids [35].

Microbial community in oil reservoirs can be considered as closed and semiclosed systems, because they exist in an environment hindered from water exchange, which is characterized by a slow mass transfer at constant temperature in the absence of atmospheric air and sunlight. In this ecosystem, oil is the main source of energy for the microbial community. Molecular nitrogen and ammonium nitrogen are sufficient to meet the needs of the microflora. The phosphorus content is small, which limits the biogenic processes in this ecosystem. Therefore, microbiological processes proceed slowly due to low water exchange and lack of nutrients. The development of oil reservoirs by water injection introduces dissolved oxygen into the system that activates microbiological processes and as result oil biodegrades [36].

Aerobic microorganisms have been found in formations with temperatures ranging from 20 to 70°C and pH ranging from 6.0 to 8.4. Some of these aerobic bacteria have been identified as *Rhodococcus ruber, Arthrobacter oxydans, Kocuria rosea, Gordonia rubropertincta, Cellulomonas cellulans, Bacillus subtilis, B. cereus, Pseudomonas fluorescens* [14, 22, 37–40]. Thermophilic microorganisms can grow at oil reservoir temperatures ranging from 40 to 70°C, at pH ranging from 6.0 to 7.8, and salinity concentrations from 0 to 5% NaCl. In high temperature oil reservoirs, hydrocarbon-oxidizing bacteria are a common component of the biocenoses in the bottom-hole areas of the water injection wells through which dissolved oxygen enters the stratum. Hydrocarbon-oxidizing bacteria found in these locations are often spore-forming, which allows survival in extreme environmental conditions [35].

Wang et al. isolated three thermophilic hydrocarbon-degrading species, such as *Bacillus* sp., *Geobacillus* sp., and *Petrobacter* sp. that could tolerate 55°C of temperature [41].

Thermophilic bacteria were isolated from a reservoir, located at Maracaibo Lake, Venezuela, which has temperatures ranging from 60 to 80°C and pressures ranging from 1200 to 1500 psi [42]. Moderately, thermophilic spore-forming sulfate-reducing bacteria (*Desulfotomaculum* and *Bacillus*) have been identified in the Zhetybay high temperature oil field in Kazakhstan [35].

The anaerobic microflora present in oil reservoirs are commonly bacteria of the genera *Bacteroides, Clostridium, Thermoanaerobacter, Thermococcus, Thermotogales* [43], *Petrotoga* [44], *Thermotoga* [45], *Desulfotomaculum* [46], *Caminicella* [47], *Geosporobacter* [48]. Screening for microbial consortia from some Omani oil wells by Al-Bahry et al. [49] showed a total of 30 genera and 69 species of microorganisms. In this study, most of the detected genera were found to be anaerobic, thermophilic, and halophilic and some of them were documented to be suitable candidates for MEOR.

2.5. MEOR oil recovery mechanisms

During the MEOR process, the components are mixed at surface facilities and injected into the oil reservoir. Inside the reservoir, MEOR-bacteria are transported by the injected water and accumulate in porous zones at the oil/rock and oil/water interfaces. Bacteria utilize very small amounts of oil and produce metabolites such as solvents, surfactants, acids, and carbon dioxide. These bioproducts interact with the oil in the reservoir to reduce the oil viscosity, interface tension at the oil/rock and oil/water interfaces, improve rock permeability by removing paraffin, mud, and other debris that plug the porous media [15, 50]. Microbial cells are continuously generated as well as the *in-situ* production of metabolites. The prolong interaction of metabolites with the oil in the reservoir, changes the oil properties in such a way that immobile unrecoverable oil is converted into movable oil that can flow to the production wells increasing oil output accordingly.

Microbial degradation of oil, which is a complex chemical compound, is the result of cometabolism of microorganisms where the metabolism's products of the hydrocarbon-oxidizing bacteria serve as the substrate for other physiological groups in the reservoir. Hydrocarbons are decomposed to produce fatty acids that can be utilized by other microorganisms [51].

The main mechanisms acting on oil recovery by MEOR are summarized as follows:

a. Formation of bioacids that could dissolve some of the minerals (i.e., clays, carbonates, etc.) contained in the formation rocks. Rock dissolution increases the porosity and permeability of the reservoir [52–54];

b. Production of solvents and biogases, leading to lower oil viscosity that facilitates oil displacement through the porous media [55–58];

c. Formation of biosurfactants, biopolymers and other compounds, that could interact with the crude oil by emulsifying the oil, reducing its viscosity, and reducing the interfacial tension at the oil-water interface [59–63];

d. Production of microbial biomass that could change the wettability of the oil rock [55, 64].

One of the most important functionalities of oil-oxidizing microorganisms is their capability of using hydrocarbons to produce biosurfactants, which emulsify hydrocarbons. The hydrocarbon-oxidizing microorganism's strains that are very active in producing biosurfactants are: *Pseudomonas aeruginosa, Bacillus subtilis, Mycobacterium rhodochrous, Rhodococcus erythropolis, Candida lipolytica*, and *Torulopsis gropengiesseri*. Microorganisms belonging to different genera have the ability to metabolize hydrocarbons including more than 300 fungal, bacterial, yeast, and actinomycetes strains. The hydrocarbon-oxidizing ability is quite common in bacteria belonging to the genera *Mycobacterium, Rhodococcus, Pseudomonas, Micrococcus*, and *Bacillus*. In fungi and yeast-like organisms, this faculty is often found in nonsporogenic *Candida, Trichosporon*, and *Exophialia*. The vast majority of *Rhodotorula* species is also capable of oxidizing hydrocarbons [65–69].

The implementation of MEOR requires low capital investment; while it offers high efficiency, and environmental friendliness. The initial phase of the MEOR process is the partial oxidation of residual oil in the bottom-hole area that yields bioproducts such as carbon dioxide, low-molecular-weight fatty acids, and other organic compounds. Further, when these bioproducts are transported by the injected water into the anaerobic zones of the reservoir, methanogenic microorganisms are activated. Production of methane is important because this is an easily extractible gas that can be dissolved into the oil phase (i.e., if the reservoir pressure is high enough) improving the oil mobility [70].

During waterflooding, dissolved oxygen in the water is delivered to the strata. This oxygen is rapidly consumed at the bottom-hole area during the microbial oxidation of residual oil, which causes the stimulation of anaerobic bacteria, particularly, methanogens, in the oxygen-free zone of the stratum [70]. The number of aerobic hydrocarbon-oxidizing and oligocarbophilic bacteria grows to a less extent, however, at the same time the content of anaerobic metabolism products in oil formation waters increases significantly. During this process, carbonate and sulfate content increases.

Foam-forming organic substances that reduce the interfacial tension at the oil/water interface by a factor of 100 have been identified to be caused by microbiological oil oxidation products in the bottom-hole area [71].

Oil recovery by waterflooding can be viewed as a natural fermenter, where continuous microbial cultures could be maintained. These microbial cultures could be activated by the injection of microorganisms and nutritional medium components. In this case, residual oil serves as the main substrate for microorganisms; while in the bottom-hole area, a specific microbial community is formed whose activity can be regulated [71].

The temperature of the oil reservoirs determines the types of microbial communities. In the bottom-hole areas of the injection wells, the temperature corresponds to the temperature of the injected water. In high temperature reservoirs, as is the case of the Zhetybay oil field, cold water is injected, therefore mesophilic bacteria prevail at these conditions compared to the thermophilic communities of the Uzen oil field in Kazakhstan, where hot water is injected [71].

The implementation of MEOR starts with the addition of biological materials to the injection water. Microorganisms enter the reservoir mixed with the injected water through the existing flooding system without affecting the injection rate or pressure. The implementation of MEOR process requires very small modifications, if any, to the existing water injection equipment, so that the flooding process is not interrupted [6].

After the implementation of the MEOR project, it is continuously monitored through bacteria population growth and the oil output rate within certain period of time. The hydrocarbon-oxidizing bacteria population is kept under continuous surveillance after the injection of MEOR fluids. The population size is compared to that of the indigenous hydrocarbon-oxidizing bacteria before the beginning of the process. Normally, such population starts to grow slowly. In addition, the fluids produced are also monitored for the presence of hydrocarbon-oxidizing bacteria in order to assess how far the microorganisms have moved into the reservoir after injection [6].

2.6. Field tests applications of MEOR

There is extensive MEOR published literature on laboratory research data and pilot field trials. Although at present widespread commercial use of the MEOR technology has not taken place yet.

Biotechnological methods for increasing oil recovery have to solve a number of practical problems [72], which are summarized as follows:

a. The preparation of suitable microorganisms and microbial associations highly active at the specific conditions of the reservoir, including the composition and properties of the crude oil. Most of the microorganisms that adapt to the conditions of the field could have little effect on the composition and properties of the crude oils. Industrial applications require new strains of microorganisms with the following qualities: tolerant to high temperatures and salinities concentration, as well as capable of synthesizing surfactants and polysaccharides.

b. The establishment of techniques to create appropriate reservoir conditions to favor the growth and activity of specific microorganisms. This requires further exploration of ways to introduce additional nutrients, primarily nitrogen and phosphorus compounds.

c. The development of cost-effective methods for sulfate reduction. Reservoir conditions are ecological niches for sulfate-reducing bacteria. It is necessary to control the generation of hydrogen sulfide because it creates the problem of a toxic aggressive environment, corrosion, higher sulfur content in the crude oil, toxic products, and other undesirable consequences.

Maudgalya et al. [73] reviewed 407 MEOR field trials worldwide. The field trials were classified according to the following parameters: reservoirs' lithology and properties, microorganisms, nutrients, type of test, and type of recovery mechanism. From the total 407 field trials, 333 field trials were applied following the well stimulation method, 26 of the trials were conducted using the waterflooding and 44 field trials were conducted as single well (huff-puff scheme) applications; while details of the application method for the remaining four field trials were not provided. This survey indicated that the primary mechanisms for MEOR were permeability profile modification, increase of capillary number (i.e., biosurfactants, alcohols, biopolymers, and acids), biodegradation of heavy crude oil components making the oil less viscous, and the swelling of the oil due to the absorption of biogas (i.e., CO_2 and CH_4) within the bulk oil phase.

Careful review of the common characteristics and results observed from these 407 MEOR field trials indicate that successful field trials were obtained at the following conditions:

- Minimum reservoir permeability of 75 md to ensure propagation of bacteria and nutrients deep into the reservoir;
- Reservoir temperature <200°F;
- Brine salinity <100,000 ppm;

- Bacteria species commonly used: anaerobic bacteria (i.e., *Clostridia*). The bacterium *Clostridium* showed to be effective in both sandstone and carbonate reservoirs. *Bacillus* (i.e., aerobic) species were also used or combination of them. The use of indigenous bacteria is strongly recommended because they only need the supply of nutrients and have a greater chance of growing at reservoir conditions, making the process less costly;
- Nutrient: the most common organic nutrient used was molasses; while phosphorus and nitrogen fertilizers were the most common inorganic nutrients;
- Oil saturation: ranging between 45 and 70%;
- Candidate fields most suitable for MEOR are waterflooded fields with relatively high oil saturations [73].

