EFFECT OF CRUDE OIL COMPOSITION ON WETTABILITY ALTERATION DURING IMMISCIBLE CO_2 FLOODING

BY

MUZZAMMIL SHAKEEL

A Thesis Presented to the
DEANSHIP OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

PETROLEUM ENGINEERING

December 2014

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN 31261, SAUDI ARABIA

DEANSHIP OF GRADUATE STUDIES

This thesis, written by **MUZZAMMIL SHAKEEL** under the direction his thesis advisor and approved by his thesis committee, has been presented and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE IN PETROLEUM ENGINEERING**

Dr. Sidqi Abu Khamsin
(Advisor)

Dr. Abdullah Saad Sultan
Department Chairman

Dr. Hasan Al-Yousef
(Member)

Dr. Salam A. Zummo
Dean of Graduate Studies

DEANSHIP OF GRADUATE STUDIES

Dr. Enamul Hossain
(Member)

14/5/15

Date

Dedication

I dedicate my work to my family and friends who had been a constant support in all my endeavors.

ACKNOWLEDGEMENTS

I would like to express my sincere appreciation and gratitude to my thesis advisor Dr. Sidqi Abu Khamsin and my thesis committee members Dr. Hasan Al-Yousef and Dr. Enamul Hussain for their continuous support throughout my research period. I especially acknowledge the support of Dr. Sidqi Abu Khamsin and I am thankful to him for his precious time and commitment. His precious guidance and advice helped me grow confidence and ultimately making me capable of achieving and completing this research.

I would like to express my deepest appreciation to Mr. Abdul Samad and Mr. Muhammed Ali Sahito, who both showed good support and had the substance of ultimate guidance. Without their help and guidance, this research would not have been possible.

I would like to thank my family for their strong support and encouragement throughout my study period and who were a source of continuous inspiration throughout my Master’s degree.

Special thanks are due to the Department of Petroleum Engineering at King Fahd University of Petroleum & Minerals and Research Institute (RI), including Faculty, Staff and Fellow Graduate Students and Friends who contributed directly or indirectly to the accomplishments of this work.

I also gratefully acknowledge the help of Dr. Abdullah Sultan, Chairman of Petroleum Engineering Department, who cooperated in the arrangement of material and equipment from abroad.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

USBM	:	United States Bureau of Mines
SEM	:	Scanning Electron Microscopy
NMR	:	Nuclear Magnetic Resonance
EOR	:	Enhanced Oil Recovery
CO_2	:	Carbon Dioxide
cP	:	Centipoise
MPa	:	Mega Pascal
MMP	:	Minimum Miscibility Pressure
SARA	:	Saturates Aromatics Resins & Asphaltenes
HPLC	:	High-Performance Liquid Chromatography
PVT	:	Pressure-Volume-Temperature
API	:	American Petroleum Institute
mD	:	Milli-Darcy
µL	:	Micro Liter
µm	:	Micro Meter
psig	:	Pounds Per Square Inch (gauge)
^{o}C	:	Centigrade
^{o}F	:	Fahrenheit
cc	:	Cubic Centimeter
N_2	:	Nitrogen
KCL	:	Potassium Chloride
SCCM	:	Standard Cubic Centimeters per Minute
SCF	:	Standard Cubic Feet

ft^3/day	:	Cubic Feet per Day
S_{wi}	:	Initial Water Saturation
S_{ori}	:	Initial Residual Oil Saturation
IOIP	:	Initial Oil In-Place
S_{gi}	:	Initial Gas Saturation
S_{oi}	:	Initial Oil Saturation
lb/ft^3	:	Pound per Cubic Feet
PV	:	Pore Volumes
min	:	Minute
ml	:	Milli-litre

ABSTRACT

Full Name : Muzzammil Shakeel

Thesis Title : Effect of Crude Oil Composition on Wettability Alteration During Immiscible CO_2 Flooding

Major Field : Petroleum Engineering

Date of Degree : December, 2014

With increasing demand for hydrocarbons in the world, it is important to utilize all the possible tools and techniques to produce maximum hydrocarbon from the sub-surface. Since hydrocarbons are a non-renewable resource, research is always being carried out to increase the recovery from existing reservoirs. Facts and figures show that carbonate reservoirs contain more than half of the world's hydrocarbon reserves. Thus various recovery methods are used to maximize recovery from carbonate reservoirs.

Wettability is an influential factor in the recovery of oil from reservoirs in general. Carbonate rocks are usually oil-wet; therefore, considerable amount of oil remains adhered to the rock surface and is not recovered from the reservoir by water flooding, thereby causing low oil recovery.

Carbon dioxide flooding is a proven technique which can be employed in order to enhance oil recovery from such reservoirs. Carbon dioxide injection is more desirable compared to other gases due to easy availability, low injectivity problems and low formation volume factor. Carbon dioxide not only swells the oil and decreases the oil viscosity, but also alters the wettability of the reservoir rock. This increases the oil

recovery which was previously low due to the oil-wet nature of the rock. However, in reservoirs at shallow depths or incompatible oil compositions miscible displacement is unfeasible. For such reservoirs, immiscible carbon dioxide flooding where the gas is injected below the minimum miscibility pressure could be promising.

Because of low injection pressure in immiscible CO_2 flooding, the beneficial effects of carbon dioxide on the oil are certainly reduced. Therefore, it is necessary to study the extent of wettability alteration of the reservoir rock during the process as this could constitute the bulk of the improvement in displacement.

This study focuses on the effect of immiscible CO_2 flooding on the wettability of Indiana limestone, a carbonate rock, employing three different crude oils. By varying the API gravity of the oil, the most influential crude oil property(s) on wettability alteration are determined. Core-flooding experiments are conducted and their results are carefully analyzed. An existing mathematical model developed to incorporate continuous wettability alteration in immiscible CO_2 flooding process is also verified based on the experimental results.

ملخص الرسالة

الاسم الكامل: م. مزمل شكيل

عنوان الرسالة: تأثير تركيب الزيت الخام على خاصية القابلية-للبلل أثناء عملية ضخ ثاني أكسيد الكربون الغير قابل للذوبان

التخصص: هندسة البترول.

تاريخ الدرجة العلمية: ديسمبر 2014

مع ازدياد الطلب على الطاقة في العالم، فإنه من المهم استغلال كل الوسائل والإمكانيات لإنتاج أقصى كمية من الهيدروكربونات من سطح الأرض. وبما أن الهيدروكربونات من وسائل الطاقة الغير متجددة، فإن الأبحاث مستمرة لزيادة الإنتاج من الخزانات اللتي تم اكتشافها مسبقاً. والحقائق تشير إلى أن الخزانات-الكربونية تحتوي على أكثر من نصف مخزون من الهيدروكربونات. ولهذا فإن طرق إستخراج متنوعة يتم استخدامها لتضخيم الإنتاج من الخزانات-الكربونية.

تعتبر خاصية قابلية-البلل عنصر مؤثر في عملية استخراج الزيت من الخزانات بوجه عام. الخزانات-الكربونية تكون مبللة بالزيت عادة؛ ولهذا يتبقى بها كميات كبيرة من الزيت ملتصقة بالصخر ولا تستخرج من الخزان بضخ الماء، مما يسبب انتاج قليل للزيت.

ضخ ثاني أكسيد الكربون أثبتت أنها طريقة يمكن استخدامها لتحسين انتاج الزيت من تلك الخزانات. وحقن ثاني أكسيد الكربون بالتحديد مفضل على غيره من الغازات لسهولة توفيره وقلة المشاكل التي يسببها بالإضافة إلى صغر حجمه الطبقيّ. وثاني أكسيد الكربون لا يعمل فقط على الذوبان في الزيت وتقليل لزوجته، لكنه كذلك يغير من خاصية القابلية-للبلل الخاصة بالخزان. وهذا التغيير ينتج عنه زيادة في انتاج الزيت بسبب تغيير طبيعة الصخر المحبة للزيت. ولكن في حالة وجود الزيت على أعماق قليلة أو في صور مركبات غير متوافقة، يكون استخدام الإزاحة-المذابة غير مجدي. وفي تلك الخزانات، هناك احتمال بتحسين العملية في حالة ضخ ثاني أكسيد الكربون الغير قابل للذوبان (حيث تتم عملية الضخ أسفل أقل قيمة للضغط يحدث عندها الذوبان).

بسبب قلة الضغط المستخدم في ضخ ثاني أكسيد الكربون الغير قابل للذوبان، فإن الفوائد الأساسية لإستخدام ثاني أكسيد الكربون يقل تأثيرها. ولهذا، فإن دراسة مقدار التغيير في قابلية-البلل للصخر يصبح ذو أهمية بالغة باعتباره التأثير الأهم في العملية.

هذا البحث يقوم بالتركيز على تأثير ضخ ثاني أكسيد الكربون الغير قابل للذوبان على خاصية القابيلة-للبلل الخاصة بصخر الجير الحجري بإنديان، وهو صخر كربوني يحتوي على ثلاث أنواع مختلفة من الزيت. بتغيير قيمة الكثافة الخاصة بالزيت، يتم دراسة أكثر الخصائص المؤثرة على خاصية القابلية-للبلل. تم اجراء تجارب الضخ على العينات الصخرية وتم تحليل نتائج تلك التجارب بعناية. تم تطوير نموذج رياضي موجود بحيث يستوعب التغيير المستمر في خاصية القابلية-للبلل في حالة ضخ ثاني أكسيد الكربون الغير قابل للذوبان، وتم التحقيق كذلك بناء على نتائج التجارب.

CHAPTER 1

INTRODUCTION

With the increasing demand of oil in the world and limited resources at the other end, petroleum engineers strive to produce maximum amount of hydrocarbons from the available producing reservoirs. Typically about two-third of the original oil in place is left behind even after primary and secondary recovery (water flooding). This remaining oil may be constituted as trapped and bypassed oil [1]. Therefore a need of enhanced oil recovery techniques becomes imperative in increasing the oil recovery from existing reservoirs. Wettability of the reservoir rock plays a vital role and a major determining factor in terms of total oil recovery, along with many other factors.

In this introductory chapter, the phenomenon of wettability of rocks and its importance in increasing the oil recovery will be discussed. Enhanced oil recovery techniques with emphasis on CO_2 flooding will also be a part of this chapter.

1.1 Wettability of Rocks

Wettability is a measure of the preferential tendency of a rock to allow a fluid to adhere to (spread over or wet) its surface, in the presence of another fluid. With respect to two immiscible fluids in a porous medium, wettability is the relative adhesion of one of the fluids to the surface of the rock [2].

There are four states of wettability: water-wet, oil wet, fractionally wettability and mixed wettability. A rock system is considered to be water-wet when water is adhered to the surface of the rock and the rock has more affinity for water. Alternatively, a rock is oil-wet when oil is adhered to the surface of the rock. A rock is termed fractionally-wet when the rock is neither preferentially water-wet nor oil-wet, both water and oil are adhered to the surface of the rock in different areas. In mixed-wet scenario, small pores in the rock are water-wet and filled with water while the larger pores are oil-wet and filled with oil to form a continuous phase [2]. When the rock has no strong preference for either oil or water, the rock system is said to be neutral-wet. Donaldson and Crocker (1977) presented colored photographs of residual oil saturation that are visual verification of the four states of wettability.

Wettability is considered as an important factor that controls the distribution and flow of fluids in the reservoir (Anderson, 1986). It is one of the parameters that control the remaining oil-in-place. Originally, reservoir rocks are water-wet, which means that the rock surfaces are covered with a thin water film. The original wettability is altered by the adsorption of polar compounds or deposition of asphaltenes from the crude oil (Dubey and Waxman, 1991; Croker and Marchin, 1988). Some polar compounds are soluble in water; they diffuse through the water film and become adsorbed on the rock surface making it oil-wet.

Most of the world's oil reserves are found in either sandstone or carbonate rocks. The wettability of sandstone rock generally ranges from neutral to strongly water-wet. However, carbonates generally exhibit mixed-wet to strongly oil-wet states. Thus, a large amount of oil is left behind in oil-wet reservoirs after water flooding that cannot be produced. This takes us to the idea of wettability alteration is such reservoirs to produce the oil left behind.

Wettability of reservoir rocks can be measured, both quantitatively and qualitatively, by a number of methods. Amott method and USBM method are the quantitative wettability measurement methods while relative permeability, SEM (scanning electron microscopy), NMR and contact angle measurement are regarded as qualitative measurement methods of wettability [3]. The contact angle is measured through the denser liquid phase and it has a range of 0 to 180^0. A contact angle of 180^0 implies complete oil-wet characteristics, while 0^0 means complete water-wet. Anderson (1986) classified wettability in terms of contact angle as water-wet (0-75^0), intermediate (75-115^0) and oil-wet (115-180^0).

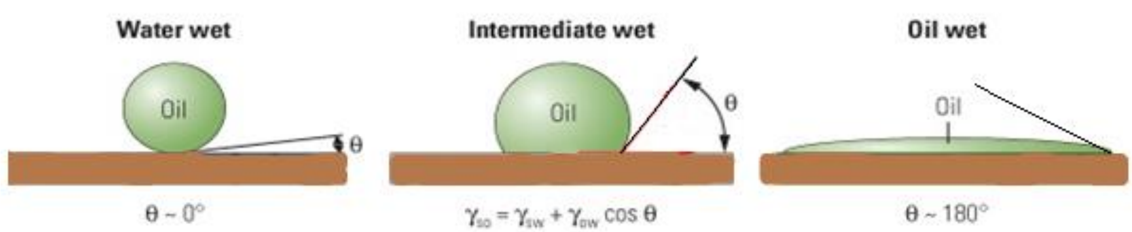

Figure 1.1: Classification of wettability by contact angle measurement

1.2 Enhanced Oil Recovery (EOR)

Water injection is very common and has been implemented since the late 19th century, and has become a standard practice since the second half of the 20th century. Enhanced oil recovery (EOR) is all about going beyond the simple water or gas injection for pressure maintenance [4]. EOR is defined as the techniques that are implemented in order to increase the oil recovery from reservoirs after primary and secondary recovery. EOR may involve the injection of substances in the reservoir that alter the reservoir rock and fluid properties.

EOR techniques are broadly categorized as gas injection (miscible) methods, thermal methods and chemical methods. These three broad categories are further divided into main categories as shown in Figure 1.2 below.

