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-THEME-

Experimental Investigation of CO_2-EOR Efficiency In Sandstone Reservoirs with NMR Technology

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Dedications

In the name of Allah, the Most Gracious, the Most Merciful

I humbly dedicate this work to the Almighty, who has guided me through every step of my academic journey. With profound gratitude, I acknowledge the blessings, strength, and wisdom bestowed upon me, enabling me to undertake this endeavor.

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Dedications

This work is dedicated to:

The sake of Allah, my Creator and my Master.

My mother the source of tenderness and love, the one who sacrificed and gave her all for us. To you *Nacira Aiad.*

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To all the people in my life who touch my heart.

Abdelkader Bouchenafa

Abstract

CO2 injection presents a promising approach for enhanced oil recovery by combining efficient oil extraction with the reduction of CO2 emissions. In this innovative study and the first of its kind in Algeria. An experimental investigation was conducted to assess the efficiency of CO2 flooding in sandstone core samples taken from the reservoir rock of Hassi Messaoud's field. A pure supercritical CO2 was used to flood the core samples, as a tertiary recovery technique, targeting the residual oil that remains unrecovered after secondary recovery (Waterflooding). The experiments were conducted under representative reservoir conditions. To monitor the process. The main objective of this study is to evaluate the impact of miscible CO2 flooding on the recovery of residual oil that remains after waterflooding.

Keywords: CO2-EOR; miscible displacement; sandstone reservoirs; residual oil; OOIP;

Résumé

L'injection de CO2 présente une approche prometteuse pour améliorer la récupération du pétrole en combinant une récupération efficace avec réduction des émissions de CO2. Ce nouveau travail est désormais comme la première étude en Algérie. Une investigation expérimentale a été menée pour évaluer l'efficacité de l'injection de CO2 dans des échantillons de grès prélevés de la roche réservoir du champ de Hassi Messaoud. Le CO2 pur en état supercritique est utilisé pour drainer l'échantillon, en tant que méthode de récupération tertiaire, ciblant l'huile résiduelle restant piégée après la récupération secondaire (injection d'eau). Les expériences ont été effectuées sous conditions réservoir représentatives. A fin d'assurer le processus, la technologie RMN a été appliquée. L'objectif principal de cette approche est d'évaluer l'impact de l'injection miscible par CO2 et déterminer les taux de récupération des quantités résiduelles.

Mots-clés : CO2-EOR ; déplacement miscible ; réservoirs gréseux ; huile résiduelle ; OOIP ;

ملخص

حقن ثاني أكسيد الكربون يمثل نهجاً واعداً لتعزيز استخراج النفط من خلال توفير استخلاص فعال للزيت مع تقليل انبعاثات ثاني أكسيد الكربون. في هذه الدراسة المبتكرة والأولى من نوعها في الجزائر، تم إجراء تحقيق تجريبي لتقييم كفاءة حقن ثاني أكسيد الكربون في عينات صخرية رملية مأخوذة من صخور خزان حقل حاسي مسعود. تم استخدام ثاني أكسيد الكربون فوق الحرج والنقي لحقن العينة الصخرية كتقنية استرجاع ثالثية للزيت، مستهدفة الزيت الباقي الذي يظل غير مسترد بعد مرحلة الإسترجاع الثانوية (حقن الماء). تمت التجارب تحت شروط ممثلة للحوض المخزني لمراقبة العملية، تم استخدام تكنولوجيا الرنين المغناطيسي النووي. الهدف الرئيسي من هذه الدراسة هو تقييم تأثير حقن ثاني أكسيد الكربون الممزوج على استرداد الزيت الباقي بعد حقن الماء.

الكلمات المفتاحية: تعزيز إستخراج البترول بثاني أكسيد الكربون، إزاحة متجانسة، خزان صخر رملي، زيت متبقي، الزيت الأصلي في المكان،

Table of Contents

Chapter I: Basic concepts in reservoir engineering

Chapter II: Principles and Applications of CO₂-EOR

Chapter III: Experimental Work

Chapter IV Results and discussion

List of Figures

List of Tables

Nomenclature

Φ	Porosity	fraction
V_p	Pore volume	ml
V_b	Bulk volume	ml
V_g	Grain volume	ml
u	Fluid velocity	cm/s
q	Flow rate	ml/s
k	Permeability	Darcy
A_c	Cross section area	cm^2
μ	Fluid viscosity	cp
l	Length of rock sample	cm
dp	Pressure gradient	atm/cm
S	Saturation	fraction
S_o	Oil saturation	ml
S_w	Water saturation	ml
S_g	Gas saturation	ml
P_c	Capillary pressure	psi
P_{nw}	Non wetting phase pressure	psi
P_w	Wetting phase pressure	psi
σ	Interfacial tension	dyne/cm
θ	Contact angle	degree
r	Pore radius	cm
C_r	Matrix compressibility	psi^{-1}
C_p	Pore compressibility	psi^{-1}
C_b	Bulk volume compressibility	psi^{-1}
σ_3	Overburden stress	psi
E	Displacement efficiency	fraction
M	Mobility ratio	fraction
K_r	Relative permeability	mD
N_c	Capillary number	/

E_v	Volumetric displacement efficiency	/
V_o	Oil volume	m^3
B_o	Volumetric factor of ol	RB/STB
B_{oi}	Initial volumetric factor	RB/STB