The Activated Environment for Recovery Optimization (AERO) technology has been developed for improving waterflood performance. The AERO system is a microbial process designed to increase oil recovery during waterflooding by the following mechanisms: improved sweep efficiency due to microdiversion of fluid pathways at the pore level, interfacial tension reduction, and residual oil mobilization (i.e., biosurfactants). This technology has been successfully implemented by Statoil offshore Norway and in the Stirrup field in southwest Kansas, USA. Highlights of this technology are minimum to none capital investment with very low risk for implementation and high performance efficiency at low operational costs [74].

Research conducted to establish the potential for MEOR application at the heavy oil Schrader Bluff formation on the North Slope of Alaska indicated that the viable mechanisms for driving incremental heavy oil recovery are:

- Wettability alteration;
- Permeability modification causing improvement of reservoir conformance;
- Some reduction of the interfacial tension between oil and water.

This study also demonstrated that the most important criteria for selecting a reservoir for MEOR applications are the reservoir temperature and formation brine salinity, which must favor bacterial growth. Furthermore, an effective MEOR application depends on the optimal use of the appropriate microbes and nutrients and their proper application in the reservoir [75].

DuPont possesses a solid expertise in MEOR and considers it a low-risk and low-cost technology to produce incremental oil from mature fields. DuPont has established a set of reservoir criteria for its successful application as follows:

- Reservoir temperatures <160°F;
- Moderate salinity levels up to 100,000 ppm;
- Reservoir permeability above 30 md to ensure the propagation of the microbes and nutrients deep into the reservoir;
- The reservoir must be under a waterflooding recovery.

http://dx.doi.org/10.5772/64805

According to DuPont's experience, the main mechanisms for oil recovery are permeability modification due to the formation of a biofilm on the rock surface and wettability modification. Successful field trials conducted by DuPont indicate that oil recovery from mature fields can be increased up to 25% with a cost of $10 per incremental barrel of oil. Furthermore, DuPont considers the MEOR technique to be more cost effective compared to other EOR processes, such as CO_2 flooding or polymer flood [76].

A biopolymer, Schizophyllan, has been developed by Wintershall. The unique properties of this biopolymer are tolerance to high salinity (up to 19 wt%), tolerance to temperatures as high as 275°F, mechanical stability, and high viscosity. Therefore, the Schizophyllan biopolymer would make possible the application of polymer flooding in harsh reservoir environments. The main downside of this biopolymer is its susceptibility to bacterial degradation; however, this has been prevented by the addition of biocides. A pilot test has indicated that the performance of polymer flooding using this biopolymer has rendered oil recoveries ranging from 20 to 25 % higher than the oil recoveries expected from conventional waterflooding [77].

Successful MEOR application in a mature waterflooded reservoir in Saskatchewan, Canada has been reported [78]. This MEOR application consisted in the stimulation of indigenous bacteria through the injection of the appropriate nutrients. Production data obtained from this MEOR field application indicate higher oil production rates, incremental oil recovery, and decreased water cuts (up to 10%), which decreased operating costs due to reduced lifting and water treatment costs. In this field application, it was considered that the main MEOR mechanism was modification of the oil and water relative permeability driven by the interactions at the oil-water-microbes interface. Several benefits of this MEOR approach compare to other MEOR applications schemes and other EOR processes are as follows [78]:

- Low application costs;
- Low process cost per incremental oil production, on average it was US$ 6 per barrel of oil produced;
- No capital outlay required to implement the MEOR project;
- Low risk to implement;
- Environmentally friendly.

Numerical modeling has been used to attempt the quantitative prediction of the performance of the MEOR process [73]. A study conducted by Eduarda et al. [79] in which a finite difference method was applied, indicated that appropriate bacterial growth within the reservoir is the determining variable affecting the oil recovery factor.

3. Conclusion

MEOR technology makes use of special indigenous or exogenous microbial strains and nutrients that are injected into the reservoir to enhance oil production. The metabolic action of the injected exogenous microbial strains and the indigenous reservoir microflora produce metabolites such as gases, alcohols, and surface active compounds (biosurfactants) that interact with the crude oil. Biogases provide additional reservoir driving pressure; while bioalcohols and biosurfactants reduce oil viscosity and surface tension between oil-water and oil-rock, respectively. Under the effect of metabolites, the crude oil flowing properties are modified causing its release and mobilization toward the production wells enhancing the oil flow output.

The following metabolites interact with the crude oil changing its physicochemical properties:

- Organic acids (i.e., acetic, propionic, and butyric acids);
- Solvents (i.e., acetone, aldehydes, low-molecular-weight alcohols, ketones, etc.);
- Biomass (i.e., cell debris);
- Biopolymers (i.e., xanthan, scleroglucan, polysaccharides);
- Biosurfactants (i.e., rhamnolipid, surfactin);
- Biogases (i.e., methane, CO_2, etc.).

MEOR is an easy-to-use process which requires minimum, if any, upgrade of the existing process equipment and facilities. This process has the potential to recover oil reserves that otherwise would remain immobile and unrecoverable. This process overcomes natural and chemical barriers in oil deposits that hinder microbial growth. MEOR is safe and environmentally friendly that does not cause any threat to plants, animals, and humans.

Author details

Aliya Yernazarova[1,2*], Gulzhan Kayirmanova[1], Almagul Baubekova[1] and Azhar Zhubanova[1]

*Address all correspondence to: aliya.yernazarova@gmail.com

1 Department of Biotechnology, Al-Farabi Kazakh National University, Almaty, Kazakhstan

2 Institute of Ecology, Almaty, Kazakhstan

References

[1] Sandrea I, Sandrea R. Global oil reserves – recovery factors leave vast target for EOR technologies. Oil and Gas Journal.2007;105(41):44–47.

[2] Beckman JW. The action of bacteria on mineral oil. Industrial and Engineering Chemistry, News Edition. 1926;4:23–26.

[3] Zobell CE. Bacterial release of oil from oil-bearing materials. World Oil. 1947; 26:36–47.

[4] Yarbrough HF, Coty VE. Microbially enhanced oil recovery from the Upper Cretaceous Nacatoch formation, Union County Arkansas. In: Proceeding of International Conference on Microbial Enhancement of Oil Recovery, USA; 1983. p. 149–153.

[5] Kryanev D, Zhdanov S. Use of advanced reservoir recovery methods in Russia and abroad. Drilling and Oil. 2011;2:22–26 (in Russian).

[6] Portwood JT. (Company Alpha Environmental Midcontinent, Inc.). A commercial microbial enhanced oil recovery technology: Evaluation of 322 projects. In: Proceedings of the SPE Production Operations Symposium; 2–4 April, Oklahoma City, Oklahoma: SPE; 2007. p. 693–709.

[7] Meyer RF, Attanasi E. Heavy oil and bitumen – strategic petroleum resources. U.S. Geological Survey Fact Sheet 2003-70-03. http://pubs.usgs.gov/fs/fs070-03/fs070-03.html.

[8] Schmitt DR. Heavy and Bituminous Oils: Can Alberta Save the World/ Australian SEG Preview magazine. 2005;118:22–29.

[9] Guseva UZ, Ovsyannikova VS, Svarovskaya LI, Altunina LK. Role of microorganisms during EOR. http://www.ipc.tsc.ru/proekts/1/10/index.htm (in Russian).

[10] Miroshnikov V, Kurbanbayev MI, Tolokonskyi S. EOR at fields in Kazakhstan. In: Proceeding of International Symposium on Theory and Practice of Application of Enhanced Oil Recovery Methods, Moscow; 2011. p. 34–41 (in Russian).

[11] Abdolhamid HR, Sadiq Al-Baghdadi MAR, El Hinshiri AK. Evaluation of biosurfactants enhancement on bioremediation process efficiency for crude oil at oilfield: strategic study. Ovidus University Annals of Chemistry. 2009;20:25–30.

[12] Feng Z, Feng M, Rongjiu S, Jie Z, Siqin H, Ying Z. Production of rhamnolipids by *Pseudomonas aerugin*osa is inhibited by H_2S but resumes in a co-culture with P. stutzeri: applications for microbial enhanced oil recovery. Biotechnology Letters. 2015;37(9): 1803–1808. DOI: 10.1007/s10529-015-1859-4.

[13] Gudina EJ, Rodrigues LR, Teixeira JA, Pereira JFB, Coutinho JAP, Soares LP. Biosurfactant producing microorganisms and its application to enhance oil recovery at lab scale. In: Proceedings of the SPE EOR Conference at Oil and GasWest Asia 2012 (OGWA). Muscat, Oman; 2012. V.1, p. 363–370.

[14] Al-Bahry SN, Al-Wahaibi YM, Elshafie AE, Al-Bemani AS, Joshi SJ, Al-Makhmari HS, Al-Sulaimani HS. Biosurfactant production by *Bacillus subti*lis B20 using date molasses and its possible application in enhanced oil recovery. International Biodeterioration and Biodegradation. 2013;81:141–146.

[15] Lazar I, Petrisor IG, Yen TF. Microbial enhanced oil recovery. Petroleum Science and Technology. 2007;25:1353–1366.

[16] Chai LuJun, Zhang Fan, She YueHui, Banat Ibrahim M, Hou DuJie. Impact of a microbial-enhanced oil recovery field trial on microbial communities in a low-temperature heavy oil reservoir. Nature Environment and Pollution Technology. 2015;14(3): 455–462.

[17] Fatkullina AS, Sadchikov AV. Use of biogas installation products for oil recovery. Electronic Scientific Journal "Modern Problems of Science and Education". 2014;3.

[18] Jimoh IA. Microbial enhanced oil recovery. PhD thesis. Luma Print; 2012. 6700 Esbjerg.

[19] Belyaev SS, Borzenkov IA, Nazina TN, Rozanova EP, Glumov IF, Ibatullin RR. Use of microorganisms in the biotechnology for the enhancement of oil recovery. Microbiology. (Maik Nauka Interperiodica). 2004;73:590–598 (in Russian).

[20] Van H, Singh A, Ward O. Recent advances in petroleum microbiology. Microbiology and Molecular Biology Review. 2003;67(4):503–549.

[21] Wang X, Li D, Hendry P, Volk H, Rashid A, et al. Effect of nutrient addition on an oil reservoir microbial population: implications for enhanced oil recovery. Journal of Petroleum & Environmental Biotechnology. 2012;3:118. DOI: 10.4172/2157-7463.1000118.