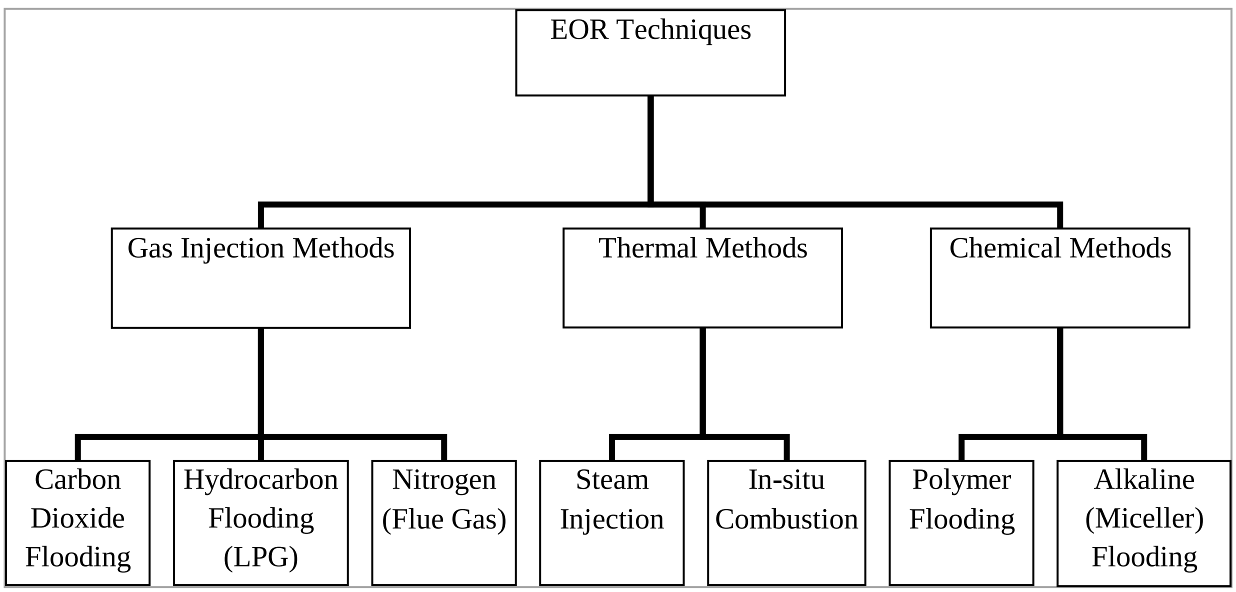

Figure 1.2: Classification of enhanced oil recovery techniques

The type of EOR technique to be implemented in a field or reservoir is based on certain selection criteria. The selection criteria may include parameters like reservoir pressure, reservoir temperature, depth, average permeability, net thickness, formation type, API gravity and viscosity of the crude oil. The decision of implementing an EOR technique depends on the extent of how much the reservoir characteristics matches the selection criteria. It also depends on the availability of resources and feasibility of a particular technique.

The most widely used EOR technique is thermal flooding, which currently constitutes the largest portion of EOR oil production. It involves heating up the reservoir – by steam injection or in-situ combustion – to make the oil less viscous. Carbon dioxide flooding is the second most common EOR technique used worldwide as shown in the Figure 1.3. This technique is discussed in detail in the next section.

Some of the successful applications of EOR projects around the world include Prudhoe Bay oilfield in Alaska with a recovery of 60%, the Permian Basin in the US, Weyburn oilfield and Midale oilfield in Saskatchewan and Midland Farms in Texas [5].

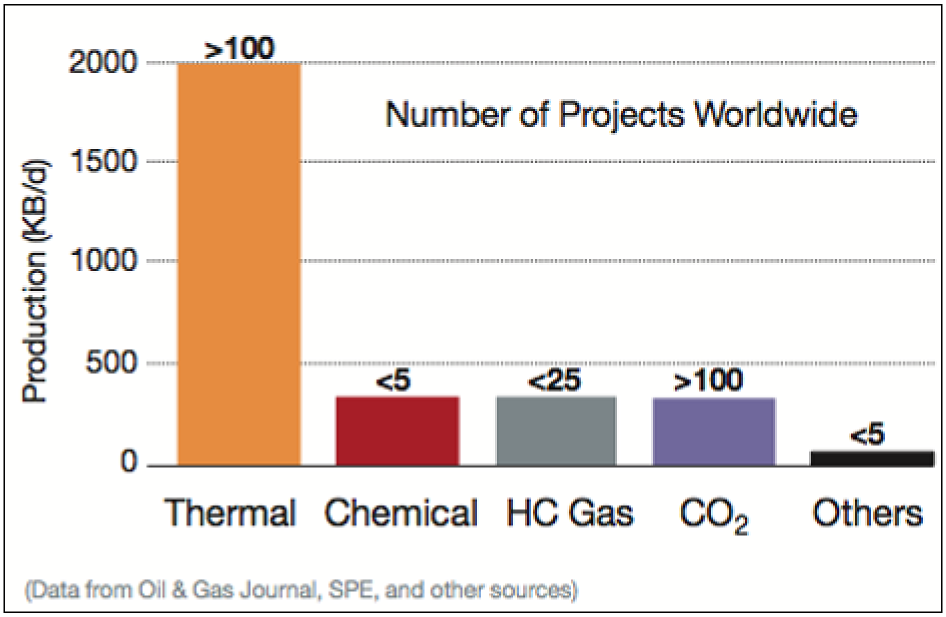

Figure 1.3: World oil production volumes by various EOR methods (2010)

1.3 Carbon Dioxide Flooding

Carbon dioxide is a colorless, odorless, non-reactive and non-combustible gas. CO_2 has a molecular weight of 44 and is 2-10 times more soluble in oil as compared to water. It has a viscosity of 0.0335cp at its critical point (1070 psia and 87.8 ºF). Its critical pressure is 7.38 MPa and its critical temperature is 87.8 ºF (31.0 ºC). The density of carbon dioxide varies between 0.1 and 0.8 g/cm^3, which is close to that of a typical light oil [6].

In carbon dioxide flooding, CO_2 gas is injected into the reservoir at or significantly above the reservoir pressure. Carbon dioxide flooding was first tried in 1972 in Scurry County, Texas, and has been very successful with a large number of CO_2 projects throughout the world [7]. According to a survey conducted in 2010, there were about 125 CO_2 flooding projects worldwide, with 110 in the U.S. [25], at least five in Canada, three in Hungary, four in Trinidad and a huge (10,700 acre) project in Turkey [8].

Usually in CO_2 flooding, most of the gas that is being injected for the purpose of EOR comes from naturally occurring reservoirs. However, technologies are being developed in order to produce CO_2 by natural gas processing, fertilizer, ethanol and hydrogen plants in areas where CO_2 is not naturally occurring [7].

Some of the fields where CO_2 flooding was used and are currently producing are Weyburn Field and Midale Field in Saskatchewan, Swan Hills Field in Edmonton, Heidelberg Field in Mississippi and West Hastings Field in Texas [5].

Carbon dioxide flooding can be conducted in both the miscible and immiscible mode. These modes are discussed in detail in the following sections.

1.4 Miscible Carbon Dioxide Flooding

When two fluids are said to be miscible, this entails that the two fluids dissolve in each other at all proportions. Miscibility between an injected fluid and the reservoir oil can be achieved through two mechanisms: first-contact miscibility and multiple-contact miscibility. First-contact miscibility occurs when the injected fluid mixes completely with the reservoir oil forming a single phase. Multiple-contact miscibility takes place in stages involving contact between a progressively modified injected fluid and the reservoir oil. By definition, miscible CO_2 flooding is the technique in which the gas is injected into the reservoir at or above the minimum miscibility pressure. Under such conditions, mass transfer between the oil and CO_2 occurs that leads to oil swelling and viscosity and surface tension reductions. Thus, miscible CO_2 flooding greatly improves the microscopic displacement efficiency, because as the CO_2 displaces the oil miscibly, the interfacial tension between the oil and CO_2 is also significantly reduced. Consequently, a lot of the entrapped oil could be mobilized enabling to achieve very low residual oil saturation [26]. In both mechanisms, miscibility requires a certain threshold pressure before it occurs; this pressure is called the minimum miscibility pressure (MMP). Thus in order to assure miscibility - both immediately or through multiple contacts - the operating pressure should be maintained at a pressure above the MMP.

Miscibility between CO_2 and crude oil is achieved through multiple contacts. When CO_2 flows through the reservoir, a vaporizing-condensing process takes place where CO_2 gas vaporizes the light to intermediate hydrocarbon components from the reservoir oil into the CO_2 gas and then later condenses them into the oil phase [9]. This process is depicted in Figure 1.4.

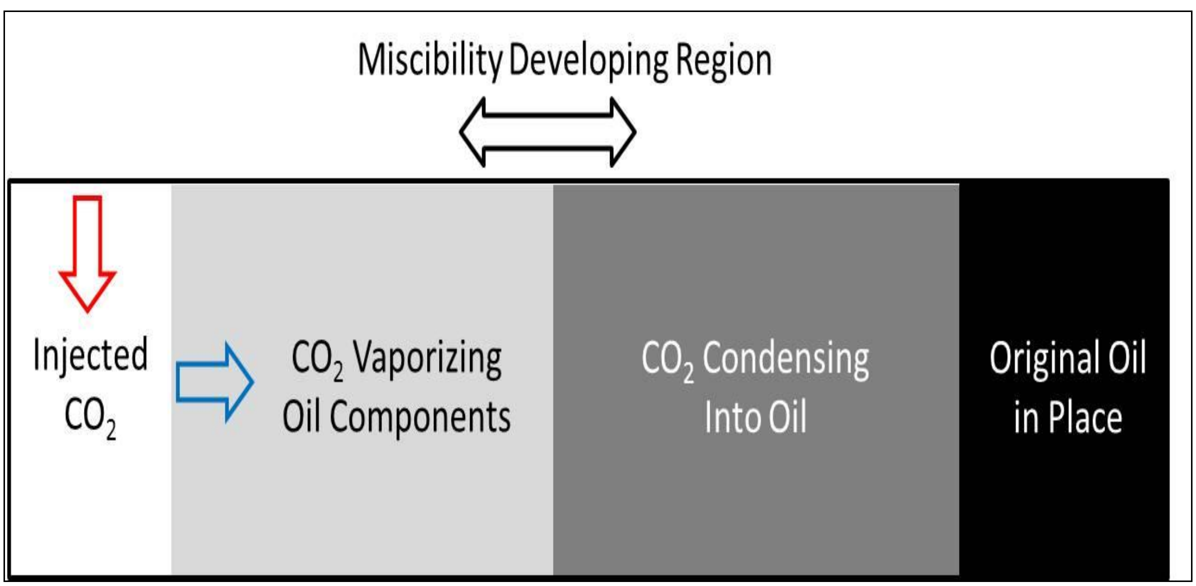

Figure 1.4: Developing miscibility during CO_2 injection

Along with pressure, temperature is a key contributing factor for the miscibility development between the reservoir oil and CO_2. [15]. The oil composition is also important since a high percentage of intermediate hydrocarbons (especially C_5 through C_{12}) is beneficial [16].

Miscible CO_2 flooding is usually feasible in deeper reservoirs where the reservoir pressure is naturally above the MMP, which is not the case with shallower reservoirs. Attempting to inject CO_2 – or any other fluid - at a pressure much larger than the reservoir pressure could cause reservoir fracturing, which is unfavorable.

The MMP for a given reservoir fluid and an injected fluid is usually determined through laboratory experiments. These experiments may use the slim-tube technique or the rising bubble experiment. Correlations are also available to provide a rough estimate of the MMP.

1.5 Immiscible Carbon Dioxide Flooding

In immiscible CO_2 flooding, the operating pressure is less than the MMP for the reservoir fluid and the injected fluid, thus miscibility is not achieved between the two phases. Thus, two distinct phases separated by a sharp interface are maintained [10]. Immiscible CO_2 flooding has a considerable potential for the recovery of moderately viscous oils, and thin formations, which are not suitable for other EOR techniques like thermal recovery techniques [11]. Immiscible CO_2 flooding can also be implemented in depleted reservoirs with low pressure in which increasing the reservoir pressure is not technically or economically feasible [18]. Besides the normal gas-liquid displacement, the recovery mechanism in this process involves reduction in oil viscosity, oil swelling, dissolved-gas drive and - possibly - wettability alteration. The effect of CO_2 on oil properties is discussed in detail in the following section.

Carbon dioxide interacts with the reservoir fluid, namely oil, by three mass transfer mechanisms. These mechanisms include solubility, diffusion and dispersion. Solubility is more significant while diffusion and dispersion take place to a lesser extent [11]. However, the success of the immiscible drive process depends on the amount of gas dissolving and diffusing into the oil and eventually improving oil properties.

As the most significant mechanism during CO_2 flooding, solubility of CO_2 in crude oil depends mainly on the temperature and pressure of the system and the oil composition. Solubility increases with pressure and reduced API gravity and decreases with temperature [11]. It is to be noted that carbon dioxide is more soluble in hydrocarbons as a gas rather than as a liquid [12].

Carbon dioxide mixes with the crude oil by solution as well as by diffusion. Diffusion is the microscopic transport of mass due to random molecular motion and is not dependent on any convection within the system [13]. Diffusion helps carbon dioxide penetrate into heavy oil, which may help to reduce gravitational and viscous instabilities [11]. Unlike solubility, diffusivity increases with increasing temperature [17].

Dispersion is the additional mixing of fluid that occurs in the porous medium due to velocity [11]. This additional mixing is due to the dispersive force of attraction, which occurs in highly polarizable molecules like hydrocarbons [14]. Thus, the physical and chemical phenomena that take place in the pore spaces during the travel of gas particles is regarded as dispersion.

1.6 Effect of CO_2 on Oil Properties

When dissolved in crude oil, carbon dioxide effects oil properties. It reduces the oil viscosity, promotes oil swelling and reduces the interfacial tension with water. Another interesting phenomenon that occurs, specifically in carbonate rocks, is rock wettability alteration. Therefore, under immiscible conditions, the oil recovery is highly improved because of all those effects.

Oil viscosity is a function of temperature, pressure and the amount of CO_2 dissolved in it [11]. The reduction in viscosity helps reduce the mobility ratio and enhance macroscopic displacement efficiency [22]. Swelling (increase in volume) of the crude oil causes disconnected oil blobs in the pore spaces to reconnect resulting in higher oil recovery [19]. It also leads to a lower residual oil saturation and better microscopic displacement efficiency [23]. The swelling factor increases dramatically at pressures below the oil's bubble point pressure [20]. The interfacial tension between water and oil is also reduced in the presence of CO_2 [21].

CHAPTER 2

LITERATURE REVIEW

Extensive study of the literature was done in order to shed light on the topic in detail, as the subject was challenging and requires knowledge of various aspects of CO_2 flooding and wettability alteration. A review of previous research works carried out on the subject is presented and discussed briefly in the following paragraphs.