List of Abbreviation

OOIP	Original oil in place
EOR	Enhanced oil recovery
CO2	Carbon dioxide
CO2-EOR	CO2 enhanced oil recovery
NMR	Nuclear magnetic resonance
MMP	Minimum miscibility pressure
IFT	Interfacial tension
OWC	Oil water contact
GOC	Gas oil contact
GOR	Gas oil ratio
ASP	Alkaline surfactant polymer
WAG	Water alternating gas
STB	Stock tank barrel
MBE	Material balance equation
CCS	Carbon capture and storage
LPG	Liquefied petroleum gas
HC	Hydrocarbon
DLCC	Direction Laboratoires & Carothèque Centrale
CINA	Centrale industrielle Naili Abdelhalim
HMD	Hassi Messaoud
CFS 350	Core flooding system 350 bar
BPR	Back pressure regulator
RF	Recovery factor
PVI	Pore volume injected
IPCC	Panel on Climate Change
IEA	International Energy Agency
BP	British Petroleum

Introduction

Introduction

The global energy consumption is projected to increase by almost 50% between 2020 and 2050 [1]. This is due mainly to the required industrial development to meet the rapid increase of the world's population, which is expected to reach about 9.7 billion by 2050 [2]. Crude oil currently dominates the world's primary energy consumption, accounting for over 31% of the world's total primary energy consumption, which includes (oil, natural gas, coal, hydroelectric, nuclear energy, and renewables) [3]. The demand for crude oil is estimated to reach 108.2 million barrels per day by 2045, necessitating continuous growth in crude oil production [4]. However, crude oil reserves are depleting, and new discoveries of easy-to-find crude oil fields are becoming more difficult. Hence, improving oil recovery from the existing and depleted mature petroleum reservoirs through advanced recovery techniques has become a vital scheme in the oil and gas industry.

During the primary (natural drive and artificial lift) and secondary (waterflooding and immiscible gas injection) oil recovery stages, roughly one-third of the original oil-in-place (OOIP) can be recovered from mature reservoirs, implying that significant amounts of crude oil are left unrecovered following these two recovery stages. The remaining oil in the reservoirs is attributed to the low oil mobility and poor displacement efficiency, directly related to the high oil viscosity and surface tension, as well as unfavorable interfacial fluid/fluid and fluid/rock properties. Therefore, tertiary recovery or enhanced oil recovery (EOR) methods have been thoroughly investigated and implemented to boost the production of the immobile oil left in the reservoirs by improving the microscopic and macroscopic (volumetric) sweep and oil displacement efficiencies [5].

Among the existing EOR methods, The CO_2 injection method for miscible oil recovery is gaining an increasing interest in the oil and gas industry because, in addition to its high oil recovery, CO_2-EOR has the ability to lower the emission of CO_2 by storing the gas permanently underground after it is utilized. At well-selected storage sites the rock formation are likely to preserve more than 99% of the injected CO_2 for over 100 years [6]. This is an environmental friendly win-win situation where both oil recovery is increased and the emission of greenhouse gases to the atmosphere is reduced.

In light of these realities, it is crucial to thoroughly study and assess the viability of CO2 injection as an enhanced oil recovery (EOR) method, particularly in the Algerian context where

this technology remains unavailable and understudied. Therefore, the objective of our study is to investigate the impact of CO2 injection on oil recovery in sandstone reservoirs following water flooding, under reservoir-representative conditions. This investigation was conducted using a combination of a Core Flooding system and NMR technology in the NMR laboratory of Direction Laboratoires & Carothèque Centrale (DLCC), SONATRACH, HMD.

The experimental procedure involved injecting CO_2 into a sandstone core sample at the Minimum Miscibility Pressure (MMP) and comparing the recovery achieved through water flooding with that achieved through CO_2 injection. Notably, the utilization of NMR technology played a pivotal role in this study, enabling precise measurements of various parameters such as porosity, saturations, and recovery factors associated with all the conducted experiments. In contrast to the conventional visual reading method, which is prone to errors and does not provide accurate results due to the inclusion of the dead volumes of the core flooding system, NMR technology ensures precise and reliable outcomes.

This thesis work will be structured according to the following plan:

The first chapter " Basic concepts in reservoir engineering" aims to provide readers with a comprehensive understanding of the processes, mechanisms, and influential factors involved in oil recovery. Chapter two "CO_2-EOR Principles and Applications" explores the fundamental principles of CO_2-EOR (Carbon Dioxide Enhanced Oil Recovery). It covers topics such as miscibility, Minimum Miscibility Pressure (MMP), and the various oil recovery mechanisms facilitated by CO_2. It also examines studies on coupled CO_2 injection with EOR techniques. By providing a concise overview of CO_2-EOR principles and applications, this chapter sets the foundation for further analysis in subsequent chapters. Chapter three provides an overview of the experimental setups and procedures employed in the study. The forth chapter presents the results of the conducted experiments and provides a thorough analysis of the outcomes. Finally, this thesis ends with a conclusion and recommendations.

Chapter l

Basic Concepts in Reservoir Engineering

Chapter I: Basic concepts in reservoir engineering

This chapter offers a comprehensive introduction to the essential principles of reservoir engineering while also delving into a range of techniques and methodologies used in oil recovery. Its purpose is to provide readers with a comprehensive understanding of the processes and mechanisms involved in the recovery of oil. Additionally, this chapter examines key factors influencing oil displacement efficiency, thus establishing a solid foundation for the subsequent chapters.

I.1 Fundamentals of rock properties

The nature of reservoir rocks containing oil and gas dictates the quantities of fluids trapped within the void space of these rocks, the ability of these fluids to flow through the rocks, and other related physical properties. The measure of the void space is defined as the porosity of the rock, and the measure of the ability of the rock to transmit fluids is called the permeability. A knowledge of these two properties is essential before questions concerning amount of fluids, rates of fluid flow and fluid recovery estimates can be answered **[7].**

I.1.1 Porosity

Sand grains and particles of carbonate materials that make up sandstone and limestone reservoirs usually never fit together perfectly due to the high degree of irregularity in shape. The void space created throughout the beds between grains, called pore space or interstice, is occupied by fluids (liquids and/or gases). The porosity of a reservoir rock is defined as that fraction of the bulk volume of the reservoir that is not occupied by the solid framework of the reservoir **[7]**. This can be expressed in mathematical form as:

$$\phi = \frac{V_b - V_{gr}}{V_b} = \frac{V_p}{V_b} \qquad (I.1)$$

Where

ϕ: Porosity, fraction.