[22] Nazina TN, Pavlov NK, Tatarkin Y, Shestakov NM, Babich TL, Sokolov DS, Ivoylov VS, Turov TP, Hisametdinov MR, Ibatullin RR, Belyaev SS, Ivanov MV. The development of biotechnology increase the degree of oil recovery from carbonate oil reservoirs on the territory of the Republic of Tatarstan. Electronic Scientific Journal Georesources. Geoenergetika. Geopolitics. 2012;2(6):1–6 (in Russian).

[23] Wagner M, Lungershausen D, Murtada H, Rosenthal G. Development and application of a new biotechnology of the molasses in-situ method; detailed evaluation for selected wells in the Romashkino carbonate reservoir. In: Proceeding of Fifth International Conference on Microbial Enhanced Oil Recovery and Related Biotechnology for Solving Environmental Problems, BDM-Oklahoma, Tulsa; 1995. p. 153–173.

[24] Joshi S, Bharucha C, Jha S, Yadav S, Nerurkar A, Desai AJ. Biosurfactant production using molasses and whey under thermophilic conditions. Bioresource Technology. 2008;99(1):195–199.

[25] Eduardo J, Gudiña E, Fernandes C, Rodrigues AI, Teixeira JA, Rodrigues LR. Biosurfactant production by *Bacillus subti*lis using corn steep liquor as culture medium. Frontiers in Microbiology. 2015;6:59.

[26] Tech Fu Yen, editor. Microbial Enhanced Oil Recovery: Principle & Practice. Boca Raton, FL: CRC Press Inc.; 1990. 257 p.

[27] Stetter KO, Huber R, Blochl E, Kurr M, Eden RD, Fielder M, Cash H, Vance I. Hyperthermophilic archaea are thriving in deep North Sea and Alaskan oil reservoirs. Nature. 1993;365(6448):743–745.

[28] Tardy-Jacquenod C, Caumette P, Matheron R, Lanau C, Arnauld O, Magot M. Characterization of sulfate-reducing bacteria isolated from oil-field waters. Canadian Journal of Microbiology. 1996;42(3):259–266.

[29] Ng TK, Weimer PJ, Gawel LJ. Possible nonanthropogenic origin of two methanogenic isolates from oil producing wells in the San Miguelito field, Ventura County, California. Geomicrobiology Journal. 1989;7(3):185–192.

[30] Birkeland NK. Chapter 14: The microbial diversity of deep subsurface oil reservoirs. In: Duhalt RV, Ramirez RQ, editors Petroleum Biotechnology, Volume 151: Developments and Perspectives (Studies in Surface Science and Catalysis) 1st ed. Elsevier Science: Amsterdam; 2004. 545 p. DOI: 10.1016/j.fuel.2006.10.012.

[31] Davey ME, Wood WA, Key R, Nakamura K, Stahl DA. Isolation of three species of Geotoga and Petrotoga: two new genera, representing a new lineage in the bacterial line of descent distantly related to the Thermotogales. Systematic and Applied Microbiology. 1993;16(2):191–200.

[32] Grassia GS, McLean KM, Glenat P, Bauld J, Sheehy AJ. A systematic survey for thermophilic fermentative bacteria and archaea in high temperature petroleum reservoirs. FEMS Microbiology Ecology. 1996;21(1):47–58.

[33] Brown F, Maure A, Warren A. Microbial-induced controllable cracking of normal and branched alkanes in oils. United States Patent 6905870; 2005.

[34] Bahrami A, Shojaosadati SA, Mohebali G. Biodegradation of dibenzothiophene by thermophilic bacteria. Biotechnology Letters. 2001;23(11):899–901.

[35] Annual Report of Project 4933/GF. The effective microbial consortium with high target activities; 2015. 45 p.

[36] Grigoryan A.A. Physiology and ecology of aerobic organotrophic bacteria oil reservoirs. PhD dissertation, Moscow;, 2004. Pp. 154.

[37] Jenneman GE, McInerney MJ, Knapp RM, Clark JB, Feero JM, Revus DE, Menzie DE. A halotolerant, biosurfactant producing *Bacil*lus species potentially useful for enhanced oil recovery. Developments in Industrial Microbiology. 1983;24:485–492.

[38] Fan Zhang, Yue-Hui She, Hua-Min Li, Xiao-Tao Zhang, Fu-Chang Shu, Zheng-Liang Wang, Long-Jiang Yu, Du-Jie Hou. Impact of an indigenous microbial enhanced oil recovery field trial on microbial community structure in a high pour-point oil reservoir. Applied Microbiology and Biotechnology. 2012;95:811–821. DOI: 10.1007/s00253-011-3717-140.

[39] Al-Sulaimani H, Al-Wahaibi Y, Al-Bahry SN, Elshafie A, Al-Bemani AS, Joshi SJ, Zargari S. Experimental investigation of biosurfactants produced by *Bacil*lus species and their potential for MEOR in Omani oil field. In: Proceedings of

the SPE EOR Conference at Oil and GasWest Asia 2010 (OGWA'10), Muscat, Oman; 2010. p. 378–386.

[40] Al-Sulaimani H, Al-Wahaibi Y, Al-Bahry SN, Elshafie A, Al-Bemani AS, Joshi SJ, Zargari S. Optimization and partial characterization of biosurfactants produced by *Bacil*lus species and their potential for ex-situ enhanced oil recovery. SPE Journal. 2011;16(3): 672–682.

[41] Wang T, Ma J, Liu QK, Zhao LX, Liang FL, Liu RL. Isolation of functional bacteria guided by PCR-DGGE technology from high temperature petroleum reservoirs. Huan Jing Ke Xue. 2008;29(2):462–468.

[42] Sanchez G, Marin A, Vierma L. Isolation of thermophilic bacteria from a Venezuelan Oil Field. Developments in Petroleum Science. 1993;39:383–389.

[43] Lien T, Madsen M, Rainey FA, Birkeland NK. *Petrotoga mobi*lis sp. nov., from a North Sea oil production well. International Journal of Systematic Bacteriology. 1998;48:1007–1013.

[44] Magot M, Olliver B, Patel BKC. Microbiology of petroleum reservoirs. Antonie Van Leeuwenhoek. 2000;77:103–116.

[45] Ollivier B, Cayol JL. Fermentative, iron-reducing and nitrate-reducing microorganisms. In: Ollivier B, Magot M, editors. Petroleum Microbiology. Washington, DC: ASM Press; 2005. p. 71–88.

[46] Eden B, Laycock P, Fielder M. Oilfield Reservoir Souring. HSE Books; 1993. 90 p.

[47] Alain K, Pignet P, Zbinden M, Quillevere M, Duchiron F, Donval JP, Lesongeur F, Raguenes G, Crassous P, Querellou J, Cambon-Bonavita MA. *Caminicella sporoge*nes gen. nov., sp. nov., a novel thermophilic spore-forming bacterium isolated from an East-Pacific Rise hydrothermal vent. International Journal of Systematic and Evolutionary Microbiology. 2002;52:1621–1628.

[48] Klouche N, Fardeau ML, Lascourrиges JF, Cayol JL, Hacene H, Thomas P, Magot M. *Geosporobacter subterran*eus gen. nov., a spore-forming bacterium isolated from a deep subsurface aquifer. International Journal of Systematic and Evolutionary Microbiology. 2007;57:1757–1761.

[49] Al-Bahry SN, Elshafie AE, Al-Wahaibi YM, Al-Bemani AS, Joshi SJ, Al-Maaini RA, Al-Alawi WJ, Sugai Y, Al-Mandhari M. Microbial consortia in Oman oil fields: a possible use in enhanced oil recovery. Journal of Microbiology and Biotechnology. 2013;23(1): 106–117.

[50] Youssef N, Elshahed MS, McInerney MJ. Microbial processes in oil fields: culprits, problems, and opportunities. In: Laskin AI, Sariaslani S, Gadd GM, editors. Advances in Applied Microbiology. Burlington: Academic Press; 2009. Vol. 66. p. 141–251.

[51] Omoniyi OA, Abdulmalik FA. Review of microbial enhanced oil recovery: current development and future prospects. International Journal of Scientific & Engineering Research. 2015;6(1):1378–1389.

[52] Al-Sulaimani H, Joshi S, Al-Wahaibi Y, Al-Bahry S, Elshafie A, Al-Bemani A. Microbial biotechnology for enhancing oil recovery: current developments and future prospects. Biotechnology, Bioinformatics and Bioengineering. 2011;1(2):147–158.

[53] Adkins JP, Cornell LA, Tanner RS. Microbial composition of carbonate petroleum reservoir fluids. Geomicrobiology Journal. 1992;10:87–97.

[54] Gray M, Yeung A, Foght J, Yarranton HW. Potential microbial enhanced oil recovery processes: a critical analysis. In: Proceeding of the SPE Annual Technical Conference and Exhibition; 21–24 September 2008; Denver. Colorado. USA; 2008. V.1. p. 303–327.

[55] Research Priorities in Microbially Enhanced Hydrocarbon Recovery (MEHR) [Internet]. 2007. Available from: http://www.energybiosciencesinstitute.org/media/MEHR%20White%20Paper%20Final.pdf [Accessed: 2007-10–24] .

[56] Bryant RS, Stepp AK, Bertus KM, Burchfield TE, Dennis M. Microbial enhanced water flooding field pilots. Developments in Petroleum Science. 1993;39:289–306.

[57] Nielsen SM, Shapiro A, Stenby EH, Michelsen ML. Microbial Enhanced Oil Recovery – Advanced Reservoir Simulation. Kgs. Lyngby, Denmark: Technical University of Denmark (DTU); 2010. 145 p.

[58] Youssef NH, Duncan KE, McInerney MJ. Importance of 3-hydroxy fatty acid composition of lipopeptides for biosurfactant activity. Applied and Environmental Microbiology. 2005;71:7690–7695.

[59] Pommerville J. Alcamo's Laboratory Fundamentals of Microbiology. 8th ed. Massachusetts: Jones and Bartlett Publishers; 2007. 352 p.

[60] Pruthi V, Cameotra SS. Production of a biosurfactant exhibiting excellent emulsification and surface active properties by *Serratia marcesc*ens. Short communication. World Journal of Microbiology and Biotechnology. 1997;13(1):133–135.

[61] Youssef N, Simpson DR, Duncan KE, McInerney M, Folmsbee M, Fincher T, Knapp RM. In situ biosurfactant production by Bacillus strains injected into a limestone petroleum reservoir. Applied and Environmental Microbiology. 2007;73(4): 1239–1247.

[62] Singh A, Van Hamme JD, Ward OP. Surfactants in microbiology and biotechnology: Part 2. Application aspects. Biotechnology Advances. 2007;25(1):99–121.

[63] Cooper DG, Macdonald CR, Duff SJB, Cosaric N. Enhanced production of surfactin from *Bacillus subti*lis by continuous product removal and metal cation additions. Applied and Environmental Microbiology. 1981;42(3):408–412.