Jackson et al. (1985) conducted dimensionless scaled experiments to evaluate the effects of rock wettability on CO_2 flooding. Wettability was found to be a major factor affecting the flood performance. Gravity forces dominated the flooding in water-wet conditions while viscous (fingering) forces controlled the flooding in oil-wet conditions. Maximum recovery was achieved by gravity forces with continuous CO_2 injection [27].

Potter (1987) conducted experiments studying the effects of CO_2 flooding on the wettability of West Texas dolomitic cores. The selected cores represented three types of wettability states: oil-wet, neutral (intermediate) and water-wet. Changes in relative permeability were examined before and after CO_2 flooding. Rock wettability was then inferred from changes in relative permeability trends. The results showed that the cores became slightly water-wet suggesting extraction of the rock surface caused by CO_2 [28].

Vives et al. (1999) studied the effect of wettability on adverse mobility in immiscible flooding systems. A quarter 5-spot pattern experiment was used in both drainage and imbibition conditions and the macroscopic bypassing in adverse mobility immiscible floods was measured. The experimental results suggested that the macroscopic viscous fingering was present in adverse mobility immiscible floods. Viscous fingering and gravity override were larger for the drainage process than for imbibition process. In water-wet media, continuous injection of CO_2 is better than WAG injection if the viscosity ratio of the oil-CO_2 mixture is about 20. However, at higher viscosity ratios and density differences a WAG ratio of 3 to 5 is more effective than continuous injection of CO_2 [29].

Chalbaud et al. (2007) addressed the role of wettability during CO_2 flooding. Core experiments were conducted on a carbonate reservoir for two wettability conditions: water-wet and intermediate-wet. CO_2 flooding was performed in glass micro-models to trace the distribution of fluids under the same conditions. The results showed that CO_2 did not contact the solids in water-wet media while for intermediate-wet media the CO_2 partially wetted the solids [30].

Okasha et al. (2007) conducted a detailed study and survey of wettability evaluation for Arab-D carbonate reservoir (Upper Jurassic) in Saudi Arabia. Wettability results were collected from various quantitative and qualitative methods over fifty years using preserved and restored core material. Amott wettability results and USBM wettability indices indicated a general trend of slightly oil-wet to intermediate wettability behavior of Arab-D core material. However samples located below the oil-water contact demonstrated an intermediate to slightly water-wet behavior [3].

Zekri et al., (2007) investigated the possible alteration of tight limestone core properties such as porosity, permeability, wettability and the effect of water shielding on a water driven slug of super critical CO_2 under miscible conditions. Core-flooding experiments were conducted using actual rock cores and fluids obtained from a field in Abu Dhabi at reservoir conditions of 4000 psia and 250^oF. Results showed that super critical CO_2 flood changed the wettability of water-wet limestone cores to more favourable condition of wettability, i.e. more water-wet condition [31].

Al-Otaibi et al. (2010) conducted extensive wettability studies to determine the optimum brine salinity which results in higher oil recovery at high pressure (upto 2000 psi) and elevated temperature (upto 270^oF) in carbonate rocks. Contact angle and Amott imbibition methods are the most common methods to measure the wettability or preferential affinity of reservoir rocks. Through contact angle measurements, it was determined that calcium carbonate substrates were oil-wet when sea water or formation water was used but became water-wet when aquifer or de-ionized water was used [32].

Fjelde and Asen (2010) presented their work on wettability alteration during water flooding and carbon dioxide flooding of chalk reservoir. Spontaneous imbibition experiments were conducted to evaluate the wettability conditions for five core plugs obtained from a fractured chalk reservoir in the North Sea. The work was carried out at reservoir conditions during water and CO_2 flooding. The results showed that in the first cycle of a CO_2-WAG process, the wettability was changed from mixed-wet or preferential oil-wet to more water-wet [33].

Sahin et al. (2012) discussed the successful application of immiscible CO_2 project in the Bati Raman heavy oil field. The project is running for the last twenty-five years and is still active. The recovery from the 1.85 billion barrels of initial oil in place has reached up to 10% from less than 2% primary recovery. Apart from immiscible CO_2, conformance improvement plan was also implemented in several parts of the field based on geological variations of the field. The conformance improvement plan included chemically improved WAG, gel treatment to plug natural fractures and CO_2/foam injection for reduced mobility ratio in severe CO_2 channeling areas [34].

Al-Mutairi (2013) developed a model for wettability alteration of carbonate rock in the presence of oil and carbonated water. The model was based on experiments that monitored the variation of the contact angle with time [35]. Also, Al-Mutairi, Abu-Khamsin and Hossain (2012) developed a new, modified Corey relative permeability model to calculate the phase relative permeability as a function of wettability. They then incorporated the two models into a displacement model that was solved using a numerical, 1-dimensional, two-phase immiscible simulation scheme utilizing MATLAB programming. The displacement model also addressed the swelling of the oil and reduction of its viscosity due to contact with CO_2. The combined model is designed to predict the performance of immiscible CO_2 flooding process where wettability of the reservoir rock is altered continuously. Core flooding experiments were also conducted under immiscible conditions to test the validity of the model [36].

Jalili et al. (2014) analyzed the chemical interaction between sea water ions, asphaltene colloids and silicate/calcite mineral as a substrate during water/low salinity water flooding. The wettability change to a less oil-wet condition was observed for both types of sandstone and carbonate reservoirs during low salinity water. This is because of the fact that the total interaction potential in a calcite/brine/asphaltene system is positive (repulsive) in low salinity sea water. Low salinity seawater for tertiary improved oil recovery is proposed after sea water injection for both sandstone and carbonate reservoir rocks, yielding an additional oil recovery from 5% to 15% from water-flooded sandstone and carbonate rocks [37].

CHAPTER 3

PROBLEM STATEMENT

3.1 Knowledge Gap

As observed in the literature review, numerous works have been conducted on CO_2 flooding, both in the laboratory as well as pilot and field projects. However, the literature lacks laboratory work on CO_2 flooding carried out in carbonate rocks under immiscible conditions. Since wettability alteration of these rocks along with changes in oil properties may improve the flooding efficiency significantly, these aspects of the process deserve more investigation.

Changes in oil properties are known to occur when the oil is contacted by CO_2. The extent of those changes depends, among other parameters, on the crude oil composition. Also, the wettability of carbonate rock has been observed to alter from oil towards water when exposed to CO_2. Therefore, it is necessary to look into the effect of oil composition on the extent of such changes, which could aid in screening successful CO_2 flooding candidates.

Furthermore, a 1-dimensional, numerical, continuous wettability alteration model (Al-Mutairi, 2012) was built to represent oil-CO_2 immiscible flow in porous media using a modified Corey relative permeability model. To verify the accuracy of the model against experimental data, the model employed CO_2 solubility and oil swelling data that was obtained from the literature, which is believed to be the cause of major errors in the model's prediction. Therefore, that model needs to be verified again using laboratory data on the oil to be tested.

3.2 Objectives

There were two primary objectives of this work:

- To study the effect of oil composition on wettability alteration by CO_2 in carbonate rocks through core-flooding experiments under immiscible conditions.
- To generate oil swelling data and incorporate it in the mathematical model of Al-Mutairi et al. to verify the model employing the core-flooding data.

3.3 Research Approach

Three different crude oils were selected over a range of API gravity, from light crude oil to heavy crude oil. Initial tests on each oil included SARA analysis, solubility of CO_2 and the resulting oil swelling factor. The CO_2-saturated oil viscosity was estimated by an accurate correlation.

CO_2 core-flooding experiments under immiscible conditions were conducted on Indiana limestone core plugs at reservoir conditions, using a different crude oil for each experiment. The contact angle was measured to determine the wettability of rock samples before and after CO_2 flooding.

The mathematical model (Al-Mutairi, 2012) will be tested by using the experimental data of the core-flooding experiments on the three crude oils. After inputting the oil test data into the model, the model's predictions will be compared with the results of the flooding experiments.

CHAPTER 4

EXPERIMENTAL WORK

This chapter presents all laboratory work that was conducted during this research. The work is divided into four stages. These are:

a. Oil characterization.

b. Measurement of oil swelling due to CO_2.

c. Core flooding experiments

d. Measurement of rock wettability before and after core flooding.

4.1 Oil Properties

Three Saudi Arabian crude oils were used in this study. Crudes 1 and 3 have API gravities of 40^o and 28.56^o, respectively, while Crude 2 was a blend of two other Saudi Arabian crudes (API gravities of 31.18^o and 37.74^o) with an API gravity of 34.30^o. Properties of the three crudes are listed in Table 4.1.

Table 4.1: Properties of crude oils

Parameter	Crude Oil 1	Crude Oil 2	Crude Oil 3
API Gravity	40 ^{o}API	34.30 ^{o}API	28.56 ^{o}API
Specific Gravity (@23.5^{o}C)	0.820	0.853	0.876
Density (@23.5^{o}C)	0.8187 g/cm^3	0.8508 g/cm^3	0.8737 g/cm^3
Density (@55^{o}C)	0.789 g/cm^3	0.826 g/cm^3	0.847 g/cm^3
Dead-Oil Viscosity (@55^{o}C)	1.741 cp	3.791 cp	13.98 cp

The oil composition was determined by SARA analysis. The technique provides the saturates, aromatics, resins and asphaltene fractions of the crude oil. The instrument used is a High-Performance Liquid Chromatograph, which employs refractive index and ultraviolet detectors [24]. Table 4.2 lists compositional analysis of the three crude oils.

Table 4.2: Summary of crude oil composition

Crude Oil	API Gravity	Saturates	Aromatics	Resins	Asphaltenes	Polarity
1	40 ^{o}	32.84%	57.90%	8.66%	0.63%	9.26%
2	34.30 ^{o}	36.77%	52.40%	8.66%	2.72%	10.83%
3	28.56 ^{o}	25.16%	62.11%	9.33%	3.40%	12.72%

4.2 Rock Core Properties

Core plugs, 3” x 1.5”, were cut from the same Indiana limestone core sample and were used in all experiments. Their porosity and permeability were measured at room conditions and were found to be 15% and 70 mD, respectively.

4.3 Swelling of Oil by CO_2

Since CO_2 dissolution in the crude oil changes the oil volume significantly and, thus, affects the displacement efficiency, tests were conducted to measure variation of oil volume with CO_2 (the swelling factor) at the experimental conditions. The conditions were set at 500 psig and 55 ºC (131 ºF).

4.3.1 Experimental Setup

The experimental setup used was a PVT system manufactured by Chandler. It contains an ISCO pump, a vacuum pump, an oil transfer cell, CO_2 cylinder, N_2 cylinder, a gasometer, and a 500-cc PVT cell with a displacement piston and a mixer. The windowed PVT cell is housed inside an air bath for temperature control. Real time images of its contents can be obtained by a camera. The top of the PVT cell has a flowline through which crude oil and gas can be injected. A valve at the top of the cell facilitates the flow into and out of the PVT cell.

4.3.2 Experimental Procedure

A carefully designed procedure was devised in order to carry out these tests. First, the PVT cell was thoroughly cleaned using nitrogen gas and calibrated before starting any test. The test was started by filling the PVT cell with CO_2 gas from a CO_2 cylinder through the flowline at the top of the cell. The cell's piston was lowered in order to allow the amount of CO_2 gas being charged in. A sufficient amount of CO_2 gas was injected into the PVT cell and the temperature of the cell was set at the test temperature of 55 ^oC. The cell was set at a test pressure of 500 psig.

Once the cell's temperature and pressure stabilized, 20 cc of the crude oil were injected into the PVT cell from an oil transfer cell by the ISCO pump. The crude oil sample was injected at a pressure of 550 psig. The cell was then left for a while to allow the crude oil to be fully saturated with CO_2. Equilibrium conditions were reached when the cell's pressure stopped declining.

After stabilization, the excess CO_2 gas was then carefully bled out of the cell in a step-wise manner without dropping the cell's pressure below 500 psig. This was done by adjusting the piston's position every time a small amount of gas was bled out of the cell. The camera helped determine when all the excess CO_2 gas was bled out and only oil was left inside the cell. At this point, the volume of the CO_2-saturated oil is recorded. The swelling factor was then calculated from the initial and final volumes of the oil.

The amount of CO_2 gas dissolved in the crude oil sample was then determined by dropping the cell's pressure gradually and displacing the evolved CO_2 out of the cell where its volume was measured by the gasometer. The last reading was taken after the cell was left overnight in order to give sufficient time for the gas to evolve completely. The solubility of the CO_2 in the crude oil was then computed.

4.4 Core-flooding Experiment

The core-flooding experiment is the major undertaking in this research, which was performed at conditions to simulate an immiscible CO_2 flooding process in a shallow reservoir. The experimental setup and procedure is discussed in the following sections.

4.4.1 Experimental Setup

The experimental setup included a high-temperature air bath, a core holder, two transfer cells, a CO_2 cylinder, a nitrogen cylinder, a gas mass-flow controller, a back pressure regulator, an injection pump, a confining pressure pump, pressure gauges, a gas/liquid separator and a fraction collector. A schematic diagram of the setup is presented in Fig. 4.1 while a photograph is shown in Fig. 4.2.

The core holder is made up of Hasteloy with a rating of 350 ^{o}F and 10,000 psi and a capacity to facilitate a core sample 12” inches long. A rubber sleeve in the core holder provides sealed packing. Figure 4.3 shows a schematic of the core holder. The core holder and the two transfer cells - one for oil and the other for brine - were placed inside the temperature bath. The two transfer cells were connected to a pump on their inlet valves while the outlet was connected to the top of the core holder. One more flowline was connected to the top of the core holder to deliver CO_2 gas from a cylinder through a mass flow controller, which maintained the flow rate of gas passing through it at a selected value.

CO_2 flooding was carried out with the core sample held in the vertical position. Confining pressure was applied to the core holder by a hand pump which pressurizes the fluid – usually water – that filled the annulus between the core holder body and the rubber sleeve. Back pressure was applied to the core sample by a back-pressure regulator connected to a nitrogen cylinder.