V_b: Bulk volume (m^3).

V_{gr}: Grain volume (m^3).

V_p: Pore volume (m^3).

➢ **Engineering classification of porosity**

a) Total porosity

So called absolute porosity is the ratio of the total void space in the sample to the bulk volume of that sample, regardless of whether or not those void spaces are interconnected. A rock may have considerable absolute porosity and yet have no fluid conductivity for lack of pore interconnections **[8].**

$$\Phi_a = \frac{V_{pt}}{V_b} \qquad (I.2)$$

Where

V_{pt}: Total pore volume (m^3).

Φ_a: Absolute porosity, fraction.

b) Effective porosity

The effective porosity is the percentage of interconnected pore space with respect to the bulk volume **[8]**.

$$\Phi = \frac{V_p}{V_b} \qquad (I.3)$$

Where

Φ: Effective porosity fraction.

V_{pc}: Volume of connected pores (m^3).

If the petroleum occupies non-connected void spaces, it cannot be produced and is of little interest to the petroleum engineer. Therefore, effective porosity is the value used in all reservoir engineering calculations **[7]**.

➢ **Geological classification of porosity**

The original porosity of a formation is usually referred to as primary porosity. Porosity modified by post depositional processes is referred to as secondary porosity **[9].**

I.1.2 Permeability

Permeability is a property of the porous medium that measures the capacity and ability of the formation to transmit fluids. The rock permeability, k, is a very important rock property because it controls the directional movement and the flow rate of the reservoir fluids in the formation. This rock characterization was first defined mathematically by Henry Darcy in 1856. In fact, the equation that defines permeability in terms of measurable quantities is called Darcy's Law. Darcy developed a fluid flow equation that has since become one of the standard mathematical tools of the petroleum engineer. If a horizontal linear flow of an incompressible

fluid is established through a core sample of length L and a cross-section of area A, then the governing fluid flow equation is defined as **[8]**:

$$u = \frac{q}{A_c} = -\frac{k}{\mu}\frac{dp}{dl}$$

$$\text{(I.4)}$$

Where

       u: Fluid velocity, cm/s.

       q: Flow rate, ml/s.

       k: Permeability, Darcy (0.986923 μm^2).

       A_c: Cross section area, cm^2.

       μ: Viscosity of the fluid, cp.

       l: Length of the rock sample, cm.

       dp/dl: Pressure gradient in the direction of the flow, atm/cm.

I.1.3 Saturation

Saturation is defined as that fraction, or percent, of the pore volume occupied by a particular fluid (oil, gas, or water) **[8]**. This property is expressed mathematically by the following relationship:

$$S = \frac{V_f}{V_p} \qquad \text{(I.5)}$$

Where

       S: fluid's saturation, fraction.

       V_f: fluid's volume (m^3).

       V_p : Pore volume (m^3).

Applying the above mathematical concept of saturation to each reservoir fluid gives **[8]**:

$$S_o = \frac{V_o}{V_p} \qquad \text{(I.6)}$$

$$S_g = \frac{V_g}{V_p} \qquad \text{(I.7)}$$

$$S_w = \frac{V_w}{V_p} \qquad \text{(I.8)}$$

Where

    S_o: oil saturation, fraction.

    S_g: gas saturation, fraction.

S_w: water saturation, fraction.

The saturation of each individual phase ranges between 0 to 100 percent. By definition, the sum of the saturations is 100% **[8].** Therefore:

$$S_o + S_g + S_w = 100\%$$

(I.9)

I.1.4 Wettability

Wettability is defined as the tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids. The concept of wettability is illustrated in figure (I.1), small drops of three liquids. The three droplets are then observed from one side. It is noted that the mercury retains a spherical shape, the oil droplet develops an approximately hemispherical shape, but the water tends to spread over the glass surface **[8]**.

This spreading tendency can be expressed more conveniently by measuring the angle of contact at the liquid-solid surface. This angle, which is always measured through the liquid to the solid, is called the contact angle θ **[8]**.

As the contact angle decreases, the wetting characteristics of the liquid increase. Complete wettability would be evidenced by a zero contact angle, and complete nonwetting would be evidenced by a contact angle of 180°. There have been various definitions of intermediate wettability but, in much of the published literature, contact angles of 60° to 90° will tend to repel the liquid **[8]**.

The wettability of reservoir rocks to the fluids is important in that the distribution of the fluids in the porous media is a function of wettability. Because of the attractive forces, the wetting phase tends to occupy the smaller pores of the rock and the nonwetting phase occupies the more open channels **[8].**
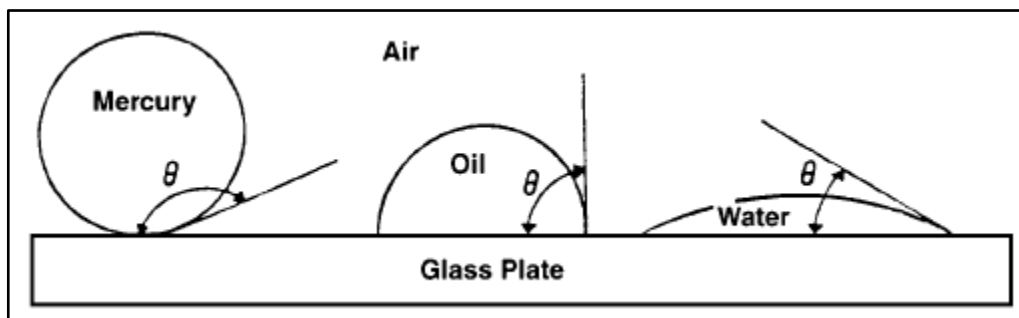
Figure I.1. Illustration of wettability **[8]**.