[64] Desai J, Banat IM. Microbial production of surfactants and their commercial potential. Microbiology and Molecular Biology Reviews. 1997;61:47–64.

[65] Chrzanowski Ł, Kaczorek E, Olszanowski A. The ability of *Candida Maltosa malt*osa for hydrocarbon and emulsified hydrocarbon degradation. Polish Journal of Environmental Studies. 2006;15(1):47–51.

[66] Prenafe ta-Boldu FX, Summerbell R, Sybren de Hoog G. Fungi growing on aromatic hydrocarbons: biotechnology's unexpected encounter with biohazard? FEMS Microbiology Reviews. 2006;30:109–130.

[67] Cheng Q, Kinney KA, Whitman CP, Szaniszlo PJ. Characterization of two polyketide synthase genes in *Exophiala lecanii-co*rni, a melanized fungus with bioremediation potential. Bioorganic Chemistry. 2004;32:92–108.

[68] Qi B, Moe WM, Kinney KA. Biodegradation of volatile organic compounds by five fungal species. Applied Microbiology and Biotechnology. 2002;58(5):684–689.

[69] Dallinger A, Duldhardt I, Kabisch J, Schauer F. Biotransformation of cyclohexane and related alicyclic hydrocarbons by *Candida malt*osa and *Trichospo*ron species. International Biodeterioration & Biodegradation. 2016;107:132–139.

[70] Nazina TN. Microorganisms oil reservoirs and their use in biotechnology enhanced oil recovery. PhD thesis; 2000. p. 67 (in Russian).

[71] Nazina TN, Ivanova AE, Blagov AV. Microbiological characterization of oil reservoirs peninsula Mangyshlak. Microbiology. 1992;61(2):316–322 (in Russian).

[72] Bekker RH, Gutorov UA, Gareev AM. Prospects of microbiological methods for enhanced oil recovery in the conditions of productive reservoirs of the Volga-Ural. Oil and Gas Business. 2012;10(3):34–39.

[73] Maudgalya S, Knapp RM, McInerney MJ. Microbial enhanced-oil-recovery technologies: a review of the past, present, and future. In: SPE Production and Operations Symposium; March 31–April 3 2007. p. 1–11. SPE 106978.

[74] Bauer BG, O'Dell RJ, Marinello SA, et al. Field experience from a biotechnology approach to waterflood improvement. In: Presented at the SPE Enhanced Oil Recovery Conference, Kuala Lumpur, Malaysia; 19–21 July 2011. SPE-144205-MS. DOI: 10.2118/144205-MS.

[75] Jackson SC, Alsop AW, Choban ER, et al. Microbial EOR: critical aspects learned from the Lab. In: SPE Improved Oil Recovery Symposium, Tulsa; 24–28 April 2010. SPE-129657-MS. DOI: 10.2118/129657-MS.

[76] Trent Jacobs T. DuPont touts MEOR technology. Journal of Petroleum Technology. 2014;66(06):34–36.

[77] Jacobs T. Wintershall sees EOR promise in new biopolymer. Journal of Petroleum Technology. 2014;66(06):36–37.

[78] Town K, Sheehy AJ, Govreau BR. MEOR Success success in Southern southern Saskatchewan. SPE Reservoir Evaluation & Engineering. 2010. ;13 (5): 773–781. SPE-124319-PA. DOI: http://dx.doi.org/10.2118/124319–PA.

[79] Lacerda E, Priimenko VI, Pires AP. Microbial EOR: A a Quantitative quantitative Prediction prediction of Recovery recovery Factorfactor. In: SPE Improved Oil Recovery Symposium held in Tulsa;, 14–18 April, 2012. SPE 153866.

Section 3

Electrorheology Technology

Application of Electrorheology to Improve Crude Oil Flowing Properties Through Pipeline

R. Tao

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/64858

Abstract

This chapter describes a new technology based on electrorheology (ER) that simultaneously reduces oil viscosity and suppresses flow turbulence. The application of a strong electric field in a small section of the oil pipeline causes the polarization of suspended particles contained in the oil phase aggregating them into short chains along the flow direction. This particle aggregation breaks the rotational symmetry and makes the oil viscosity anisotropic, which in turn reduces the oil viscosity along the flow direction. Simultaneously, oil viscosity increases in the direction perpendicular to the flow, which supresses flow turbulence. This green technology does not involve the addition of chemicals to the oil phase and is environmentally friendly. This approach is also energy efficient because it only targets the particles suspended in the oil phase causing the formation of aggregates. Furthermore, heat is not required to reduce the viscosity of the oil phase. Neutron scattering experiments and field tests demonstrate the effectiveness of this technology. Electrorheology will play an important role during enhanced heavy oil recovery and/or production operations and transportation via pipeline.

Keywords: electrorheology, crude oil viscosity, turbulence suppression, anisotropic viscosity, pipeline

1. Introduction

Currently, hydrocarbons remain as the leading energy source. While the amount of conventional light crude oil becomes less and less available, heavy crude oils and offshore crude oils are becoming very important resources. The high viscosity of these hydrocarbons becomes a critical issue during oil recovery and/or production operations. This is also a problem for offshore crude oil production, which also shows very high viscosities because of the low temperatures (i.e. 1.5–1.6°C) of the reservoirs.

The flow of high viscosity oils through pipelines is very difficult, requiring much higher pumping power. This creates complications during oil production and transportation. Therefore, reducing the viscosity of the crude oil is paramount [1–4].

Although, there has been extensive research into this issue for more than 30 years, little progress has been achieved thus far. Currently, the dominant method to reduce the viscosity of heavy crude oil remains heating by the injection of steam and/or hot water. The application of these thermal processes requires time due to heat transfer issues. Furthermore, these processes are energy-intensive and environmentally unfavorable (i.e. large volumes of CO_2 emissions during the generation of steam). Moreover, the application of thermal methods for the recovery of offshore heavy crude oils is technically difficult and expensive.

Flow turbulence is an additional issue relevant here [5–9]. The efficient transportation of crude oil via pipelines requires the suppression of turbulence, because under turbulent flow regime, much more pumping energy is required.

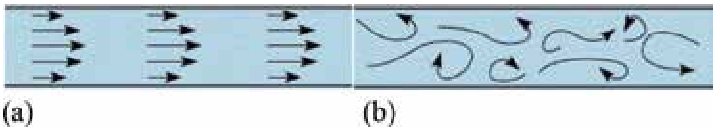


Figure 1. (a) Laminar flow in pipeline. (b) Turbulent flow in pipeline.

Flow is laminar when the Reynolds number is (**Figure 1a**):

$$N_R = \rho v D / \eta \leq 2300 \tag{1}$$

where D is the diameter of the pipeline, v is the average flow velocity, ρ is the oil density, and η is the oil viscosity. Equation (2) gives the friction factor for laminar flow:

$$f = 64 / N_R \tag{2}$$

The pressure drop ΔP is as follows,

$$\Delta P / L = \tfrac{1}{2} \rho v^2 f / D = 32 v \eta / D^2 \tag{3}$$

where L is the length of the pipeline.

Equation (4) gives the flow rate Q for laminar flow:

$$Q = \frac{\pi D^4}{128\eta}(\Delta P / L) \tag{4}$$

Figure 1b shows a turbulent flow inside a pipeline. Flow is turbulent when the Reynolds number is higher than 2300 ($N_R > 2300$), which causes an erratic flow pattern in all directions, resulting in significant loss of energy. Therefore, the flow of fluids (i.e. heavy crude oil) under turbulent flow regime requires much more pumping power.

The friction factor for turbulent flow within 2300 $N_R < 100000$ can be estimated by the Blasius equation [10] as follows,

$$f = 0.3164 / (N_R)^{0.25} \tag{5}$$

Equation (6) gives the flow rate for turbulent flow:

$$Q = 2.2526 \frac{D^{19/7}}{\rho^{3/7}\eta^{1/7}}(\Delta P / L)^{4/7} \tag{6}$$

Equations (4) and (6) indicate that flow under laminar conditions is energetically more efficient than under turbulent conditions. For example, under laminar flow conditions, a 30% increase in the oil flow rate requires a 30% increase in pumping pressure; while under turbulent flow conditions, it requires a pressure increase of 58.3%; which means that the pump needs to provide 94.3% more power. Therefore, suppressing turbulence is crucial during oil transportation by pipelines. For instance, a common practice in the field is to add drag-reducing agents, DRA (i.e. chemical additives based on polymers) to the oil before pumping it through pipelines to suppress turbulence [11]. However, the addition of DRA agents increases the oil viscosity, and it has no effect on laminar flow.

The crucial and challenging issue is clear: the efficient transportation of oil through pipelines requires the simultaneous reduction of the oil viscosity and suppression of turbulence. These issues are not only crucial for the engineering field but also important for several other technical fields, because turbulence remains as one of the most important unsolved problems of classical physics [8].

Currently, conventional pipeline transportation methods cannot simultaneously and effectively reduce fluid (i.e. crude oil) viscosity and suppress turbulence. Thermal methods for crude oil viscosity reduction cannot suppress turbulence. As the temperature increases, the oil viscosity decreases, the Reynolds number increases, and as a result turbulence increases. Other conventional technologies to reduce oil viscosity, such as heavy oil dilution with solvents, cannot accomplish the simultaneous reduction of viscosity and suppression of turbulence, either.

An unconventional technology is required to solve these challenging issues. It is necessary to enhance oil flow output by simultaneously decreasing the oil viscosity along the flow direction, while increasing it in the direction perpendicular to the pipeline axis, because turbulence always starts from the vortices and expands perpendicular to the flow direction. In other words, oil viscosity must be anisotropic: reduced along the pipeline direction and increased in the direction perpendicular to the flow, which makes the flow regime laminar along the pipeline axis even if N_R>> 2300.

This chapter describes the electrorheology (ER) technology, which provides an efficient solution for the simultaneous reduction of oil viscosity and suppression of turbulence during crude oil transportation via pipeline [2, 3, 9].

Crude oil is a liquid suspension, which depending on the chemical composition might contain particles suspended within the liquid hydrocarbon phase, such as asphaltenes, resins, fine sand particles, and wax particles. The application of a strong electric field in a small section of the pipeline causes the polarization of the suspended particles contained in the oil phase, aggregating them into short chains along the flow direction. This ER application is significantly different from traditional ER fluids, where the applied electric field is perpendicular to the flow direction, leading to increase the effective viscosity or even solidify the ER fluids [12]. Here the applied electric field and the aggregated chains are in the flow direction (**Figure 2**).

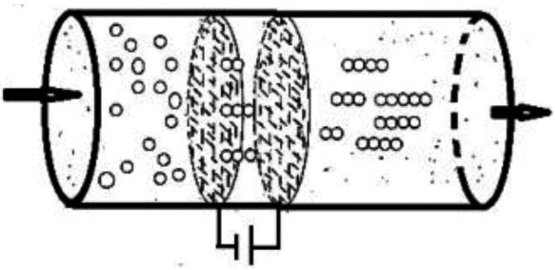


Figure 2. Aggregation of suspended particles into short chains under the influence of a local electric field.