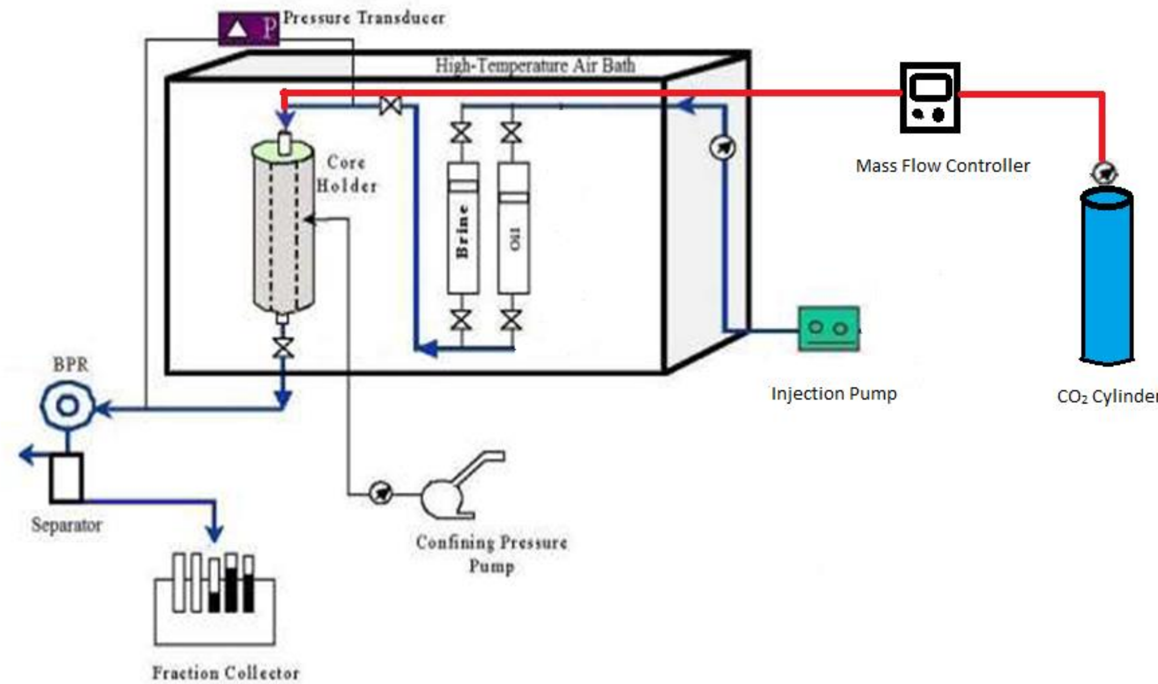

Figure 4.1: Schematic diagram of experimental setup

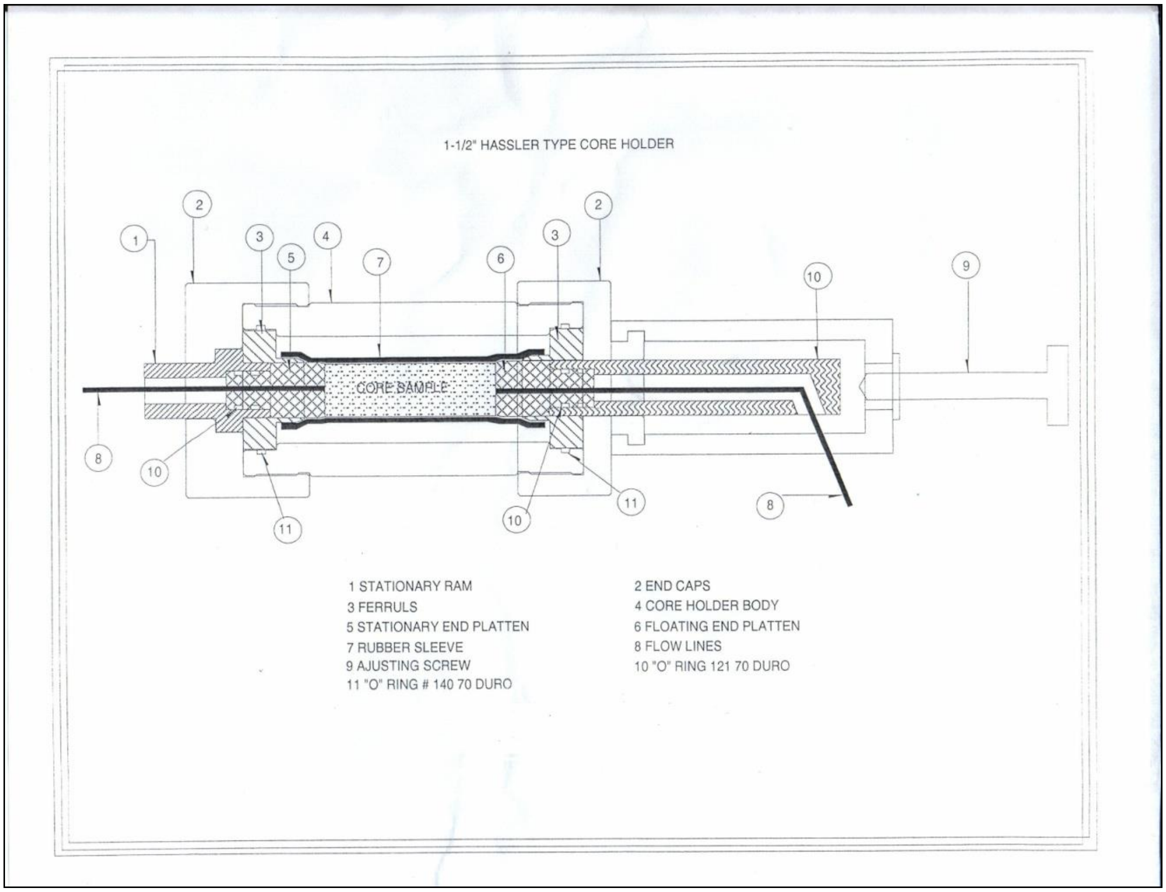

Figure 4.2: Schematic diagram of the core holder

4.4.2 Core Preparation

Before performing a CO_2 flooding run, the core plug was heated to dry any moisture, vacuumed and then saturated with the crude oil using the experimental setup. The saturated core sample was then aged with the respective crude oils. Aging was done at a temperature of 55 ^oC. The saturated core plug was submerged under the crude oil and kept in a glass beaker. The beaker was then covered and placed inside an oven for three weeks at a temperature of 55 ^oC.

After aging, the core plug was loaded into the core holder and placed inside the air bath. A confining pressure of 900 psi was applied to the core holder and a back pressure of 500 psi. All other connections were then made and the air bath temperature was set at 55 ^{o}C. Sufficient time was given to the system to stabilize at this temperature.

The oil-saturated core plug was then flooded with 5% KCl brine down to the residual oil saturation. This was followed by an oil flood of the same crude oil down to the irreducible water saturation. These saturations were computed by mass balance on the oil and brine.

4.4.3 Core Flooding Procedure

To initiate a flooding run, the core holder was isolated from the two transfer cells and connected to the mass flow controller. The CO_2 cylinder was set at a pressure of 550 psig. While the core holder was still under confining (900 psig) and back (500 psig) pressures, the mass flow controller was set at 2 SCCM and the CO_2 valve was opened. The CO_2 injection rate at the test conditions is approximately 0.0027 ft^3/day.

Crude oil produced from the core plug due to CO_2 flooding was collected in graduated cylinders through the separator. Time and production volume were noted at every step. A close eye was kept on the production flowline to observe the appearance of the first gas bubble which marked CO_2 breakthrough. The breakthrough time and cumulative oil production volume were recorded. The experiment was continued until no more oil was produced. CO_2 supply was then stopped and the setup was left to cool down to room temperature. The back pressure was then released and the core plug removed from the core holder for contact angle measurement. A typical experimental run lasted around 7 hours.

4.5 Contact Angle Measurement

Wettability alteration was determined by contact angle measurements on a droplet of the crude oil placed on the rock surface in the presence of the brine before and after flooding the core plug with CO_2. Measurements were made with an optical tensiometer, which is the state-of-the-art equipment. The equipment was specially modified and improvised to serve the purpose of measuring the contact angle of an oil droplet in the presence of brine.

4.5.1 Experimental Setup

The optical tensiometer consists of an adjustable sample platform, a high resolution built-in camera, an adjustable U-shaped injection needle, a sample collector and a desktop computer. The sample of rock surface (core plug) was placed on the adjustable sample platform and the platform was adjusted such that the camera was focusing exactly on the surface of the core. The sample collector was used to collect the sample of fluid that had to be dropped on the surface in order to measure the contact angle. The U-shaped injection needle was used to dispense (drop) the droplet of fluid on the sample surface, which was exactly in front of the camera in order to facilitate image capturing and contact angle measurement. The injection needle was very precise with respect to droplet size, fluid dropping rate and location of the droplet. More than one droplet can also be dispensed by the injection needle in a single run. The high resolution camera captures the whole process of dispensing the fluid droplet onto the rock sample surface and the interaction between the droplet and the surface.

In this special test, the core plug was suspended in 5% KCl brine (Fig. 4.4) and the crude oil droplet was introduced from beneath the core sample by the injection needle.

4.5.2 Experimental Procedure

The first step in this procedure was calibration of the equipment. The equipment was calibrated with a given sample provided with the equipment by the manufacturer. Then a transparent square container filled with the brine was placed on the platform. The saturated and aged core plug (prior to CO_2-flooding) was then suspended into the brine with the help of a clamp. A droplet of the same crude oil saturating the core plug was then introduced into the sample collector. The U-shaped injection needle was then carefully dipped into the brine and placed underneath the core plug. The equipment was then started and the oil droplet was dispensed from the needle. The droplet would rise and stick onto the lower surface of the vertically suspended core plug. Snapshots of the droplet were then taken and the contact angle was determined. This would be the initial contact angle before immiscible CO_2 flooding.

Once CO_2 flooding was completed, the contact angle was measured on the flooded core plug following the same procedure above.

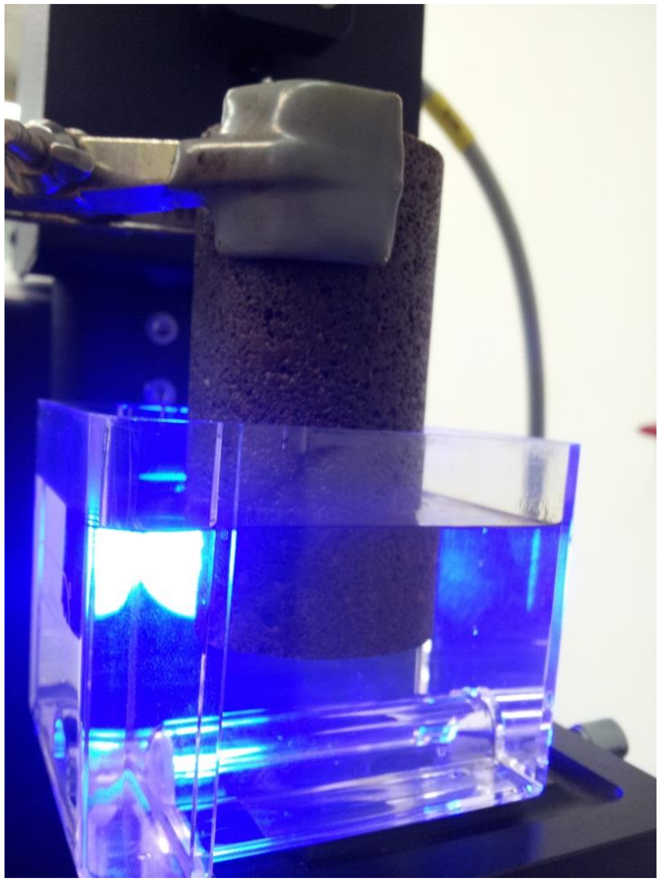

Figure 4.3: Core plug during contact angle measurement

CHAPTER 5

RESULTS AND DISCUSSIONS

This chapter presents and discusses the results of the experimental work described in Chapter 4. It also presents the predictions of Al-Mutairi's model as compared with the core-flooding results. Flooding calculations with an inert gas are also presented in order to validate the experimental results and to demonstrate the advantage of CO_2 flooding.

5.1 PVT Results

The gas solubility and oil swelling experiments yielded the results listed in Tables 5.1 and 5.2. Table 5.1 provides the volume of CO_2 gas dissolved in 20 cc of crude oil at the test conditions of 500 psig and 55 ^oC. Table 5.2 provides the oil swelling factor and CO_2 solubility at those conditions for the three crude oils of the study.

Table 5.1: CO_2 – oil solubility at 500 psig and 55 ^oC

Crude Oil	**Initial Volume of Oil (std. cc)**	**Total Volume of CO_2 Gas Dissolved (std. cc)**	**Final Volume of Oil (test cc)**
40 ^{o} API	20	919.0	22.554
34.30 ^{o} API	20	965.6	26.076
28.56 ^{o} API	20	1015.1	27.260

Table 5.2: Oil swelling factor and CO_2 solubility at 500 psig and 55 ^oC

Crude Oil	Oil Swelling Factor	Solubility of CO_2 (SCF/STB)
40 ^{o} API	1.128	258.0
34.30 ^{o} API	1.304	271.1
28.56 ^{o} API	1.363	285.0

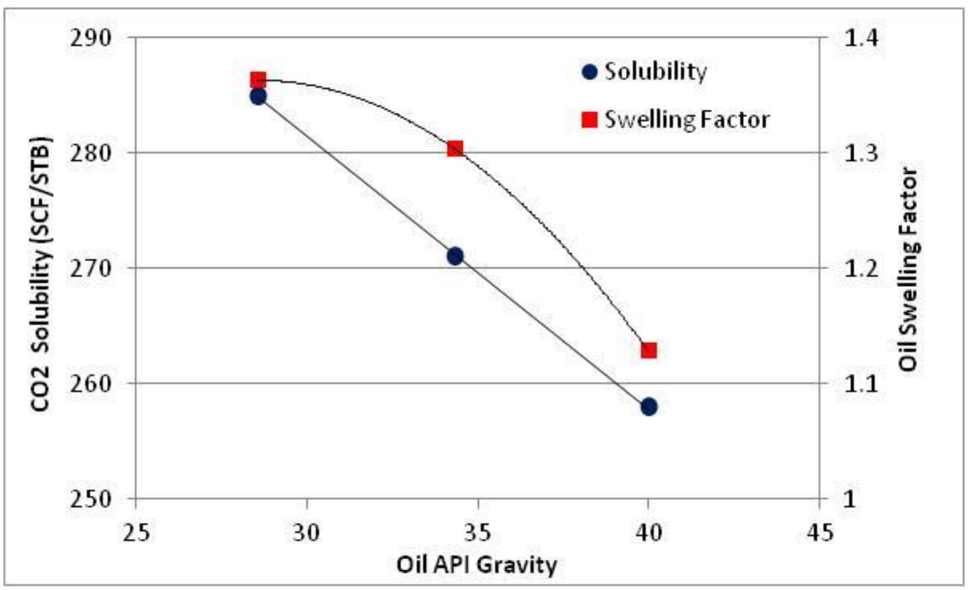

Figure 5.1: Variation of oil swelling factor and CO_2 solubility with oil API gravity

The results of Tables 5.1 and 5.2 – also plotted in Fig. 5.1 - reveal that CO_2 solubility and, consequently, the oil swelling factor increase as the oil density increases. Bennion et al. (1993) also found out that CO_2 solubility increases with decrease in oil API gravity

[38]. While the solubility appear to increase linearly with decrease in gravity, the increase in swelling factor appears to approach a limit. These trends cannot be confirmed without more data at higher and lower gravities, and are limited to the type of oils used in this study.