I.1.5 Capillary pressure

Capillary pressure is the pressure difference across the curved interface between two immiscible fluids in contact in a small capillary tube as shown in figure (I.2). The pressure difference is expressed in terms of wetting and nonwetting phase pressures **[10]**.

$$P_c = P_{nw} - P_w \qquad (I.10)$$

Where

P_c: capillary pressure (Psi).

P_{nw}: non wetting phase pressure (Psi).

P_w: wetting phase pressure (Psi).

Capillary pressure is related to interfacial tension, contact angle, and pore radius by **[10]**:

$$P_c = \frac{2\sigma\cos\theta}{r} \qquad (I.11)$$

Where

P_c: capillary pressure (dyne/cm^2).

r: pore radius (cm).

θ: contact angle (degree).

σ: interfacial or surface tension (dyne/cm).

The above expression shows that capillary pressure in reservoirs depends on the IFT between two immiscible fluids; θ, the contact angle between rock and fluid, which is a function of wettability; and r, pore radius, a microscopic rock property. An increase in pore radius leads to a decrease in Pc. Thus, high permeability rocks with relatively large pore radii have lower Pc than lower permeability rocks containing the same fluids **[10]**.
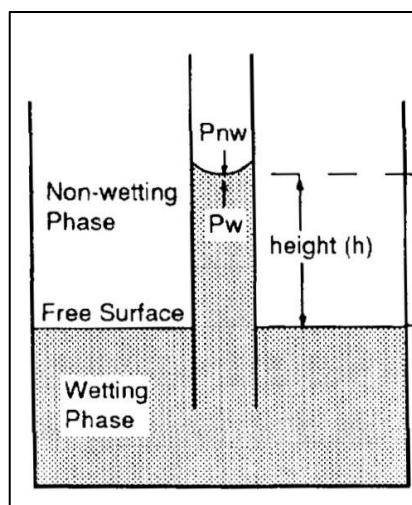
Figure I.2. Capillary tube in contact with two immiscible fluids **[11].**

I.1.6 Rock compressibility

The weight of the overburden simply applies a compressive force to the reservoir. The pressure in the rock pore spaces does not normally approach the overburden pressure. A typical pore pressure, commonly referred to as the reservoir pressure, is approximately 0.5 Psi per foot of depth, assuming that the reservoir is sufficiently consolidated so the overburden pressure is not transmitted to the fluids in the pore spaces [8].

The pressure difference between overburden and internal pore pressure is referred to as the effective overburden pressure. During pressure depletion operations, the internal pore pressure decreases and, therefore, the effective overburden pressure increases. This increase causes the following effects [8]:

- The bulk volume of the reservoir rock is reduced.
- Sand grains within the pore spaces expand.

These two volume changes tend to reduce the pore space and, therefore, the porosity of the rock. Often these data exhibit relationships with both porosity and the effective overburden pressure. Compressibility typically decreases with increasing porosity and effective overburden pressure [8].

There are three different types of compressibility.

The fractional change in grain volume per unit change in rock stress is called the rock or matrix compressibility, Cr in (psi^{-1}) [9].

$$C_r = \frac{1}{V_r}\frac{dV_r}{d(\sigma_3 - P)}$$
(I.12)

Where

V_r: the grain or matrix volume (cf).

The fractional change in total or bulk volume per unit change in rock stress is called the bulk volume compressibility, C_b in (psi^{-1}) [9].

$$C_b = \frac{1}{V_b}\frac{dV_r}{d(\sigma_3 - P)}$$
(I.13)

Where

V_b: the bulk volume (cf).

The fractional change in pore volume per unit change in rock stress is called the pore volume or formation compressibility, C_p in (psi^{-1}) [9].

$$C_p = \frac{1}{V_p}\frac{dV_p}{d(\sigma_3 - P)}$$

Where

V_p: the pore volume (cf).

P: pore pressure (psi).

σ_3: overburden pressure (psi).

I.2 Oil recovery processes

During the life of a producing oil field, several production stages are encountered. Initially, when a field is brought into production, oil flows naturally to the surface due to current reservoir pressure in the primary stage. As reservoir pressure drops, water is typically injected to boost the pressure to displace the oil in the secondary stage. Lastly, the remaining oil can be recovered by a variety of methods such as CO2 injection, natural gas miscible injection, and steam recovery in a tertiary or enhanced oil recovery (EOR) phase [12].