Such aggregation breaks the rotational symmetry and makes the oil viscosity anisotropic, accomplishing two goals: the reduction of the viscosity along the flow direction and the substantial increase in the viscosity in the direction perpendicular to the flow. These viscosity changes supress all vortices and rotating motions; hence, turbulence is suppressed, which enhances the flow parallel to the pipeline horizontal axis. This green technology does not involve the application of chemical additives to the oil phase and is environmentally friendly. It is also energy efficient since it only aggregates the particles and does not heat the bulk of the oil phase. Neutron scattering experiments and field tests on pipelines fully support the theoretical approach of this technology. It is anticipated that electrorheology (ER) will play an important role during heavy crude oil recovery and/or production, enhanced oil recovery applications, and transportation through pipelines.

2. The New Technology (ER)

Refined fractions of crude oil such as gasoline, kerosene, and diesel have very low viscosities and low dielectric constants. Paraffinic and heavier oils have higher viscosities because these oils contain randomly suspended paraffin, asphaltenes, resins, sulfur, and other solid compounds having large molecular weights. These suspended particles have higher dielectric constants that make them polarized in a strong electric field (**Figure 2**). Under the influence of a strong electric field, similar to conventional electrorheological fluids, these particles in crude oil form chains that aggregate into thick columns [12, 13, 15].

During the aggregation of dipoles into chains or chain-based columns, the total energy $U(N)$ of the system is negative making it energetically favorable. As the total number of particles, N, in the aggregated chain or column increases, the energy per particle $U(N)/N$ is more negative. The probability to have such structure of N aggregated particles is proportional to $\exp[-U(N)/k_BT]$. Therefore, an increase in N accelerates particle aggregation. The aggregated structure is more stable if it has more particles. For this reason, the formation of thick columns takes place in ER fluids under the application of an electric field.

In the ideal aggregated structure, all particles would aggregate into one thick column, body-centered tetragonal lattice [13, 14]. In reality, the aggregation process is very fast, and particle aggregation spontaneously spreads under the electric field leading to quick formation of many stable thick columns.

2.1. Neutron scattering experiments

Small-angle neutron scattering is a useful technique to confirm the induced aggregation of solid particles contained in crude oil when subjected to a strong electric field [15].

The NG7 Small-Angle Neutron Scattering or SANS facility, NCNR, is located in Gaithersburg, Maryland, USA. The SANS instrument is 30-m long, and it is equipped with a high-resolution

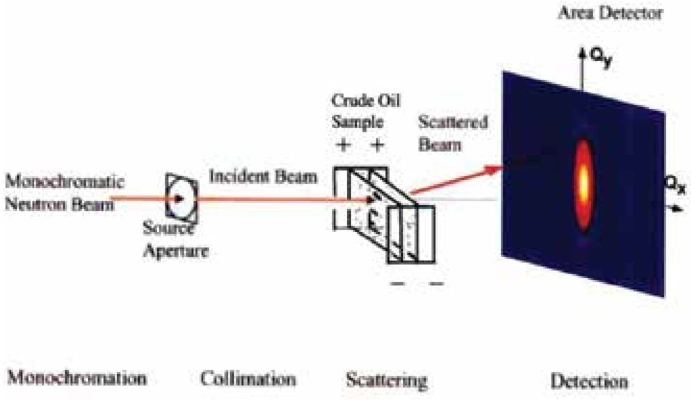


Figure 3. Neutron scattering experimental set-up.

2D detector and focusing refractive lenses. The *Q*-range of the instrument goes from 0.008 to 7.0 nm^{-1} to enable the detection of structural features in materials ranging from roughly 1 nm to over 500 nm.

As shown in **Figure 3**, the crude oil sample goes in a special capacitor, consisting of two pieces of cadmium electrodes and two pieces of quartz glass windows. The neutron beam passes through the quartz windows and through the crude oil sample into a detector. The application of a high voltage to the cadmium electrodes produces an electric field perpendicular to the neutron beam. Cadmium electrodes are suitable neutron absorbers, which reduces neutron scattering noise.

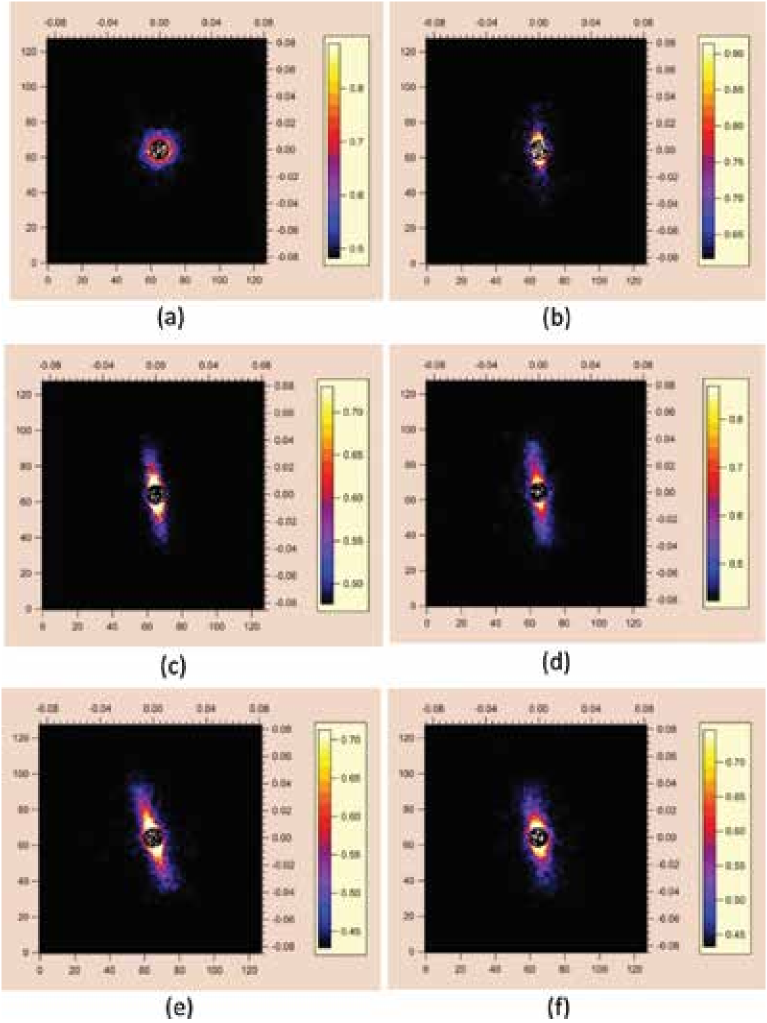


Figure 4. Scattering patterns at various electric fields obtained from a paraffin base crude oil. (a) E = 0 V/cm, (b) E = 2500 V/cm, (c) E = 4000 V/cm, (d) E = 7500 V/cm, (e) E = 11,000 V/cm, (f) E = 15,000 V/cm.

In this experimental work, the samples evaluated were a light paraffin base crude oil (API° 34) and a heavy asphalt base crude oil (API° 21). The test results have confirmed that under the influence of a strong electric field, the suspended particles from both the paraffin base crude and the asphalt base crude oil aggregated into short chains. As shown in **Figure 4a**, in the absence of an electric field, the scattering was isotropic and sparse indicating a random dispersion of particles in the oil phase. The application of an initial electric field of 250 V/mm induced the onset of particles aggregation. The scattering signal revealed that the particles suspended in the light paraffin base crude oil started to aggregate into a short chain with a length of 68 nm and a thickness of 34 nm (**Figure 4b**). As the applied electrical field increased to $E = 400$ V/mm, the neutron scattering signal indicated that the short chain acquired a prolate spheroid shape with a length of 75.2 nm and a thickness of 37.6 nm (**Figure 4c**). At a higher electrical field of $E = 750$ V/mm, the chain length increased to 94 nm long and the thickness to 38.4 nm (**Figure 4d**). At a higher electric field of 1100 V/mm, the chain reached a length of 94.8 nm and a thickness of 38.6 nm (**Figure 4e**). Finally, at the highest value of the electrical field applied of $E = 1500$ V/mm (**Figure 4f**), the chain dimensions were 94.8 nm length and 45 nm thickness. Therefore, as the electric field increases, the aggregated chains become longer and thicker (**Table 1**).

Electric field (V/mm)	Length 2a (nm)	Thickness 2b (nm)
0	~6	~6
250	68.0	34.0
400	75.2	34.8
750	94.0	38.4
1100	94.8	38.6
1500	94.8	45.0

Table 1. Aggregated short chains of light paraffin base crude oil.

The asphalt base crude oil showed similar behavior under the ER treatments at different electric field intensities. For example, under an electric field of 1000 V/mm, the asphalt particles aggregated into a short chain in a prolate spheroid shape with a length of 78 nm and a thickness of 50 nm [15].

Based on the neutron scattering information, it is possible to approximate the short chain to a prolate spheroid (**Figure 5**) with its rotational z-axis along the flow direction.

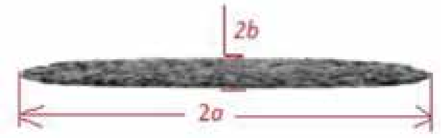


Figure 5. Aggregated short chains or prolate spheroids.

Equation (7) allows determining the dimensions of the prolate spheroid (short chain of agglomerates) as follows:

$$(x^2 + y^2) / b^2 + z^2 / a^2 = 1 \tag{7}$$

Here $a > b$ and the electric field is along the z-direction. Generally, a heavy crude oil contains numerous solid particles suspended within the bulk of the liquid hydrocarbon phase. In this case, the application of an electric field induces a strong aggregation of particles forming numerous short chains and/or prolate spheroids.

Einstein studied the viscosity of dilute liquid suspensions and found that the intrinsic viscosity for spheres is $[\eta] = 2.5$ [16]. For the prolate spheroids, the intrinsic viscosity along the z-axis $[\eta_{\parallel}]$ is smaller than 2.5, while the intrinsic viscosity along the directions perpendicular to the z-axis, $[\eta_{\perp}]$ is higher than 2.5. For crude oils with API° gravities lower than 34° (heavier crude oils), the aggregated chains will be longer than the aggregated chains observed in the nuclear scattering experiment for paraffinic oil. If for instance, it is assumed that $(a{-}b)/a = 0.8$, then $[\eta_{\parallel}] = 2.035$ and $[\eta_{\perp}] = 3.548$ [17]. This information of intrinsic viscosities enables the calculation of the viscosities using the Krieger-Dougherty equation [18],

$$\eta_i / \eta_0 = (1 - \phi / \phi_{\max})^{-[\eta_i]\phi_{\max}} \tag{8}$$

where η_i is the effective viscosity, η_0 is the viscosity of base liquid, $[\eta_i]$ is the intrinsic viscosity of the particles, and $\phi_{\max}$ is the maximum volume fraction for randomly packed particles. Recent work found that $\phi_{\max}$ strongly depends on the particle shape. For spheres, $\phi_{sphere} = 0.64$ and for spheroids $\phi_{spheroid} \geq 0.72$ [19, 20]. If the particle volume fraction $\phi = 0.5$, then the initial viscosity of the crude oil is $\eta = 11.38\eta_0$. After the electric field is applied, then the effective viscosity along the flow direction is reduced to $\eta_{\parallel} = 5.68\eta_0$, which corresponds to a viscosity reduction of 50.1%, while the effective viscosity perpendicular to the flow direction is increased to $\eta_{\perp} = 20.67\eta_0$ that represents a viscosity increase of 81.6%. The flow behaviour of this electric-field treated crude oil is similar to the flow of a nematic liquid crystal with its molecules in alignment with the flow direction [21].