CO_2 solubility has an even more pronounced effect on oil viscosity. Table 5.3 lists the original, dead oil viscosity and the viscosity of CO_2-saturated oil for all three crude oils. The CO_2-saturated oil viscosity was calculated using a recent, well-known and proven correlation (Emera and Sarma, 2006). The data of Table 5.3 shows the significant impact of CO_2 on the viscosity of the crude oil, and hence the pivotal impact of this viscosity reduction on improved oil recovery. However, the Table 5.3 also shows that all oils lost viscosity to the same degree, i.e., about 40% of the dead oil viscosity.

Table 5.3: Dead crude oil viscosity and CO_2 saturated oil viscosity

Crude Oil	**Measured Dead Crude Oil Viscosity (cP)**	**Estimated CO_2-Saturated Oil Viscosity (cP)**	**Saturated/Dead Oil Viscosity Ratio**
40 ^{o} API	1.741	1.121	0.644
34.30 ^{o} API	3.791	2.266	0.598
28.56 ^{o} API	13.98	8.996	0.643

To demonstrate the unusual effect of CO_2 on oil properties, solubility calculations were performed with natural gas for comparison purposes. Table 5.4 shows the estimated viscosity and swelling factor of each of the three crudes but saturated with 0.7 gravity natural gas at 55 ^oC and 500 psig. These values are estimated using correlations from Chevron Oil Field Research Co. (1947). The viscosity values of Table 5.4 are slightly higher than the CO_2-saturated oil viscosity estimates. This indicates that CO_2 is slightly better as a viscosity reducer than natural gas. However, CO_2 shows a greater ability to swell the oil than natural gas. Table 5.4 shows that the swelling factor with natural gas decreases as the oil API gravity decreases. This is expected since lighter oils dissolve more gas due to molecular similarity. But this is opposite to the trend seen with CO_2 as the swelling factor is largest with the heaviest oil. Nevertheless, the swelling factor with natural gas is much smaller than that with CO_2 for all three oils.

Table 5.4: Swelling factor and viscosity of oil saturated with 0.7 gravity natural gas

Crude Oil	**Oil Swelling Factor**	**Saturated Oil Viscosity (cP)**
40 ^{o} API	7.4%	1.23
34.30 ^{o} API	6.5%	2.44
28.56 ^{o} API	5.65%	9.4

5.2 Core-Flooding Results

As discussed in the previous chapter, CO_2 gas flooding was carried out on oil-saturated core plugs (with irreducible brine saturation) and was continued until oil production ceased. The core-flooding experiments mimicked immiscible CO_2 flooding in the reservoir. All the core plugs were initially oil-wet after aging as observed by the initial contact angles (Table 5.6). The end-point saturation with brine (S_{wi} and S_{orb}) of the core plugs were different from one another. Those saturations along with the results of the core-flooding experiments are summarized in the Table 5.5.

Table 5.5: Core-flooding results

Parameter	**40^o API Oil**	**34.3^o API Oil**	**28.56^o API Oil**
Initial Water Saturation (S_{wi})	25.26%	11.80%	10.00%
Residual Oil Saturation by Brine Flood (S_{orb})	46.26%	47.70%	56.63%
Pore Volumes of CO_2 at Breakthrough	0.49	0.48	0.44
Total Pore Volumes of CO_2	2.44	2.17	1.77
Oil Recovery at Breakthrough (%IOIP)	60.40	50.04	48.65
Total Oil Recovery (%IOIP)	67.59	57.36	53.75
Residual Oil Saturation by CO_2 Flood (S_{org})	24.22%	37.61%	41.63%

It can be observed from the results that the light crude oil (40^o API) showed the highest oil recovery, both at CO_2 breakthrough and total, as compared with the medium (34.30^o API) and heavy (28.56^o API) crude oils. This is attributed to the light oil having the lowest viscosity among the three oils. This leads to a lower mobility ratio – compared with other oils – and thus a better displacement efficiency. The residual oil saturation after the CO_2 flood is computed from the oil recovery values and is also listed in Table 5.5. The difference between the brine S_{or} and the gas S_{or} is caused by wettability alteration, which will be discussed in Section 5.3. The lightest oil showed the largest drop in residual oil saturation, which is believed to be the major contributor in attaining the highest CO_2-flood oil recovery.

5.3 Wettability Alteration Results

Images of the contact angle measurements are shown in Figures 5.2 to 5.7. Each image shows the core plug surface with an oil droplet lodged at the plug's bottom surrounded by brine. Figures 5.2 and 5.3 show images for the 40^o API oil before and after CO_2 flooding, respectively. Figures 5.4 and 5.5 are for the 34.30^o API oil and Figures 5.6 and 5.7 are for the 28.56^o API oil. Table 5.6 lists all initial and final contact angles.

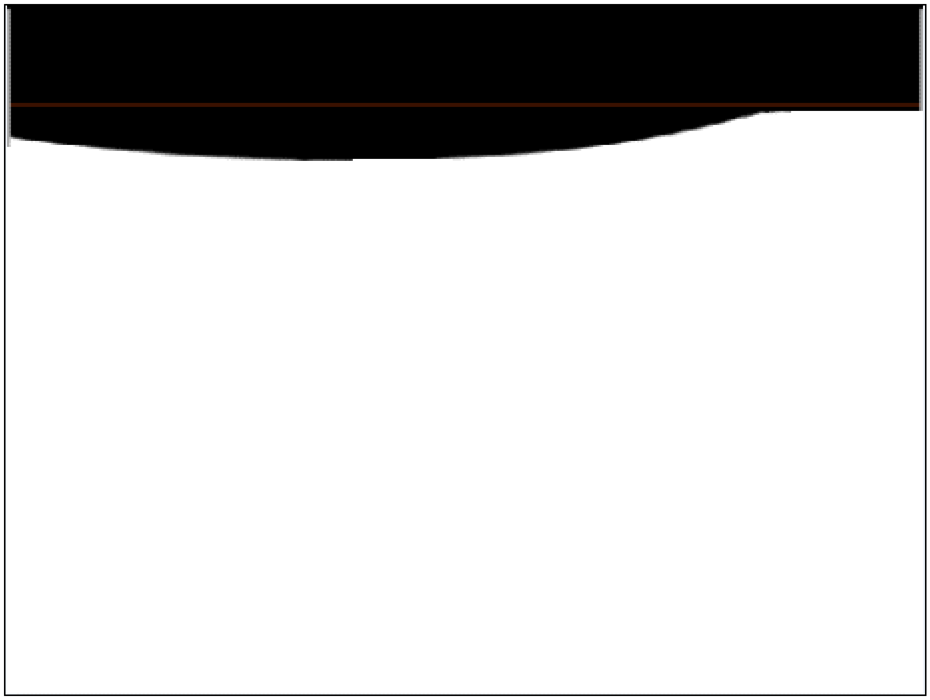

Figure 5.2: Contact angle of oil droplet before CO_2 flooding (40^o API)

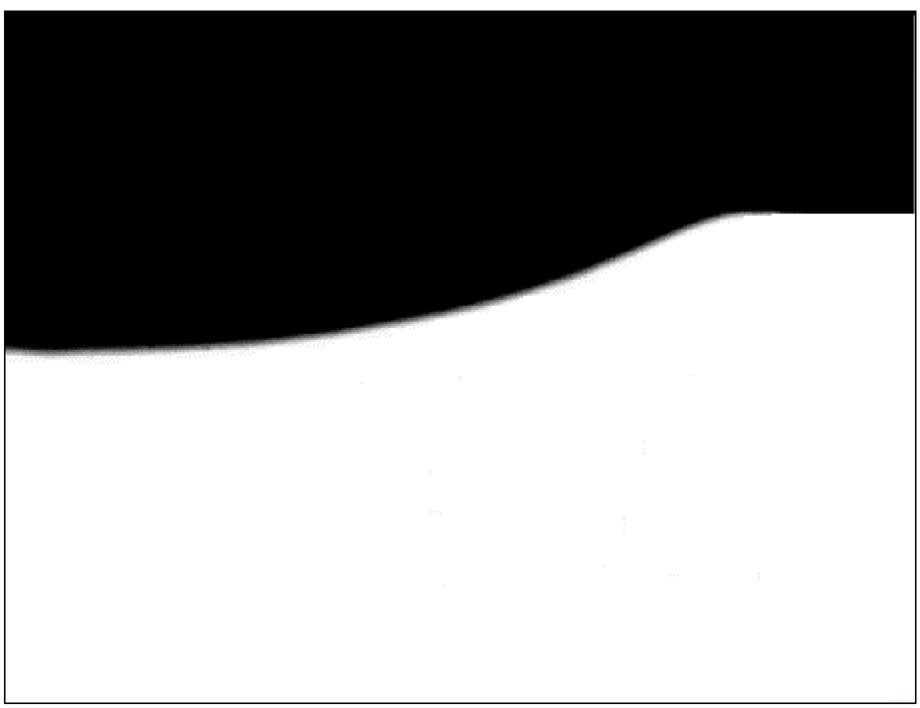

Figure 5.3: Contact angle of oil droplet after CO_2 flooding (40^o API)

Figure 5.4: Contact angle of oil droplet before CO_2 flooding (34.30^o API)

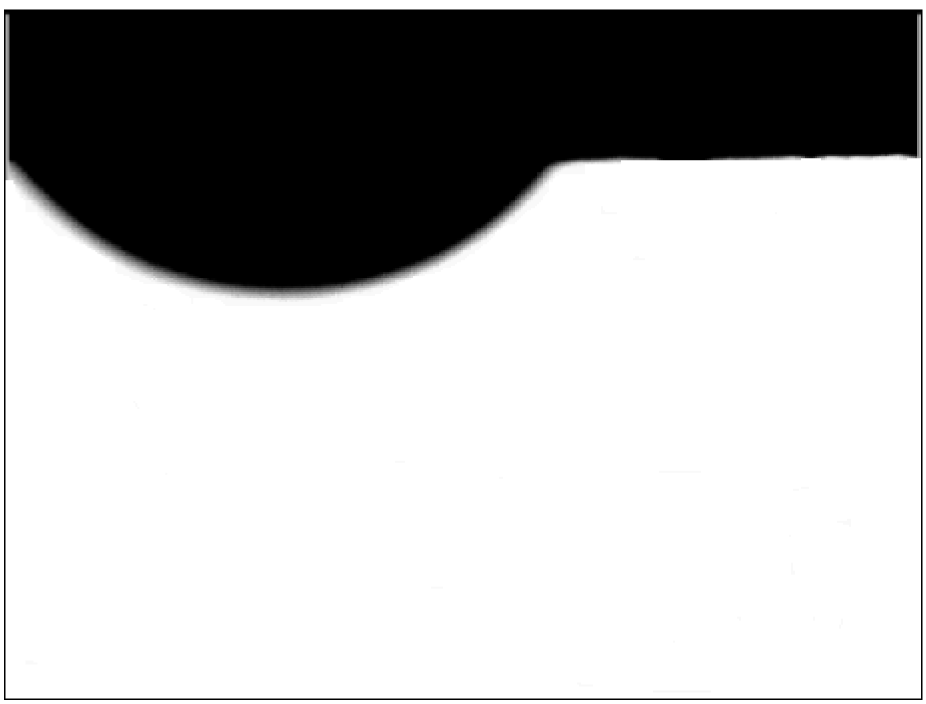

Figure 5.5: Contact angle of oil droplet after CO_2 flooding (34.30^o API)

Figure 5.6: Contact angle of oil droplet before CO_2 flooding (28.56^o API)

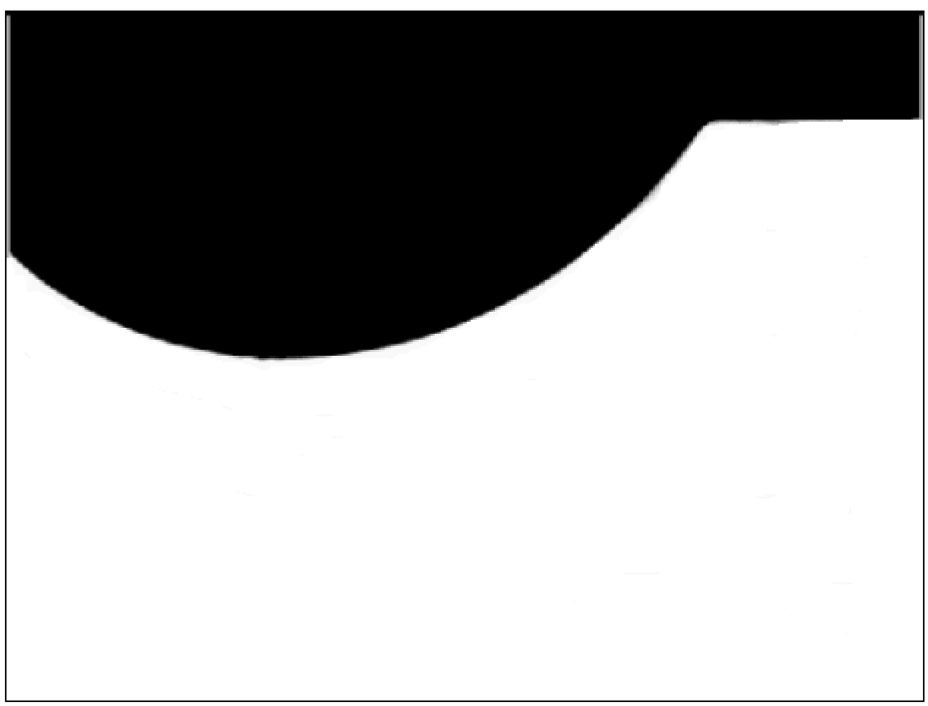

Figure 5.7: Contact angle of oil droplet after CO_2 flooding (28.56^o API)

Table 5.6: Initial and final contact angles for wettability measurement

Crude Oil	Initial Contact Angle	Final Contact Angle
40^{o} API	168^{o}	156^{o}
34.30^{o} API	165^{o}	140^{o}
28.56^{o} API	167^{o}	126^{o}

Having been cut from a clean carbonate rock and aged in oil, all core plugs were initially oil-wet with virtually the same contact angle regardless of the oil. Since asphaltenes are known to be the most influential group in causing oil wetness, and since the three oils have different asphaltene contents, it appears that only a certain – and equal - amount of the asphaltenes are adsorbed on the rock-grain surfaces in all three cases. This amount of asphaltenes depends on the rock mineralogy, specific surface area, pressure and temperature.