I.2.1 Primary recovery

Primary recovery mechanism as it is the stage when the natural energy of the reservoir is used to transport hydrocarbons towards and out of the production wells. The earliest possible determination of the drive mechanism is a primary goal in the early life of the reservoir, as its knowledge can greatly improve the management and recovery of reserves from the reservoir in its middle and later life. There are five important drive mechanisms: Solution gas drive; Gas cap drive; Water drive; Gravity drainage Combination or mixed drive. These drives can maintain the reservoir pressure, though water drive maintains much higher than the gas drives (Figure I.3) [12].
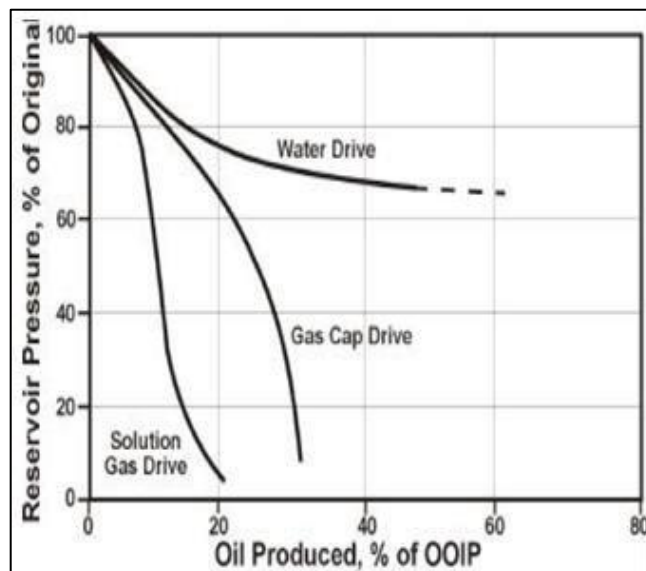
Figure I.3. Reservoir pressure trends by drive mechanisms [13].

➢ **Water drive mechanism**

The drive energy is provided by an aquifer that interfaces with the oil in the reservoir at the oil-water contact (OWC). As production continues, and oil is extracted from the reservoir, the aquifer expands into the reservoir displacing the oil. The recovery from water driven reservoirs is usually good (20-60% OOIP). Oil production from a strongly water driven reservoir remains fairly constant until water breakthrough occurs. When water breakthrough does occur, the well can either be shut-down, or assisted using gas lift. **[12]**.
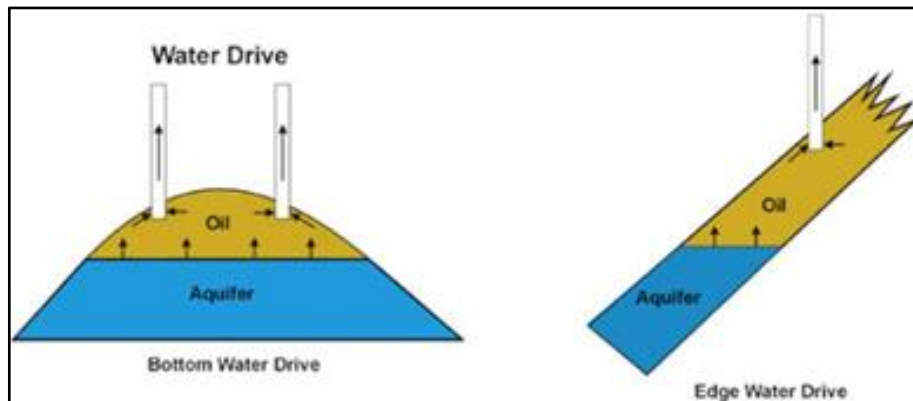
Figure I.4. Types of water drive **[14]**.

➢ **Gas cap drive mechanism**

As production continues, the gas cap expands pushing the gas-oil contact (GOC) downwards. Eventually the GOC will reach the production wells and the gas oil ratio (GOR) will increase by large amounts. The recovery of gas cap reservoirs can be (20% to 40% OOIP). Produced gas can be separated and immediately injected back into gas cap **[12]**.
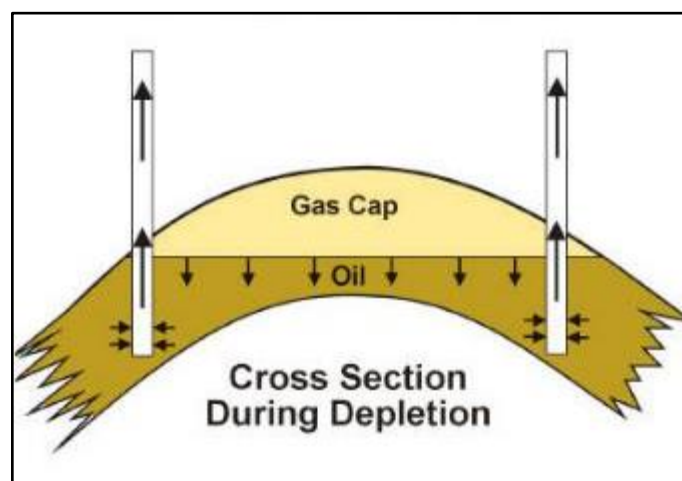
Figure I.5. Gas cap drive mechanism **[14]**.

➢ **Solution gas drive**

In solution gas drive, the expansion of the dissolved gases in the oil and water provides most of the reservoirs drive energy. Solution Gas Drive is associated to two types of Reservoirs that are related to pressure; under saturated reservoirs (no free gases in oil), drive energy is provided only by the bulk expansion of the reservoir rock and liquids; saturated reservoirs, where the pressure is less than the bubble point pressure. A decline in reservoir pressure causes bubbles of gas to expand. Thus, gas expansion is the primary reservoir drive for reservoirs below the bubble point. Oil recovery from this type is typically between 20% and 30% of original oil in place figure (I.6) [12].
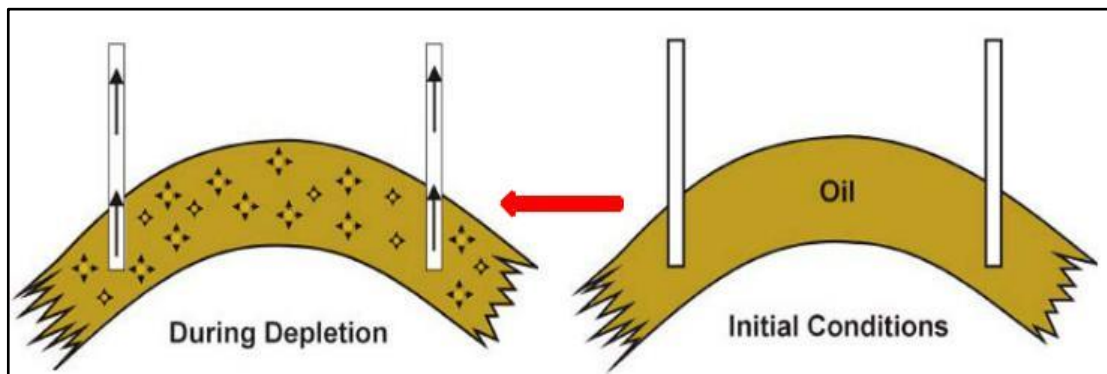
Figure I.6. Solution gas drive mechanism [14].