A viscosity increase in the direction perpendicular to the flow causes the suppression of turbulence because the vortices in turbulent flow move in the direction transversal to the pipeline axis. For this reason, the formation of aggregated short chains in the bulk of the crude oil plays a similar function as the addition of drag-reducing agents (DRA) to the crude oil. However, the addition of DRA could cause further issues at the oil refineries. Moreover, the more significant aspect of this technology is the simultaneous reduction of viscosity, which enhances the flow output, while the addition of DRA to the oil phase cannot reduce the viscosity of the oil.

Another advantage of this technology is that the aggregated chains in the laminar flow migrate toward the center of the pipe that corresponds to minimum shear rate zone due to the Segré-Silberberg effect [22]. Therefore, this technology also reduces the sedimentation and/or deposition of particles on the pipeline walls. All these factors are essential for significant improvement of oil transportation via pipelines.

2.2. Laboratory evaluation of viscosity reduction

A series of laboratory tests evaluated the performance of different types of crude oils [23]. However, this chapter summarizes only the behavior of the Daqing crude oil, which is a well-known paraffinic crude oil with a pour point of around 30°C from the Daqing oil field, China.

The experimental procedure was as follows. The crude oil sample was loaded at the top of a cylindrical container. Underneath the cylinder, a valve allowed the flow of crude oil through three electrodes into a long capillary tube with a diameter of 0.2673 cm. A cup on a microbalance collected the crude oil that flowed down through the capillary tube. A computer connected to the microbalance recorded the oil mass as a function of time using a LabVIEW data acquisition system, which allowed determining the flow rate, Q. This experimental device was located inside an oven to keep the target temperature at 35.1°C during the experimentation. The middle electrode was connected to the positive output of the high-voltage power supply. The other two electrodes were connected to the negative output of the power supply. After the power supply was turned on, the strong electric field was produced in both capacitors along the flow direction, one vertically up and the other vertically down, forcing the suspended particles in the crude oil to aggregate into streamlined short chains along the flow direction causing the reduction of the crude oil effective viscosity. Since there are only dipolar interactions involved, such arrangement of the electrodes works well. It reduces the requirement of high voltage and makes the technology safer. **Figure 6** shows a picture of the experimental set-up.

Figure 6. Experimental set-up.

In these experimental runs, the N_R was very low, and the crude oil flowed through the capillary tube under laminar flow conditions, which allowed determining the oil viscosity along the flow direction using Eq. (9),

$$\eta = \frac{\pi \rho^2 g R^4}{8Q}\left(1 + \frac{h}{L} - \frac{v^2}{2gL}\right) \tag{9}$$

where R and L are the respective radius and length of the capillary tube, h is the height of the oil level above the capillary tube, ρ is the density of the oil, and g is the acceleration of gravity. Equation (10) allows estimating the average flow velocity,

$$v = Q/(\rho \pi R^2) \tag{10}$$

where Q is the flow rate, R is the radius of the capillary tube, and ρ is the density of the oil.

In all the experimental runs, crude oil flowed down by gravity in the absence of electric field to allow the stabilization of the oil and to obtain the baseline behavior of the crude oil (i.e. initial oil viscosity). Afterwards, crude oil flowed down by gravity under the effect of different electric field intensities. The oil flow rate increased rapidly under the effect of the tested electric fields. **Figure 7** shows the mass of oil passing through the electric field as a function of time and electric field. In **Figure 7**, a sudden change of the slope corresponds to a rapid increase in the mass of oil passing down as a function of time. Therefore, it was straightforward to determine the viscosity of the oil before and after the application of the electric field.

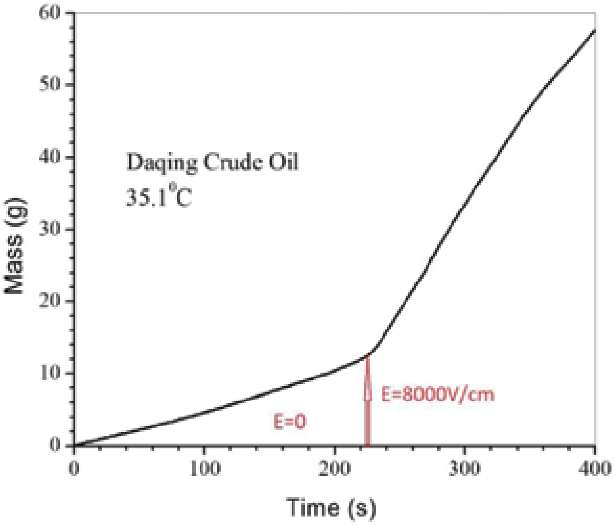


Figure 7. Mass of oil as a function of time and electric field.

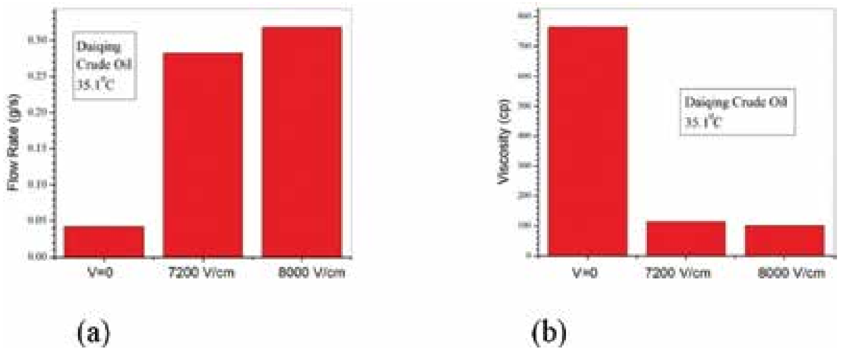


Figure 8. Effect of electric field on Daqing crude oil. (a) Mass flow rate as a function of electric field (b) Viscosity as a function of electric field. Data obtained a temperature of 35.1°C.

This study allowed determining the optimum electric field that induced the largest reduction of oil viscosity. As shown in **Figure 7**, the mass flow rate in the absence of electric field was 0.04182 g/s, which corresponded to a viscosity of 764.5 cP. The application of an electric field of 7200 V/cm increased the flow rate to 0.28252 g/s, which corresponded to a viscosity of 113.16 cP. A further increase of the electric field to 8000 V/cm increased the flow rate to 0.318095 g/s that was equivalent to a final viscosity of 100.5 cP from an initial value of 764.5 cP.

Replication tests gave consistent results and confirmed that the application of the ER treatment effectively reduces irection.

Figure 8a plots the mass flow rate as a function of electric field. The mass flow rate of the oil increased by 661% when the electric field was increased from 0 to 8000 V/cm, which induced the simultaneous reduction of the crude oil viscosity by 86.9%.

Figure 9. The photo of the AOT device installed in the pipeline.

2.3. Field tests under laminar flow conditions

These field tests employed the testing pipeline route at the Rocky Mountain Oil Test Center (RMOTC) facility near Casper, Wyoming, equipped with a positive displacement (PD) pump. The electrical device or Applied Oil Technology (AOT) device was connected at 7.219 km of the testing route (**Figure 9**). Sensors inside the pipeline (inner diameter of 14.163 cm) at various locations measured the oil pressure and temperature.

Figure 9 shows a photo of the AOT device installed at the RMOTC pipeline system. The device was connected downstream the pump, which pumped the crude oil to the top of the device. Then, the oil flowed down through the electric field and the pipeline. Several mesh electrodes (39 units) inside the vertical pipe of the device with a gap of 3 cm between two neighboring ones induced the axial electric field inside the vertical pipe.

The field tests used two loops as follows:

(1) **Close loop**. The oil flowed through the pump, the AOT device, and the pipeline for several cycles.

(2) **Open loop**. In this case, after one cycle, the oil flowed to a storage tank and fresh oil from another supply tank was pumped through the device and pipeline.

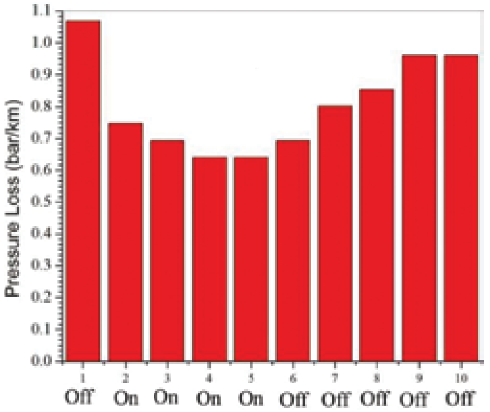


Figure 10. Pressure loss across the test loop as a function of the application of an electric field using the AOT device.

In these tests, the viscosity reduction was first determined along the flow direction under laminar flow regime (N_R = 1205.21). The pump was set at a constant Q of 46.56 m^3/h, which provided a linear velocity of 82.09 cm/s. The properties of the crude oil were API° = 34, initial viscosity = 81.6 cP at 12.1°C, and density = 0.8459 g/cm^3. As the untreated oil flowed through the pipeline, the pressure loss was 1.07 bar/km. The application of an electric field of 2300 V/cm caused a reduction of pressure loss across the loop from 1.07 to 0.641 bar/km (40% reduction). Similarly, the viscosity along the flow direction reduced from 81.6 cP to 48.95 cP (40% reduction). Then, the AOT device was turned-off and the pressure loss across the loop gradually returned to the original value in the absence of the electric field (**Figure 10**). Measurement of the pumping power requirements is useful to evaluate the effect of the ER treatment on the flow properties of the crude oil. Before the application the ER treatment, the pump required a total power of 14.2 kW. However, the ER treatment gradually reduced the pumping requirements to a steady value of 8.9 kW, which is equivalent to an energy saving of 5.3 kW. The AOT device utilized less than 100 W of electric power during the lifespan of the experimentation.