The data of Table 5.6 shows marked reductions – to varying extents - in the contact angles for the three oils indicating a change in rock wettability from strongly oil-wet to slightly oil-wet after the CO_2 flood. To explain this wettability alteration it should be remembered that in a typical carbonate rock the grain surfaces are positively charged. When the rock is aged with oil, the negative ends of the oil's polar compounds (asphaltenes) adhere to those surfaces rendering the rock oil-wet. However, when CO_2 dissolves in the oil and diffuses to the grain surfaces the slightly negative end of the CO_2

molecule tends to desorb the asphaltenes and replace them on the rock surface, thus weakening the rock's oil wettability.

To explain the varying degrees of wettability alteration - increasing with increase in oil density - attention is turned to CO_2 solubility. Obviously, the more CO_2 that dissolves in the oil, the greater is the extent of asphaltene surface desorption and replacement. It also follows that the more asphaltenes removed, the less oil wet the rock becomes and thus more reduction in the contact angle will be observed. Thus, it can be concluded that the wettability alteration of the rock depends on the solubility of CO_2 in the crude oil provided that the crude oil has a certain minimum asphaltene content to saturate the rock grain surfaces to begin with.

The large reduction in oil wetness explains the unusually large incremental oil recovery beyond breakthrough with the heavy oil. This incremental recovery would have been very low had wettability alteration not occurred.

An interesting observation would be to notice the behavior of wettability at higher pressures, where the solubility of CO_2 in the crude oil could increase to a point where the rock becomes water-wet.

The above reasoning works for oils whose asphaltene content increases with the oil's density. This is because CO_2 solubility increases with oil density regardless of composition. Variation of rock oil wetness with dissolved CO_2 for heavy oils with low asphaltene content remains to be investigated.

5.4 Numerical Model Verification

A 1-dimensional, continuous wettability alteration, displacement mathematical model had been previously developed by Al-Mutairi (2013) to describe and predict the performance of immiscible CO_2 flooding of a linear, oil-saturated porous medium. The model used a modified Corey relative permeability correlation to simulate the immiscible CO_2 flooding process at in-situ conditions. The model was tested against the core-flooding results of this study and a comparison was performed.

The assumptions in the mathematical model are as follows:

- The porous medium has a known geometry and initially contains mobile oil only.
- The pressure and oil saturation are initially uniform throughout the medium.
- The flow is assumed to be linear and parallel to the medium's length (x-axis).
- CO_2 is injected at one end of the medium.
- CO_2 remains in the gas phase throughout the process.
- CO_2 injection rate is constant.
- Flooding is immiscible with no gas slippage.
- Capillary pressure is neglected.
- The system is compressible and isothermal.
- The rock is initially strongly oil-wet.

- Connate water saturation is known.

In each time step, the gas saturation in a cell is examined. If it is above 0.01, the viscosity of the crude oil and the oil volume are adjusted accordingly. The gravity effect is also incorporated in the displacement model since the CO_2 core flooding experiments were conducted in vertical direction. The gravity effect is reflected in the pressure equation of the model. The model equations were solved using a numerical scheme by MATLAB programming.

The input data required viscosity and solubility data for the CO_2-saturated oil. Previously, those were obtained from charts for general CO_2-oil mixtures published in the literature. To improve the accuracy of the model's predictions, the experimentally-determined oil swelling factor and solubility values of this study were employed. Also, viscosity values for the CO_2-saturated oils were estimated using the Emera and Sarma correlation (Emera and Sarma, 2006).

Table 5.7 shows the input data to the numerical model to simulate the 3 core-flooding runs. The end point saturations are also included in the input data to adjust the relative permeability curves. The viscosity reduction and oil swelling factor values for the respective oil are also included into the model in order to predict the results accurately. The CO_2 injection rate was kept the same for the three oils, as all the experiments were conducted at the same injection rate of 0.0027 ft^3/day.

Table 5.7: Input data for numerical model verification

Parameter	**Crude Oil 1**	**Crude Oil 2**	**Crude Oil 3**
Gas Injection Rate (ft^3/day)	0.0027	0.0027	0.0027
Porosity (%)	15	15	15
S_{wi}	0.2526	0.118	0.10
S_{or}	0.4526	0.477	0.5663
S_{gi}	0	0	0
S_{oi}	0.7474	0.882	0.90
Gas Viscosity (cP)	0.03	0.03	0.03
Dead Oil Viscosity (cP)	1.741	3.791	13.98
Dead Oil Density (lb/ft^3)	49.3	51.5	52.87
CO_2-Saturated Oil Viscosity (cP)	1.121	2.266	8.996
Oil Swelling Factor (%)	12.77	30.38	36.30
c_g (psi^{-1})	0.002	0.002	0.002
c_r (psi^{-1})	0.000004	0.000004	0.000004
c_o (psi^{-1})	0.000015	0.000015	0.000015
Initial Contact Angle (degrees)	168	165	167
Final Contact Angle (degrees)	156	140	126
Time Step (days)	0.0001	0.0001	0.0001

Figure 5.8 shows the experimental flooding data along with the model's prediction for crude oil 1. The experimental data shows a total oil recovery of 67.59% as compared to a value of 61.81% predicted by the model after 2.44 pore volumes of CO_2 had been injected.

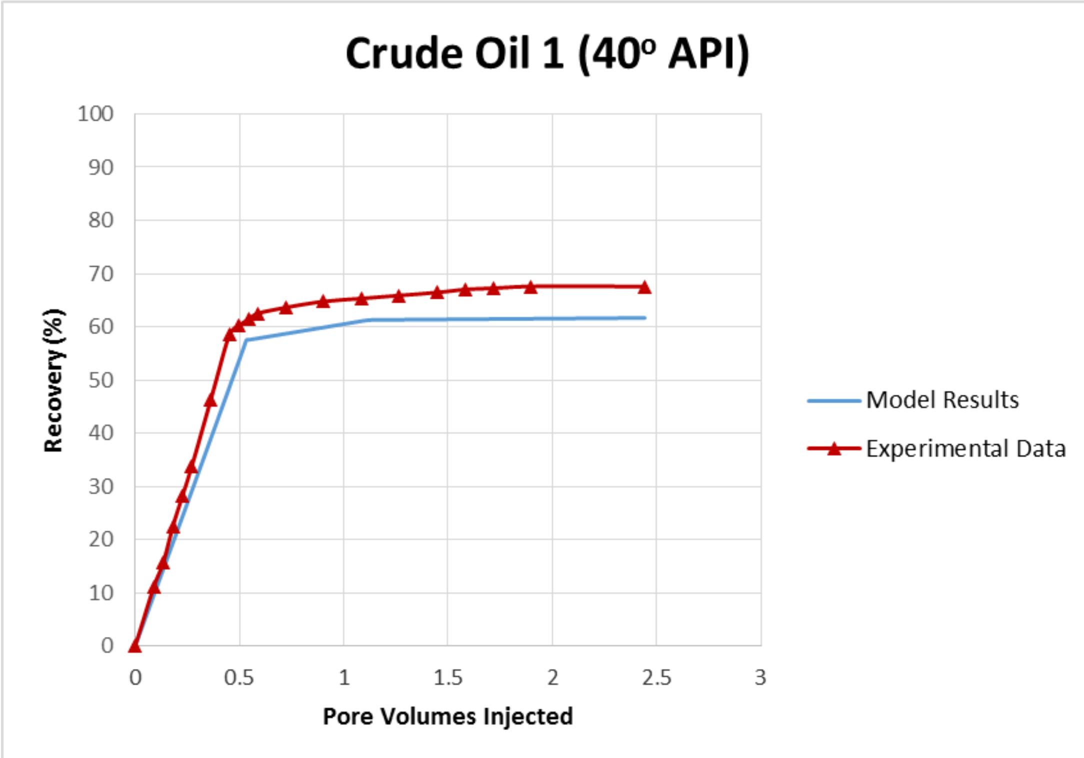

Figure 5.8: Comparison of results for crude oil 1 (40° API)

The model prediction shows a good match with the experimental data, with a difference of around 6% in the total oil recovery. The experimental data showed oil recovery at breakthrough of 60.40% at 0.49 pore volumes of CO_2 injected while the model showed 57.53% and 0.50 pore volumes, respectively. Thus, it is observed that the model is predicting slightly lower oil recovery at breakthrough and lower total oil recovery as compared to the actual experimental results. However, within experimental error, the model prediction is considered close to the actual experimental results.

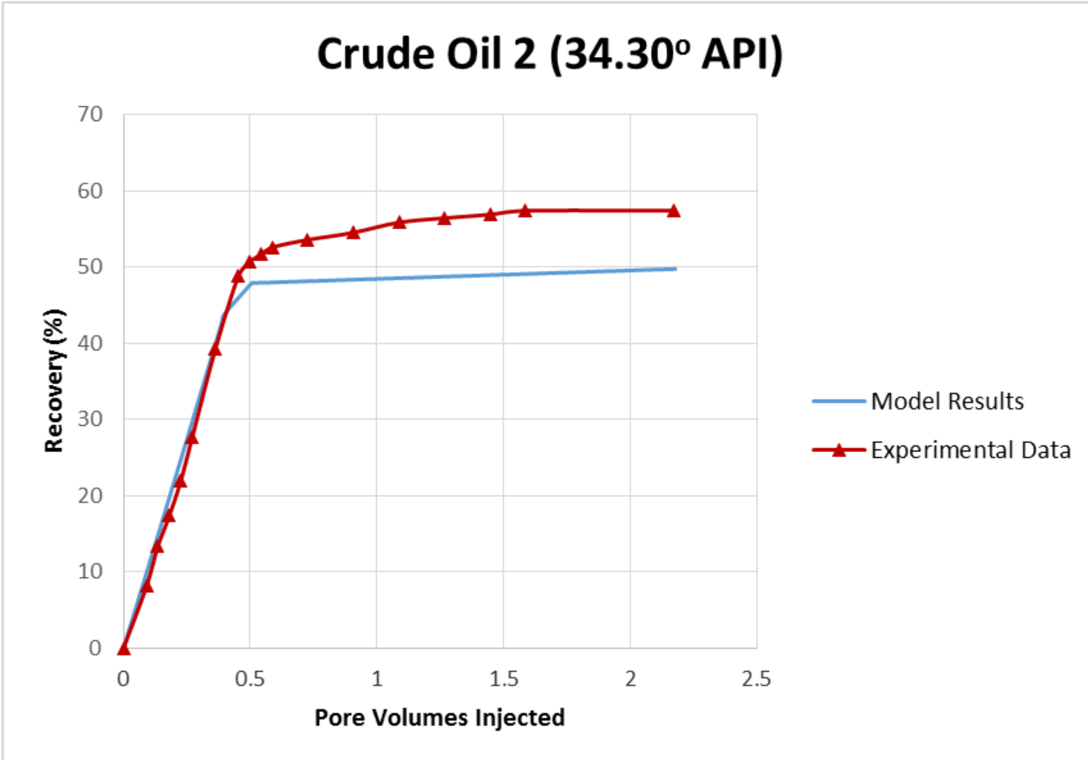

Figure 5.9: Comparison of results for crude oil 2 (34.30^o API)

Figure 5.9 shows the experimental results and the model prediction for crude oil 2 (34.30^o API). The experimental data showed oil recovery at breakthrough of 50.04% at 0.48 pore volumes of CO_2 injected while the model showed 48.53% and 0.48 pore volumes, respectively. A slight shift between the two plots is observed after breakthrough with the model predicting lesser total oil recovery. This is similar to what is noticed in crude oil 1 but with a slightly larger difference between the two plots. However, a difference of almost 7% in the total oil recovery between the experimental data and the model prediction is within the acceptable range of uncertainty.

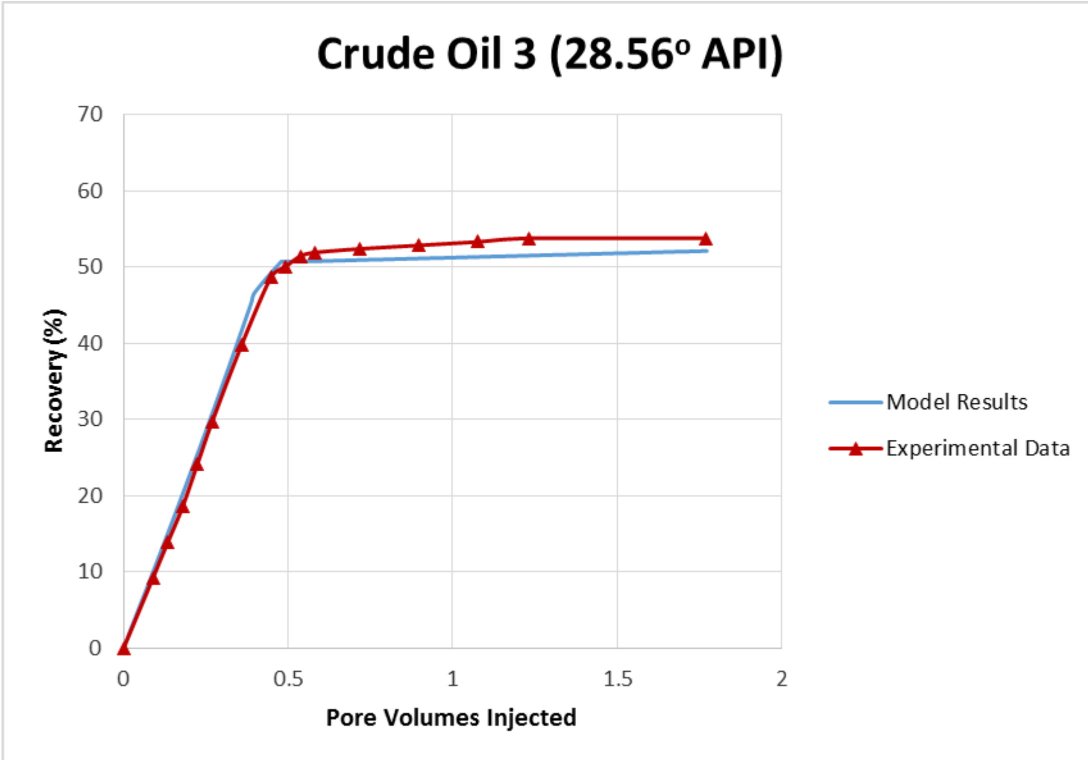

Figure 5.10: Comparison of results for crude oil 3 (28.56^o API)

Figure 5.10 compares the recovery plots for the heavy crude oil. The oil recovery plot from both the experimental data and the model are in good agreement. The experimental data showed oil recovery at breakthrough of 48.65% at 0.44 pore volumes of CO_2 injected while the model showed 48.03% and 0.43 pore volumes, respectively. A difference of about 1% in the total oil recovery between the experimental data and model prediction shows a good match.