➢ **Gravity drainage**

Gravity Drainage is the fourth drive force that might be considered for drive mechanism where the density differences between oil and gas and water result in their natural segregation in the reservoir. This process can be used as a drive mechanism, but is relatively weak, and in practice is only used in combination with other drive mechanisms [12].
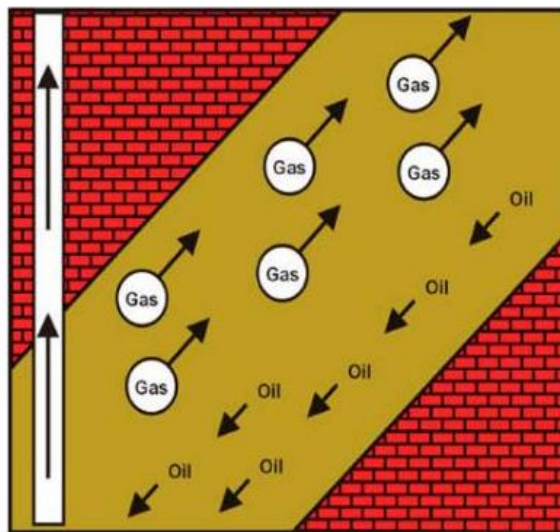
Figure I.7. Gravity drainage drive mechanism [14].

➢ **Combination drive**

In practice a reservoir usually incorporates at least two main drive mechanisms. Therefore, Combination or Mixed Drive can be accounted as the fifth type of drives [12].
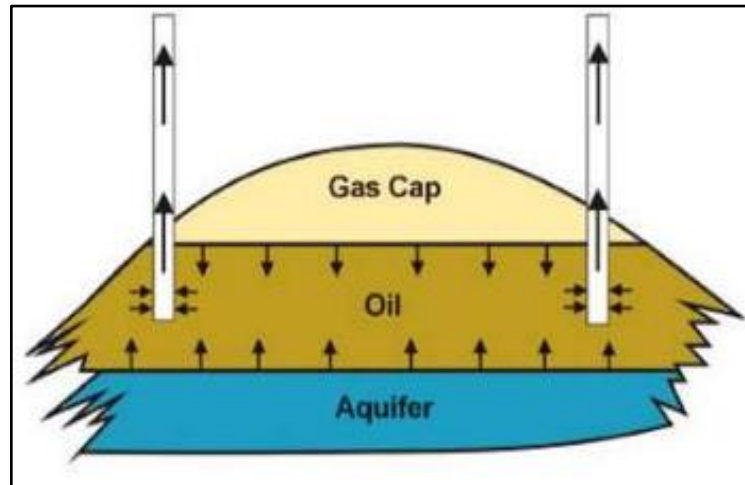
Figure I.8. Combination drive mechanism [14].

I.2.2 Secondary recovery

Secondary recovery is the result of human intervention in the reservoir to improve recovery when the natural drives have diminished to unreasonably low efficiencies. Two techniques are commonly used [13]:

- Water injection.
- Gas injection.

➢ **Water injection**

Water injection is implemented by injecting water into a set of wells while producing from the surrounding wells. Water flooding projects are generally implemented to accomplish reservoir pressure maintenance and/or dispose of brine water (or produced formation water), and/or as a water drive to displace oil from the injector wells to the producer wells [13].
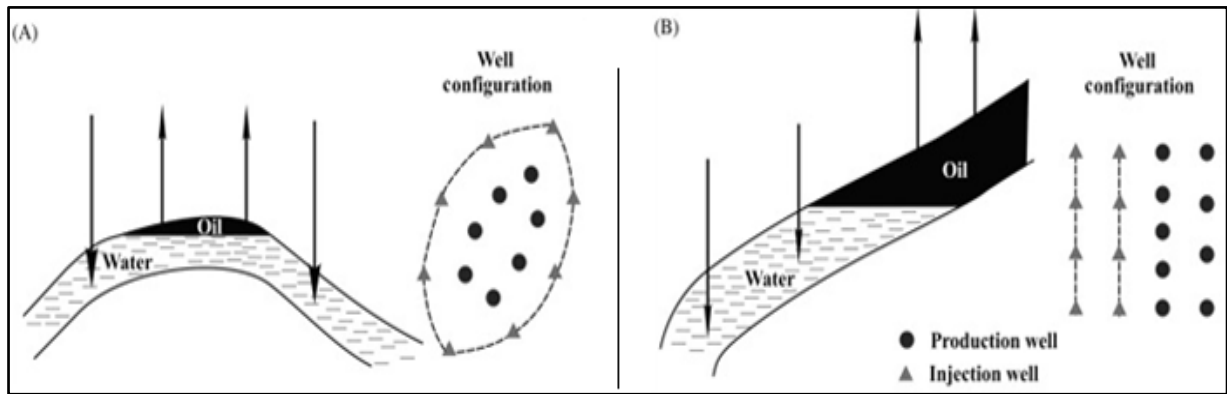
Figure I.9. Water injection in oil reservoirs **[15]**.