2.4. Suppression of turbulent flow conditions

These tests were conducted with a Reynolds number near the critical value of 2300 first, then extended to Reynolds number well above 6000. The pump was set at a constant Q of 95.392 m^3/h that corresponded to a flow velocity v of 168.2 cm/s. The conditions of the initial test were crude oil with an initial viscosity of 93.7 cP at 11.5 °C, a Q of 95.392 m^3/h, laminar flow with a N_R = 2160.82, and a pressure drop along the pipeline of 2.51 bar/km. The application of an electric field of 2300 V/cm reduced the oil viscosity to 85.5 cP, which increased the N_R to 2368.1, which corresponds to a turbulent flow regime. However, if the flow were turbulent, the pressure loss would increase to 3.85 bar/km (Eq. 3); while in fact, the pressure loss was 2.296 bar/km and the pump power requirement was 52.4 kW (reduced from 57.4 KW). This experimental run confirmed that the flow of crude oil under the influence of the ER treatment remained laminar.

A further increase of the electric field to 3000 V/cm caused an additional reduction of the oil viscosity to 75.6 cP and an increase in the N_R to 2678.2. Likewise, if the flow regime were turbulent at this condition, the pressure drop along the loop would increase to 3.73 bar/km. On the contrary, the pressure loss along the pipeline reduced to 2.03 bar/km, and the pump power requirement decreased to 48.3 kW, which corresponds to a laminar flow regime. Observations from replication tests were consistent.

Another field test evaluated the performance of the paraffin base Daqing crude oil, which has a pour point around 30°C. The transportation of this oil requires that the temperature within the pipeline system must be maintained in the range of 55–72°C through 15–20 km of insulated pipeline length (pipeline inner diameter 14.5 cm), before the pipeline system reaches another heating station.

Initially, several pre-tests established the conditions for turbulent flow regime within the temperature range previously indicated. For example, crude oil at 55.6°C and viscosity of 16.92 cP was flowed through the pipeline at a flow rate of 34.46 m^3/h and a pressure of 7.0 bar; under these conditions, N_R was 4128.3 (turbulent regime). In another pre-test, crude oil at 71.1°C and a viscosity of 12.4 cP was pumped at a pressure of 7.0 bar. The experimentally measured Q was 36 m^3/h. According to Eq. (6), under these flow conditions (i.e. pressure and oil viscosity), Q must be 36.02 m^3/h for a turbulent flow regime, which was in agreement with the experimentally measured Q. On the other hand, if the flow were laminar at the same flow conditions, the calculated Q using Eq. (1) should be 47.02 m^3/h, which is much higher than the measured Q.

In other pre-experimental run, crude oil at 55.6°C was flowed through the test loop at a pumping pressure of 8.35 bar. The measured Q was 38.1 m^3/h. If the flow were laminar, according to Eq. (1), the Q should be 41.1 m^3/h. However, the measured Q (38.1 m^3/h) was equal to the Q estimated using the Blasius formula (Eq. 6) of 38.11 m^3/h.

Overall, these pre-tests demonstrated that the flow of crude oil at 55.6 and 71.1°C was turbulent and more importantly that heating of the crude oil does not suppress turbulence.

The procedure used to evaluate the effect of the application of an electric field on the suppression of turbulence during the flow of crude oil through the test loop was as follows.

(1) AOT device turned-off

Flow conditions: temperature of crude oil = 55.6 °C, pumping pressure = 3.1 bar, Q = 16.4 m^3/h, and N_R = 1964.7 (laminar flow regime).

(2) AOT device turned-on

The application of an electric field of 13.3 kV/cm reduced the oil viscosity along the flow direction to 14.14 cP and gradually increased Q to 19.6 m^3/h. Although N_R increased to 2808.9, the flow regime was still laminar (based on the theoretical flow rate, which was in agreement with the experimentally measured Q).

In order to test the crude oil flow behavior at much higher N_R at a constant electric field of 13.3 kV/cm, the flowing pressure was increased from 3.1 to 5.0 bar and Q was increased to 31.6 m^3/h, which corresponded to an N_R of 4528.6. Nevertheless, under these conditions the flow remained laminar because the measured Q was in agreement with the theoretical estimation (Eq. 1) of Q = 31.61 m^3/h for a laminar flow regime.

A further increase in the pumping pressure to 7.0 bar, under a constant electric field of 13.3 kV/cm, caused an increase in Q to 44.3 m^3/h and an N_R of 6348.7. However, according to Eq. (1), the flow of crude oil remained laminar. **Table 2** summarizes these experimental observations.

Flow rate (m^3/h)	Viscosity (cP)	Reynolds number	Electric field (V/mm)	Pressure (bar)	Temperature (°C)	Flow regime
34.36	16.92	4128.3	0	7.0	55.6	Turbulent
36.0	12.40	5890.3	0	7.0	71.1	Turbulent
38.1	16.92	4565.6	0	8.35	55.6	Turbulent
16.4	16.92	1964.7	0	3.1	55.6	Laminar
19.6	14.14	2808.9	1333	3.1	55.6	Laminar
31.6	14.14	4528.6	1333	5.0	55.6	Laminar
44.3	14.14	6348.7	1333	7.0	55.6	Laminar

Table 2. Test results with $N_R > 2300$.

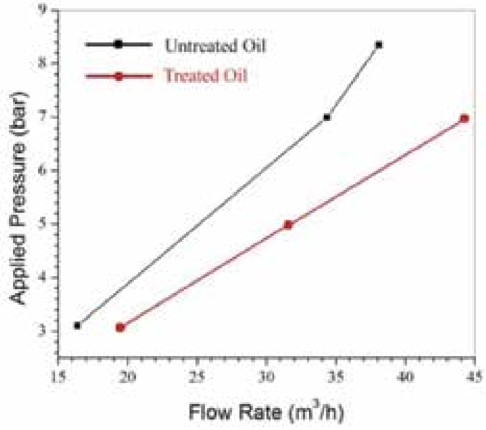


Figure 11. Pumping pressure versus flow rate.

Figure 11 plots the applied pumping pressure as a function of Q (m^3/h) for untreated and treated crude oil. It is clear that even at very high Q (40 m^3/h) and large N_R= 6348, the flow regime of the ER-treated crude oil remained laminar. On the contrary, the flow of the untreated oil became turbulent N_R >2300. These experimental observations clearly confirm that the ER treatment effectively suppresses the onset of turbulent flow regime.

2.5. Field tests on a section of the keystone pipeline

These field tests employed a section of the Keystone Phase II pipeline near Wichita, Kansas. **Figure 12** shows a picture of the AOT device installed in this pipeline system. The device was downstream of the pump, which pumped the crude oil to the top of the device, entering the four parallel cylinders through the mesh electrodes, and then to the pipeline downstream.

Figure 12. AOT device installed on the Keystone pipeline system.

These tests evaluated the performance of an asphalt base crude oil. The crude oil had a density of 0.887 g/cm^3 and a viscosity of 214.1 cP at 25°C. The inner diameter of the pipeline was 35 inch (88.9 cm) and Q was kept constant at 2280 m^3/h, which corresponds to a flow velocity of 1.02 m/s. Under these conditions, the N_R was 3757.9, which indicates turbulent flow conditions. From Eq. (5), the estimated friction factor for this turbulent flow is $f_T = 0.04011$; while the pressure difference along the pipeline was estimated using Eq. (11) as follows,

$$\Delta P = \tfrac{1}{2}\rho v^2 f_T L / D \tag{11}$$

where L is the distance between the Keystone pump station and the next downstream pump station, ϱ is the flow velocity, and D is the pipeline diameter.

Equation (12) allows estimating the required pumping power, P_{wi}.

$$Pwi = Q\Delta P = \pi\rho v^3 DLf_T / 8 \tag{12}$$

where Q is the flow rate and ΔP is the pressure difference in Eq. (11). The application of an electric field caused the reduction of the crude oil viscosity along the flow direction from 214.1 to 142.5 cP; while the viscosity of the oil in the direction perpendicular to the flow was significantly increased (>700 cP). Under these conditions, the treated oil flow was laminar. **Figure 13** shows that after the AOT device is turned-on, the treated crude oil flowing under laminar conditions pushes the rear of the untreated oil downstream the pipeline, which flows under turbulent conditions.

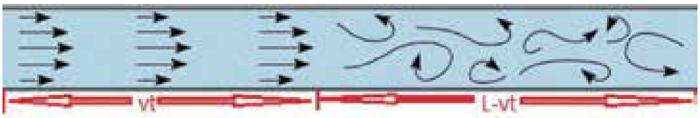


Figure 13. Treated oil under laminar flow conditions pushes the untreated oil under turbulent flow conditions downstream the pipeline.

If the AOT device was on for time t (**Figure 13**), the length of the laminar flow section is vt along the pipeline; while the turbulent flow had length of $L\text{-}vt$. The Reynolds number for the laminar flow was 5646.1, and the friction factor was $f_L = 0.011335258$. Equation (13) allows the estimation of the pump power requirements for the period $0 < t < L/v$ as follows,

$$Pw(t) = \pi\rho v^3 D[vtf_L + (L - vt)f_T] / 8 = Pwi[1 - (1 - f_L / f_T)vt / L] \tag{13}$$

Substituting the values for f_L and f_T, the pump power requirements for the period of $0 < t < L/v$ were calculated as follows (Eq. 14):

$$Pw(t) = Pwi(1 - 0.7195vt / L) \tag{14}$$

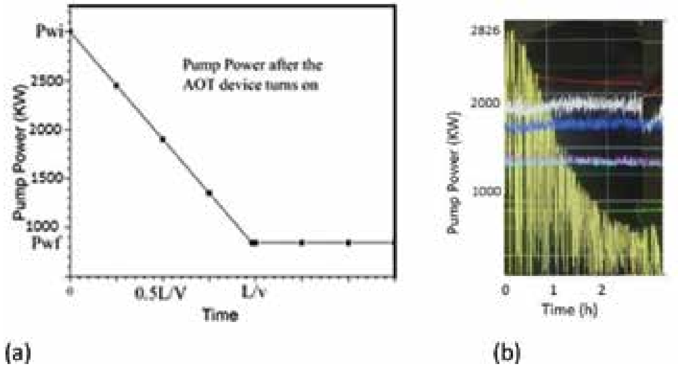


Figure 14. (a) Estimated pump power requirements as a function of time and electric field. (b) Experimental pump power versus time.

After $t \geq L/v$, only treated oil occupied the test section of the pipeline, and the calculated pump power was 0.28 P_{wi}. This indicates that the application of the ER treatment reduced the pumping requirements by 72%. **Figure 14** presents these calculated power requirements (**Figure 14a**) and the experimental pump power requirements (**Figure 14b**).

Figure 14b displays the experimental pump power reduction after the application of ER treatment. Before the treatment, the pump required a power of 2826 kW to transport the crude oil. After 2 hours of treatment, the pump power requirements stabilized at around 800 kW, while Q remained constant at 2280 m^3/h. In this case, the total reduction of pumping power requirements was 71.7%.