In conclusion, the discrepancies seen above between the experimental and simulated results, especially in crude oil 1 and crude oil 2, are a consequence of the model's structure. The model does not simulate the slow sequence of processes by which the CO_2

dissolves in the oil and changes its properties. The model assumes all these processes to take place instantaneously once the CO_2 comes into contact with the crude oil. On the other hand, diffusion by CO_2 through the oil to the rock surface and the consequent change in the rock's wettability is factored in by the model. This is simulated by an exponential decay function that reduces the contact angle with time of contact. However, the parameters of this function were borrowed from another test conducted on a different oil and a different carbonate rock. Thus, the model predictions are faster than the experimental data, yielding slightly lesser total oil recovery as compared to the experimental data.

5.5 Comparison with Inert Gas

To verify the results of both the flooding experiments and the model predictions, a flood with nitrogen was simulated. Being an inert gas, N_2 has negligible solubility in crude oil at low pressures and, thus, it does not change the oil properties noticeably. Also, no rock wettability alteration by N_2 has been reported. The objective of this comparison with an inert gas - nitrogen in this case - was only to check the reliability of CO_2 core-flooding and model results.

Fractional flow curves were plotted for vertical nitrogen flooding and Buckley-Leverett calculations were performed for the three crude oils of the study. Relative permeability curves (Fig. 5.11) for nitrogen displacing oil were obtained from the literature (William et. al). However, a few assumptions were made for nitrogen flooding calculations. The same relative permeability curves were used for all the three crude oils of the study due to limited available data.

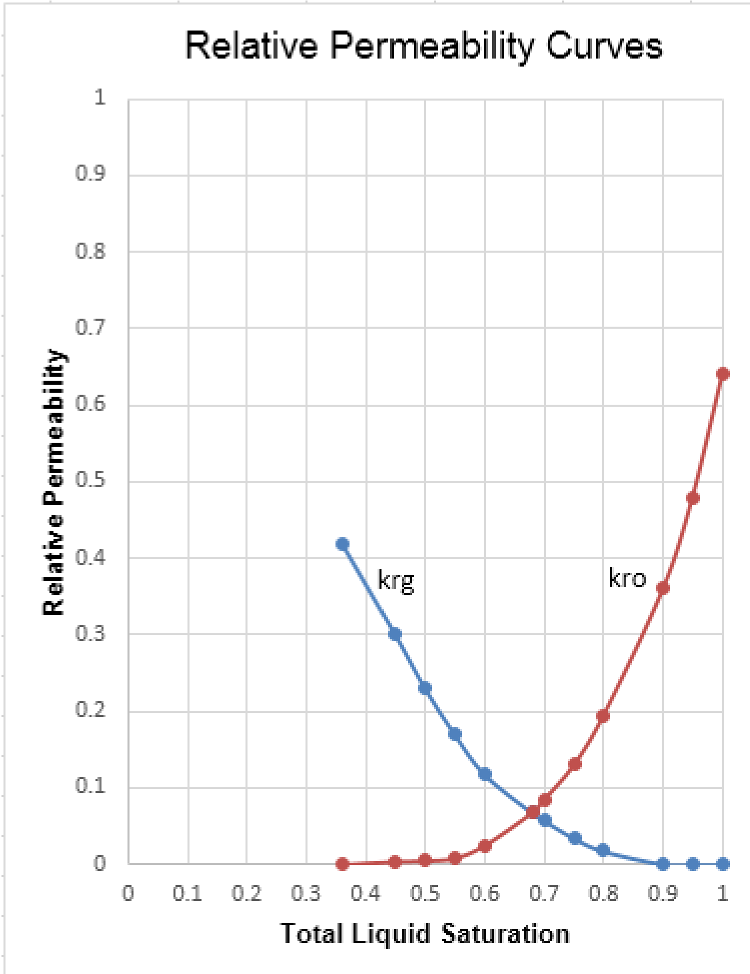

Figure 5.11: Relative permeability curve for nitrogen flood

The predicted performance of N_2 flooding for crude oil 1 is shown in Fig. 5.12. Figures 5.13 and 5.14 show the results for crude oil 2 and crude oil 3, respectively. Also shown in these figures are the experimental and simulated results of the CO_2 floods.

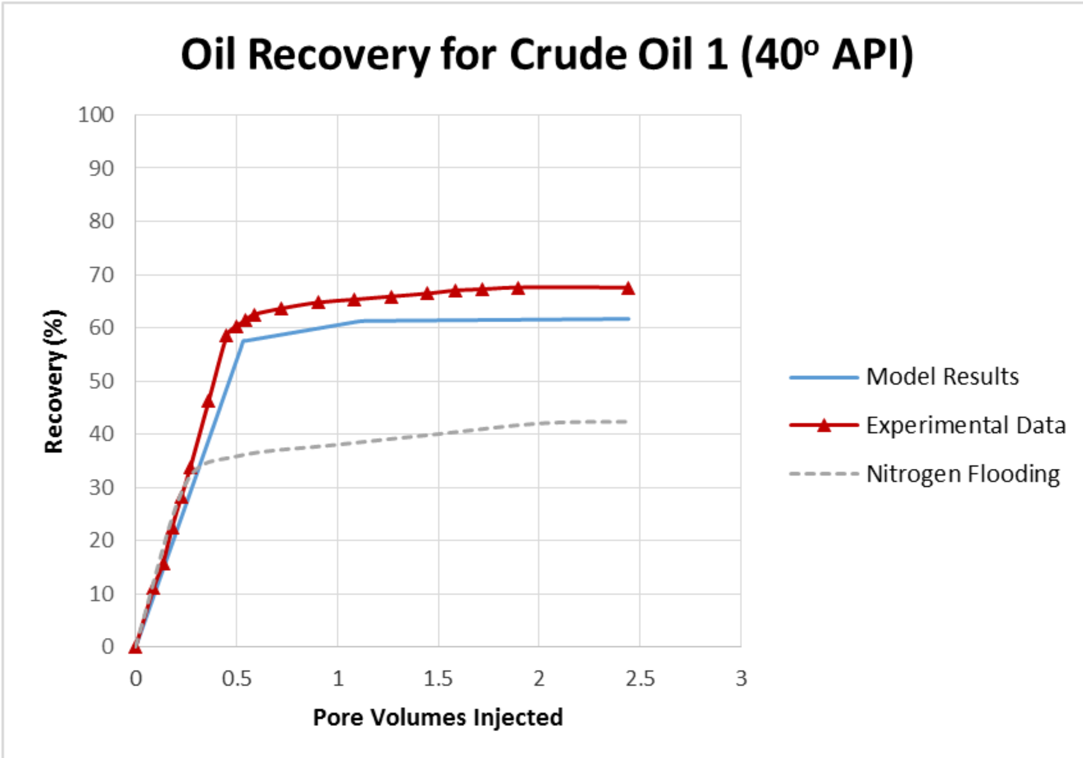

Figure 5.12: Comparison with inert gas for the crude oil 1 (40^{o} API)

As expected, Fig. 5.12 shows that the nitrogen flood yields a very low total oil recovery of 42.81% at 2.44 PV of gas injected as compared to total oil recovery of 67.59% with CO_2 flooding. It can be seen that up to gas breakthrough, the nitrogen flood is in good agreement with the CO_2 experimental data. This is because both the gases are displacing the oil in a similar fashion. However, the special effects of CO_2 are seen in the delayed breakthrough time, providing the extra oil recovery which is not achieved in the case of an inert gas. This also shows that the model incorporates the special features of oil-CO_2 interaction and is in better agreement with the experimental results.

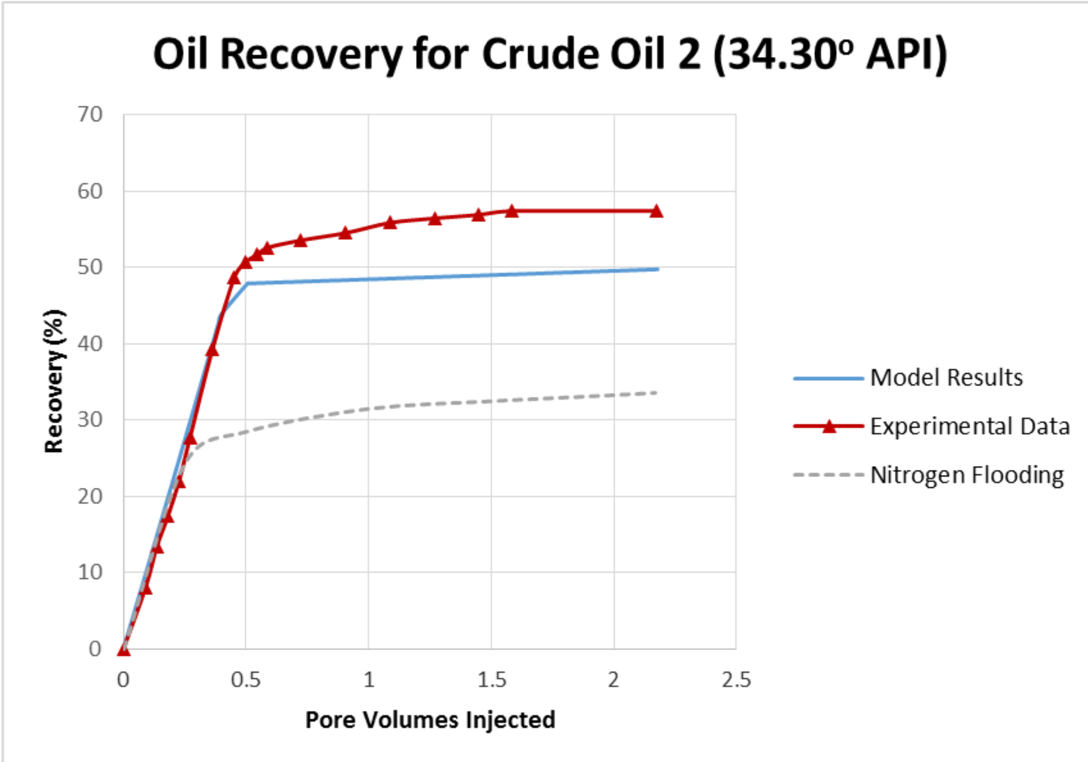

Figure 5.13: Comparison with inert gas for the crude oil 2 (34.30^o API)

Figures 5.13 shows similar comparisons for crude oil 2 where the CO_2 flood gave a total oil recovery of 57.36% while N_2 flooding gave 34.01% oil recovery at the total pore volumes of gas injected of 2.17 PV. Similar to crude oil 1, the recovery up to N_2 breakthrough is similar in both the CO_2 experimental data and the nitrogen flood but diverges greatly after breakthrough. The model shows a somewhat better match with the experimental data.

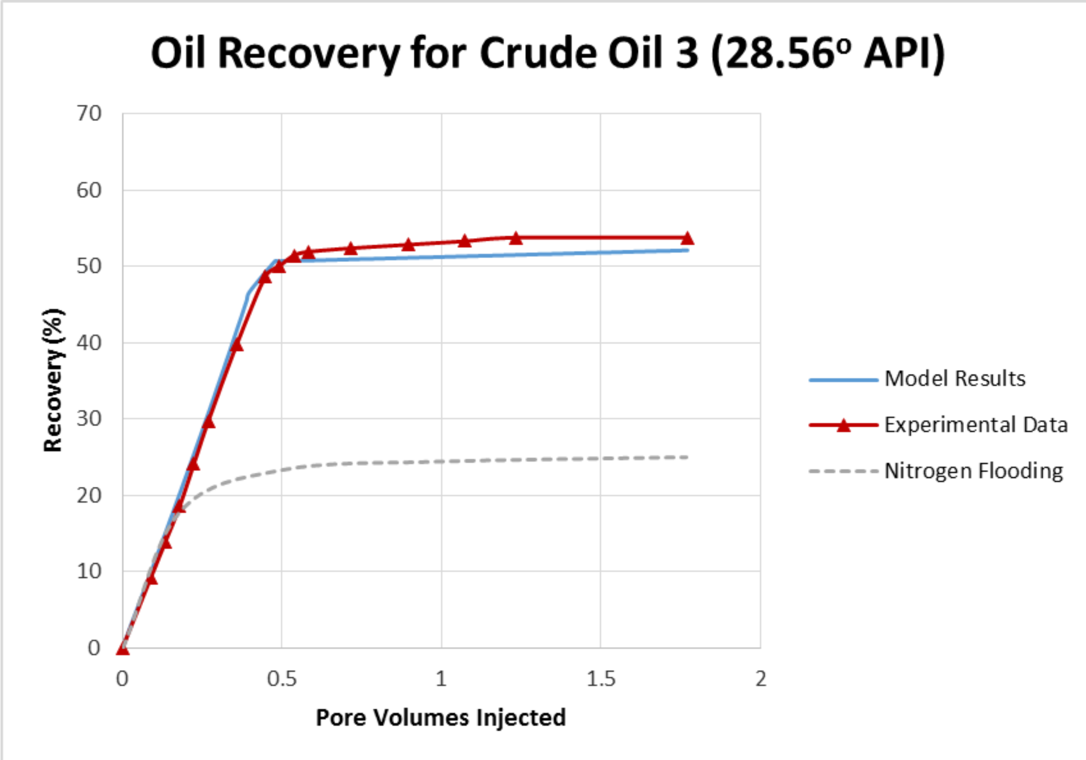

Figure 5.14: Comparison with inert gas for the crude oil 3 (28.56^{o} API)

Figure 5.14 compares the case of crude oil 3 where the nitrogen flood gave a total oil recovery of 25% compared with a total oil recovery of 53.75% with the CO_2 flood. Apart from the good agreement between the two curves up to breakthrough, an interesting thing to note here is that the difference between the two curves is higher than with the other two crude oils. Crude oil 3 yielded the highest incremental recovery as compared to the other two crude oils. This is because of the largest change in contact angle in this crude oil, which changed from 167^{o} to 126^{o}. The highest CO_2 solubility and oil swelling factor values for this crude oil also had a large impact when compared with N_2.

Thus, the results of this simulated nitrogen flood lead to two conclusions. First, the CO_2 flood experiments did capture the special effects of CO_2 on oil and rock properties and the consequent effect on oil recovery. That is even at low pressures, the experimental recovery curve with CO_2 was far different and larger from that of an inert gas. Second, the mathematical model built to account for all phenomena taking place within CO_2 flooding succeeded in simulating those phenomena as it matched the experimental data reasonably well. It can also be inferred from the results that immiscible CO_2 flooding is an effective EOR technique with a significant incremental recovery especially in heavy oil reservoirs even at low pressures.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

This chapter presents the conclusions from this research and proposes recommendations for future work as well. This study was directed to have a better understanding of the immiscible CO_2 flooding process in carbonate rocks and to quantify the recovery mechanisms and processes taking place during this process.