> **Gas injection**

This method is similar to water flooding in principle, and is used to maintain gas cap pressure even if oil displacement is not required. Usually, the produced natural gas is re-injected to the reservoir in order to maintain reservoir pressure rather than to displace the hydrocarbon **[13]**.
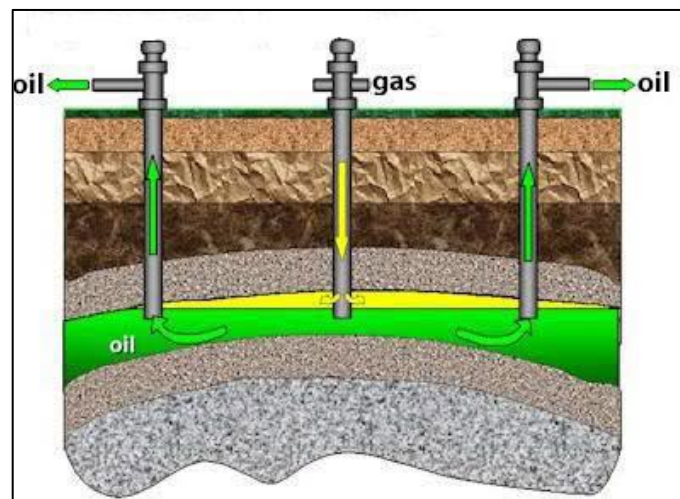
Figure I.10. Gas injection in gas cap **[16]**.

I.2.3 Tertiary recovery

Tertiary recovery or enhanced oil recovery EOR refers to the recovery of oil through the injection of fluids and energy not normally present in the reservoir. The objectives of the injected fluids are to achieve mainly two purposes; First is to boost the natural energy in the reservoir; second is to interact with the reservoir rock/oil system to create conditions favourable for residual oil recovery that leads to reduce the interfacial tension between the displacing fluid and oil, increase the capillary number, reduce capillary forces, increase the drive water viscosity, provide mobility-control, create oil swelling, reduce oil viscosity, alter the wettability of reservoir rock **[12]**.

Several techniques are implemented in tertiary recovery. Figure (I.11) illustrates oil recovery stages by the different EOR techniques **[12]**.
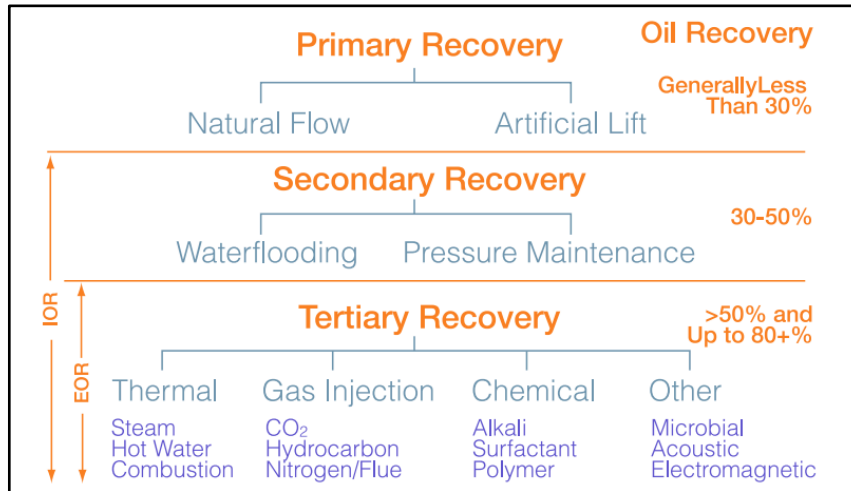
Figure I.11. The different oil recovery stages and the corresponding oil recovery factor **[12]**.

a)   Thermal techniques

Thermal methods raise the temperature of the reservoir to heat the crude oil in the formation and therefore reduce its viscosity and/or vaporize part of the oil and thereby decrease the mobility ratio. The increase in heat reduces the surface tension and increases the permeability of the oil and improves the reservoir seepage conditions. The heated oil may also vaporize and then condense to be produced. This operation, however, requires substantial investment in special equipment. Both methods also hardly damage the well bore structure, as well as pose safety risks in the larger production process. Therefore, thermal methods are not generally used very often **[12]**.

➤ **Steam injection**

Steam is injected into the reservoir either continuously or in cycles. Continuous steam injection involves both injection and production wells, whereas cyclic injection involves one well only which serves as both injection and production well. Steam floods are easier to control than in-situ combustion. For the same pattern size, the response time is 25-50% lower than the response time for additional production by in-situ combustion **[12]**.
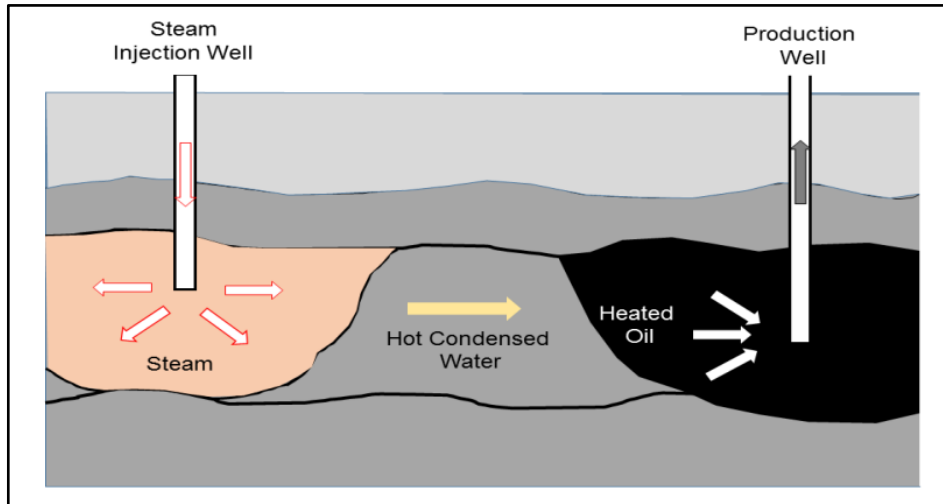
Figure I.12. Illustrative mechanism of steam flooding process **[17]**.