In this experimental study, the AOT device required <1 kW of power; while the pumping power required to transport the heavy crude oil at a Q = 2280 m^3/h was significantly reduced with overall power savings > 2000 kW. These experimental observations confirm the theoretical predictions and demonstrate the efficiency of this technology for transporting heavy crude oil via pipeline.

2.6. Lasting effect of the ER treatment on crude oil flowing properties

The anisotropic viscosity of the crude oil is the result of the aggregation of suspended particles into short chains along the flow direction under the effect of an electric field. Therefore, the reduced crude oil viscosity along the flow direction and the turbulence suppression effect will diminish if the aggregated short chains deassembled partially or completely.

Laboratory-bench scale tests evaluated the lifespan of the anisotropic viscosity effect after the ER treatment. The experimental procedure consisted in the application of the electric field to the oil sample at a pre-established temperature for about 5 seconds. Afterwards, the sample was stored at the corresponding temperature, and the crude oil viscosity was measured as a function of time. **Tables 3** and **4** summarize the experimental results obtained from the evaluation of two crude oils.

Viscosity (cP)	911	390	408	421	441	480	487
Time (h)	Untreated	0	4	8	12	23	26

Table 3. Viscosity performance of the Daqing crude oil after the ER treatment at 35.1°C. The applied electric field was 8 kV/cm for 5 seconds.

Viscosity (cP)	261.3	121.1	151.2	172.4
Time (h)	Untreated	0	12	24

Table 4. Viscosity performance of crude oil (API 34°) after the ER treatment at −3.1°C. The applied electric field was 1.6 kV/mm for 5 seconds.

These experimental results indicate that while the aggregated chains gradually deassembled as a function of time, the deaggregation process is slow and the viscosity of the crude oil increases very slowly. In these experiments, the anisotropic viscosity of the treated crude oil lasted for more than 24 hours.

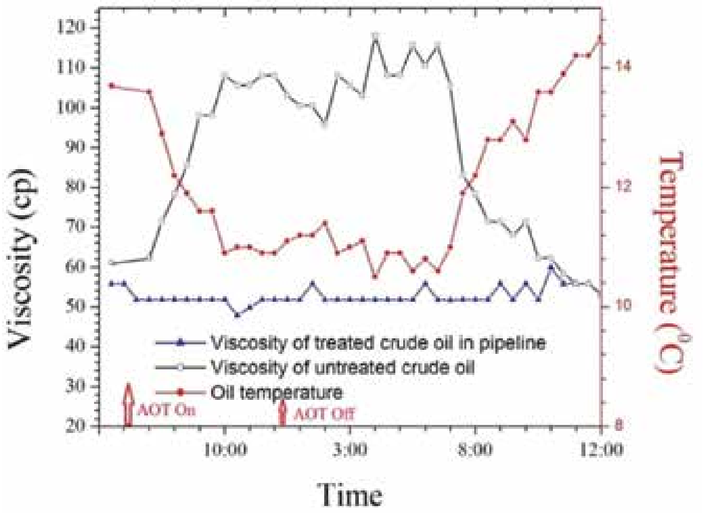


Figure 15. Crude oil viscosity and temperature as a function of time.

Tests at the RMOTC pipeline also evaluated the lifespan of the ER treatment. These field tests used the pipeline loop described in Section C and employed a crude oil with an API° 34° and an initial viscosity of 118.06 cP. The positive displacement pump drove the crude oil through the AOT device and the pipeline loop during six and half hours. The electric field applied was 2 kV/cm, which reduced the viscosity of the crude oil along the flow direction from 118.06 to 51.8 cP (viscosity reduction of 56.12%). After 6.5 hours, the AOT device was turned-off, but the crude oil circulated the pipeline loop for more than 11 hours. During this period, the pressure loss across the pipeline loop and the pump power requirements were continuously monitored.

The experimental observations indicate that the reduced viscosity of the treated oil, the pressure loss, and the pump power requirements remained stable during a period of 11 hours. Afterwards, the pressure loss and pump power requirements started to increase, signifying that the viscosity reduction effect on the treated crude oil began to disappear. **Figure 15** summarizes these experimental observations.

The lasting effect of the ER treatment (11 hours) obtained in the pipeline loop (field test) was shorter than the lasting effect determined at the laboratory scale (>24 hours). In the field test, the PD pump continuously pumped the crude oil through the pipeline loop. This continuous pumping through the PD pump could cause the disruption and breaking of the aggregated particles that induce the oil viscosity increase; while in the experiments conducted in the laboratory, only Brownian motion caused shear forces on the aggregated chains.

Nevertheless, in industrial ER applications, a treatment lifespan of 11 hours seems to be practical, considering that the electric field can be re-applied to adjust the viscosity of the crude oil as needed. Furthermore, the lasting effect of the ER treatment simultaneously suppresses turbulence [24].

3. Conclusions

Electrorheology, ER, is effective in simultaneously reducing the viscosity and suppressing turbulence during oil transportation via pipeline.

Experimental work at laboratory bench scale and field tests demonstrate the ER technology efficiently induces the aggregation of suspended particles contained in crude oils. These aggregated particles form short chains along the flow direction, which simultaneously reduce the crude oil viscosity and suppress turbulence, enhancing flow output.

Typical flow of crude oil in pipeline becomes turbulent when the Reynolds number exceeds 2300; the ER-treated crude oil remains laminar even at Reynolds numbers close to 10,000. Furthermore, field tests indicate that the ER effect on the viscosity and flow properties of the crude oil lasts 11 hours, after the ER treatment has ceased. The application of this technology for oil transportation via pipeline is in rapid development.

The ER technology shows great potential for heavy oil extraction and EOR operations; however, these applications require significant more research.

Author details

R. Tao

Address all correspondence to: rtao@temple.edu

Department of Physics, Temple University, Philadelphia, PA, USA

References

[1] R. Von Flatern. Paraffins: the scourge of deepwater development. *Offshore* 57, N3, 28-31 (1997).

[2] R, Tao & X. Xu. Reducing the viscosity of crude oil by pulsed electric or magnetic field. *Energy Fuels* 20, 2046-2051 (2006).

[3] R. Tao. Electrorheology for efficient energy production and conservation. *J Intell Mater Syst Struct*22, 1667-1671 (2011).

[4] H. Tang, K. Huang & R. Tao. Electrorheology improves transportation of crude oil. *J Intell Mater Syst Struct* 22, 1673-1676 (2011).

[5] B. Hof, J. Westerweel, T. W. Schneider, and B. K. Eckhardt. Finite lifetime of turbulence in shear flows. *Nature* 443, 59 (2006).

[6] K. Avila, D. Moxey, A. de Lozar, M. Avila, D. Barkley. The onset of turbulence in pipe flow. *Science* 333, 192 (2011).

[7] B. Hof, A. de Lozar, M. Avila, X. Y. Tu, T. M. Schneider. Eliminating turbulence in spatially intermittent flows. *Science* 327, 1491 (2010).

[8] D. Vergano. Turbulence theory gets a bit choppy. *USA Today*. September 10 (2006).http://usatoday30.usatoday.com/tech/science/columnist/vergano/2006-09-10-turbulence_x.htm.

[9] R. Tao and G.Q. Gu. Suppressing turbulence and enhancing the liquid suspension flow in pipeline with electrorheology. *Phys Rev E* 91, 012304 (2015).

[10] P. R. H. Blasi*u*, Das Aehnlichkeitsgesetz bei Reibungsvorgangen, in Flüssigkeiten. Forschungsheft 131, 1 (1913). (The law of similarity in friction processes in liquid, Research Bulletin 131, 1 (1913)).

[11] J. L. Zakin. Polymer and Surfactant, Drag Reduction In Turbulent Flows, *in Polymer Physics* (edited by L. A. Utracki and A. M. Jameson, Wiley, Hoboken, NJ, USA, 2009), 89-127.

[12] W. M. Winslow. Induced fibration of suspensions. *J Appl Phys* 20, 1137 (1949).

[13] R. Tao and J. M. Sun. Three-dimensional structure of induced electrorheological Solid. *Phys Rev Lett* 67, 398 (1991).

[14] T. J. Chen, R. N. Zitter, and R. Tao. Laser diffraction determination of the crystalline structure of an electrorheological fluid. *Phys Rev Lett* 68, 2555 (1992).

[15] R. Tao, E. Du, H. Tang, X. Xu. Neutron scattering studies of crude oil viscosity reduction with electric field. *Fuel* 134, 493 (2014).

[16] A. Einstein. The motion of elements suspended in static liquids as claimed in the molecular kinetic theory of heat, *Ann Phsik* 17 (8), 549-560 (1906); A new determination of the molecular dimensions. *Ann Phsik* 19 (2), 289-306 (1906).

[17] G. B. Jefferry. The motion of ellipsoidal particles immersed in a viscous fluid. *Proc R Soc Lond A*, 102, 161 (1922).

[18] I. M. Krieger and T. J. Dougherty. A mechanism for non-Newtonian flow in suspensions of rigid spheres. *Trans Soc Rheol* 3, 137 (1959).

[19] A. Donev, I. Cisse, D. Sachs, E. Variano, F.H. Stillinger, R. Connelly, S. Torquato, P. M. Chaikin. Improving the density of jammed disordered packings using ellipsoids. *Science* 303, 990-993 (2004).

[20] W. N. Man, et al. Experiments on random packing of ellipsoids. *Phys Rev Lett* 94, 198001:1-4 (2005).

[21] M. Miesowicz. The three coefficients of viscosity of anisotropic liquids, *Nature* 158, 27 (1946).

[22] G. Segre & A. Silberberg. Behavior of macroscopic rigid spheres in Poiseuille flow. *J Fluid Mech* 14, 136–157 (1962).

[23] R. Tao and H. Tang. Reducing viscosity of paraffin base crude oil with electric field for oil production and transportation. *Fuel* 118, 69 (2014).

[24] M. U. Babler, L. Biferale, and A. S. Lanotte. Breakup of small aggregates driven by turbulent hydrodynamical stress. *Phys Rev E* 85, 025301 (2012).

Edited by Laura Romero-Zeron

Commercial application of chemical enhanced oil recovery (cEOR) processes is expected to grow significantly over the next decade. Thus, Chemical Enhanced Oil Recovery (cEOR): A Practical Overview offers key knowledge and understanding of cEOR processes using an evidence-based approach intended for a broad audience ranging from field operators, researchers, to reservoir engineers dealing with the development and planning of cEOR field applications. This book is structured into three sections; the first section surveys overall EOR processes. The second section focuses on cEOR processes, while the final section describes the electrorheology technology. These sections are presented using a practical and realistic approach tailored for readers looking to improve their knowledge and understanding of cEOR processes in a nutshell.

Photo by kodda / iStock

IntechOpen

ISBN 978-953-51-4171-6