6.1 Conclusions

A number of conclusions can be drawn after the successful completion of this study. Conclusions made from this research are summarized as follows:

1) Immiscible CO_2 flooding in oil-wet carbonate rocks causes the wettability of the rock to change from strongly oil-wet to weakly oil-wet.
2) The extent of wettability alteration depends on the composition of the crude oil present in the reservoir.
3) Heavy oils rich in asphaltenes and have high polarity exhibit larger degrees of wettability alteration and greater incremental oil recovery.
4) Oil swelling caused by CO_2 gas dissolution is significant even at low pressures especially with heavy crude oils.
5) A mathematical model that had been built previously to describe the CO_2-oil immiscible displacement in porous media allowing continuous wettability alteration has been tested.

6) The model's predictions for ultimate recovery are close to the actual laboratory results and are in good agreement within experimental error.

7) Discrepancies between the model's predictions and the experiment, especially before gas breakthrough, could be attributed to some assumptions in the model with regards to the speed at which gas/liquid equilibrium is attained.

8) Immiscible CO_2 flooding has high prospects in shallow and low pressure carbonate (oil-wet) reservoirs.

6.2 Recommendations for Future Work

1. This work was done on a specific reservoir pressure and temperature conditions. Further research can be done on different pressure and temperature range.

2. More crude oils can be tested to confirm the relationship between the oil's asphaltene content and its effect on rock wettability alteration.

3. The study of physical and chemical interaction between the CO_2 gas and the asphaltene colloidals can also be an area of research.

4. Other carbonate rocks should be tested to check the extent of wettability alteration.

5. The change in oil viscosity with the amount of dissolved CO_2 should be measured experimentally instead of resorting to correlations.

Appendix

Table 1: CO_2 Flooding Data for Crude Oil 1

Time (min)	CO2 Injected (cc)	Production (ml)	PV Injected	Recovery (%)
0	0	0	0	0
20	40	1	0.0904	11.2663
30	60	1.4	0.1357	15.7728
40	80	2	0.1809	22.5326
50	100	2.5	0.2262	28.1658
60	120	3	0.2714	33.7990
80	160	4.1	0.3619	46.1919
100	200	5.2	0.4524	58.5849
110	220	5.35	0.4976	60.2748
120	240	5.45	0.5429	61.4015
130	260	5.55	0.5881	61.9648
160	320	5.65	0.7239	63.0914
200	400	5.75	0.9049	64.2181
240	480	5.8	1.0858	64.7814
280	560	5.85	1.2668	65.3447
320	640	5.9	1.4478	65.9080
350	700	5.95	1.5835	66.4713
380	760	5.97	1.7193	66.8093
419	838	6	1.8958	67.5980
540	1080	6	2.4433	67.5980

Table 2: CO_2 Flooding Data for Crude Oil 2

Time (min)	CO2 Injected (cc)	Production (ml)	PV Injected	Recovery (%)
0	0	0	0	0
20	40	0.85	0.0906	8.12619
30	60	1.4	0.1359	13.3843
40	80	1.82	0.1812	17.3996
50	100	2.3	0.2265	21.9885
60	120	2.9	0.2718	27.7246
80	160	4.1	0.3624	39.1969
100	200	5.4	0.4530	48.7571
110	220	5.6	0.4983	50.6692
120	240	5.65	0.5436	51.6252
130	260	5.7	0.5889	52.5812
160	320	5.76	0.7249	53.5372
200	400	5.8	0.9061	54.4933
240	480	5.84	1.0873	55.8317
280	560	5.9	1.2685	56.4053
320	640	5.93	1.4498	56.6921
350	700	6	1.5857	57.3613
480	960	6	2.1747	57.3613

Table 3: CO_2 Flooding Data for Crude Oil 3

Time (min)	CO2 Injected (cc)	Production (ml)	PV Injected	Recovery (%)
0	0	0	0	0
20	40	1	0.0896	9.2678
30	60	1.6	0.1344	14.8285
40	80	2	0.1792	18.5356
50	100	2.6	0.2240	24.0963
60	120	3.2	0.2688	29.6570
80	160	4.1	0.3585	37.9981
100	200	5.25	0.4481	48.6561
110	220	5.4	0.4929	50.0463
120	240	5.55	0.5377	51.4365
130	260	5.6	0.5825	51.8999
160	320	5.65	0.7170	52.3632
200	400	5.7	0.8963	52.8266
240	480	5.75	1.0755	53.2900
275	550	5.8	1.2324	53.7534
395	790	5.8	1.7702	53.7534

References

1. Farhadinia, M.A., SPE and Delshad, M., SPE (2010). Modeling and Assessment of Wettability Alteration Processes in Fractured Carbonates using Dual Porosity and Discrete Fracture Approaches. SPE 129749. Improved Oil Recovery Symposium held in Tulsa, Oklahoma, USA, 24-28 April 2010.
2. Donaldson, Erle and Alam, Waqi (2008). Wettability.Gulf Publishing Company, Houston, Texas.
3. Okasha, T.M., SPE, Funk, J.J., SPE and Al-Rashidi, H.N., Saudi Aramco (2007). Fifty Years of Wettability Measurements in the Arab-D Carbonate Reservoir. SPE 105114. 15th SPE Middle East Oil and Gas Show and Conference held in Bahrain International Exhibition Centre, Kingdom of Bahrain, 11-14 March 2007.
4. BP Magazine, Issue Four 2013. Enhanced Oil Recovery: Boosting Production. http://www.bp.com/en/global/corporate/press/bp-magazine/issue-four-2013/enhanced-production.html
5. Oil and Gas Journal. 2014 Worldwide EOR Survey. Issue: 07/04/2014. http://www.ogj.com/articles/print/volume-112/issue-4/special-report-eor-heavy-oil-survey/2014-worldwide-eor-survey.html
6. Dyer, S.B. and Farouq Ali, S.M., SPE (1994). Linear Model studies of the Immiscible CO_2 WAG Process for Heavy Oil Recovery. SPE Reservoir Engineering, 107-111, May 1994.
7. U.S. Department of Energy 2014. Oil and Gas. Enhanced Oil Recovery.
8. David Martin, F., SPE and Taber, J.J., SPE New Mexico (1992). Carbon Dioxide Flooding. Journal of Petroleum Technology, JPT, April 1992, 396-400.
9. Jarrel, P., Fox, C., Stein, Michael, S. and Stev, 2002. Practical Aspects of CO_2 Flooding. Henry H. Doherty Series, SPE Monograph, Volume 22 Richardson, Texas.
10. Stalkup, Fred, 1984. Miscible Displacement. Henry H. Doherty Series, SPE Series Volume 8, New York.
11. Dyer, S.B. and Farouq Ali, S.M., Univesity of Alberta. The Potential of the Immiscible Carbon Dioxide Flooding Process for the Recovery of Heavy Oil. Petroleum Society of CIM, presented at 3rd Technical Meeting of the South Saskatchewan section, held in Regina, September 25-27, 1989.
12. Holm, L.W. Carbon Dioxide Solvent Flooding for Increased Oil Recovery, Trans., AIME, 1959, 216, 225.231.
13. Crank, J. The Mathematics of Diffusion, Oxford Claredon Press, 1967.
14. Laidler, K.J. and Meiser, J.H. Physical Chemistry. Benjamin/ Cummings Publication Company Inc., Ontario (1982).
15. Yellig,W.F. and Metcalf, R.S. Determination and Prediction of the CO_2 Minimum Miscibility Pressures. Journal of Petroleum Technology, JPT, Jan 1980, 160-168.
16. Orr, F.M. Jr. and Silva, M.K. Effect of Oil Composition on Minimum Miscibility Pressure, Part 2: Correlation. SPERE (Nov. 1987), 479-491.

17. Nguyen, T.A. and Farouq Ali, S.M. Effect of Nitrogen on the Solubility and Diffusivity of Carbon Dioxide into Oil and Oil Recovery by the Immiscible WAG Process. The Jounal of Canadian Petroleum Technology, February 1998, Volume 37, No.2.
18. Mohammed-Singh, LJ, Singhal, AK. Lessons from Trinidad's CO_2 Immiscible Pilot Projects. SPE Reservoir Evaluation and Engineering, 2005.
19. Salehi, Amir. CO_2 Injection for Enhanced Oil Recovery. Stanford University, December 11, 2013.
20. Briggs, J.P. and Puttagunta, V.R. The Effect of Carbon Dioxide on the Viscosity of Lloydminster Aberfeldy Oil at Reservoir Temperature. Alberta Research Council Report, Edmonton Alberta, January 1984.
21. Beech, C.E. and Parkhurst, I.P. Effect of Dissolved Gas upon the Viscosity and Surface Tension of Crude Oils. Petroleum Development and Technology in 1926, Pet. Div. AIME, 51-69.
22. Hatzignatiou, D.G., Lou, Y.. Feasibility Study of CO_2 Immiscible Displacement Process in Heavy Oil Reservoirs. Annual Technical Meeting, Calgary, Alberta 1994.
23. Zain, Z.M.. Evaluation of CO_2 Gas Injection for Major Oil Production Fields in Malaysia – Experimental Approach Case Study: Dulang Field. SPE Asia Pacific Improved Oil Recovery Conference, Kuala Lumpur, Malaysia 2001.
24. Aske, Narve, Kallevik, Harald and Sjoblom, Johan. Determination of Saturate, Aromatic, Resin and Asphaltenic (SARA) Components in Crude Oils by Means of Infrared and Near-Infrared Spectroscopy. Energy & Fuels 2001, 15, 1304-1312, American Chemical Society, Published on 8th November 2001.
25. Stephen Melzer, L.. 2012. "Carbon Dioxide Enhanced Oil Recovery (CO_2 EOR): Factors Involved in Adding Carbon Capture, Utilization and Storage (CCUS) to Enhanced Oil Recovery". Melzer Consulting, February 2012.
26. Baljit S. Sehbi, SPE Halliburton Energy Services, Scott M. Frailey, SPE and Akanni S. Lawal, SPE, Texas Tech University. Analysis of Factors Affecting Microscopic Displacement Efficiency in CO_2 Floods. SPE 70022. Presented at SPE Permian Bsain Oil and Gas Recovery Conference held in Midland, Texas, 15-16 May 2001.
27. Jackson, D.D, Exxon Co. U.S.A.; Andrews, G.L., Shell Oil Co.; and Claridge E.L., U. of Houston. Optimum WAG Ratio vs. Rock Wettability in CO_2 Flooding. SPE 14303. Presented at the 60th Annual Technical Conference and Exhibition fo the Society of Petroleum Engineers held in Las Vegas, NV September 22-25, 1985.
28. Potter, G.F, Amoco Production Co. The Effects of CO_2 Flooding on Wettability of West Texas Dolomitic Formations. SPE 16716. Presented at the 62nd Annual Technical Conference and Exhibition of the Society of Petroleum Engineers held in Dallas, TX September 27-30, 1987.
29. Vives, M.T., SPE, Chang, Y.C. and Mohanty, K.K, SPE, U. of Houston. Effect of Wettability on Adverse-Mobility Immiscible Floods. SPE Journal 4 (3), September 1999, pg 260-267.
30. Chalbaud, C., SPE, Lombard, J.M., SPE, Martin, F. and Robin,M., SPE, Institut Francais du Petrole; Bertin, H., SPE, Universite de Bordeaux; and Egermann, P.,

Institut Francais du Petrole. Two Phase Flow Properties of Brine-CO_2 Systems in Carbonate Core: Influence of Wettability on Pc and kr. SPE 111420. Presented at the 2007 SPE/EAGE Reservoir Characterization and Simulation Conference held in Abu Dhabi, U.A.E., 28-31 October 2007.

31. Zekri, Abdulrazag Y., SPE, United Arab Emirates U.; Shedid, Shedid A., SPE, UWA; and Almehaideb, Reyadh A., SPE, United Arab Emirates U. SPE 104630. Presented at the 15th SPE Middle East Oil and Gas Show and Conference held in Bahrain International Exhibition Center, Kingdom of Bahrain, 11-14 March 2007.
32. Alotaibi, M.B., Nasralla, R.A. and Nasr-El-Din, H.A., Texam A&M University, all SPE members. SPE 129972. Presented at the 2010 SPE Improved Oil Recovery Symposium held in Tulsa, Oklahoma, USA, 24-28 April 2010.
33. Fjelde, Ingebret, SPE, and Asen, Siv Marie, SPE, IRIS. Wettability Alteration During Water Flooding and Carbon Dioxide Flooding of Reservoir Chalk Rocks. SPE 130992. Presented at the SPE EUROPEC/EAGE Annual Conference and Exhibition held in Barcelona, Spain, 14-17 June 2010.
34. Sahin, Secaeddin, Kalfa, Ulker, Celebioglu, Demet, Duygu, Ersan and Lahna, Hakki, Turkish Petroleum Corp. (TPAO). SPE 157865. Presented at the SPE Heavy Oil Conference Canada held in Calgary, Alberta, Canada, 12-14 June 2012.
35. Al-Mutairi, Saad M., 2013. “Modeling Wettability Alteration during Immiscible Carbon Dioxide Flooding Process”, Ph.D. dissertation, KFUPM, Dec. 2013.
36. Al-Mutairi, Saad M., Abu Khamsin, Sidqi A. and Hossain, M. Enamul, 2012. “A Novel Approach to Handle Continuous Wettability Alteration during Immiscible CO_2 Flooding Process”, paper SPE 160638. Presented at Abu Dhabi International Petroleum Exhibition & Conference held in Abu Dhabi, UAE, 11-14 November 2012.
37. Jalili, Zohreh, Norwegian University of Science and Technology, and Tabrizy, Vahid Alipour, Asgard Petroleum Technology, Statoil ASA. Mechanistic Study of the Wettability Modification in Carbonate and Sandstone Reservoir during Water/Low Salinity Water Flooding. Energy and Environment Research; Vol. 4, No. 3, 2014. Published by Canadian Center of Science and Education.
38. Bennion, D. Brant and Thomas, F. Brent. The Use of Carbon Dioxide as an Enhanced Recovery Agent for Increasing Heavy Oil Production. Presented at the Joint Canada/Romania Heavy Oil Symposium, 7-13 March, 1993 at Sinia, Romania.

Vitae

Name	: Muzzammil Shakeel
Nationality	: Pakistani
Date of Birth	: 01/14/1990
Email	: muzammil.shakeel@hotmail.com
Address	: Bahadurabad, Karachi, Pakistan.
Academic Background	: **Masters in Petroleum Engineering**
	King Fahd University of Petroleum & Minerals
	Dhahran, Saudi Arabia
	BE in Petroleum Engineering
	December, 2011
	NED University of Engineering & Technology, Karachi
	Pakistan