➢ **In-situ combustion**

In-situ combustion or fire flooding is a process in which an oxygen containing gas is injected into a reservoir where it reacts with the oil contained within the pore space to create a high temperature self-sustaining combustion front that is propagated through the reservoir. The heat from the combustion thins out the oil around it, causes gas to vaporize from it, and vaporizes the water in the reservoir to steam. Steam, hot water, and gas, all act to drive oil in front of the fire to production wells. In-situ combustion is possible if the crude-oil/rock combination produces enough fuel to sustain the combustion front. Severe corrosion and increased sand oil production are some of the problems that encountered by implementation of this technique **[12]**.
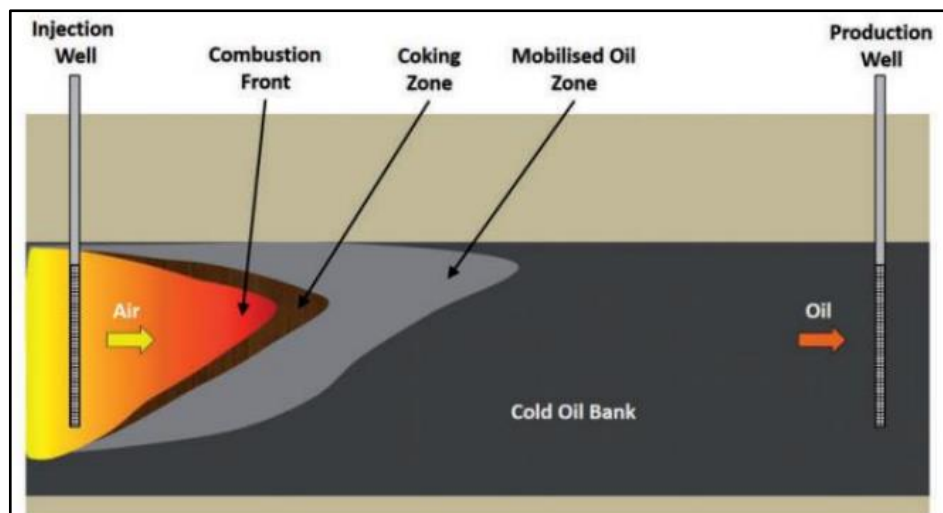
Figure I.13. Schematic of conventional in-situ combustion process **[18]**.

b) **Chemical flooding**

The best times for using chemical EOR methods were in the 1980's. Polymer flooding was the most important chemical EOR method. However, since 1990's, production from chemical EOR methods has been insignificant around the world except for China. These processes use chemicals added to water in the injected fluid of a water flood to alter the flood efficiency in such a way as to improve oil recovery by: Increasing water viscosity (polymer floods); Decreasing the relative permeability to water (cross-linked polymer floods); Increasing the relative permeability to oil (micellar and alkaline floods) **[12].**

➢ **Polymer flooding**

Polymers improve both vertical and areal sweep efficiency by reducing water-oil ratio. Polymers are injected through water injection wells in order to displace the residual oil. Increasing the displacing fluid's viscosity and lowering its relative permeability through plugging will improve the mobility ratio and this will make an improvement in areal and vertical sweep efficiency **[12]**.
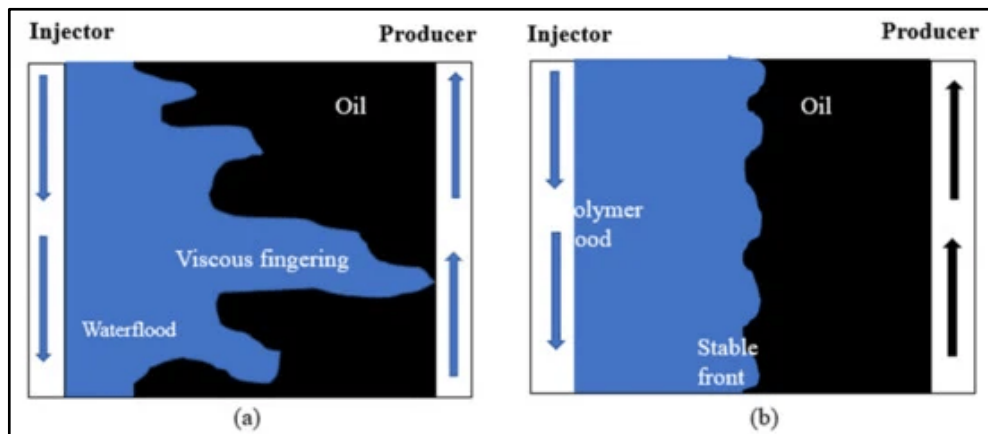
Figure I.14. (a) Waterflooding process (b) polymer flooding process **[19]**.

➢ **Alkaline-surfactant-polymer flooding**

During water flooding residual oil is trapped due to low water viscosity and high water-oil interfacial tension, therefore another way is to inject the three chemicals; Alkaline to minimize surface adsorption; Surfactant to lower interfacial tension and stabilizes the emulsion. On the other hand, Polymer is used to increase viscosity and to improve mobility control and sweep efficiency **[12]**.
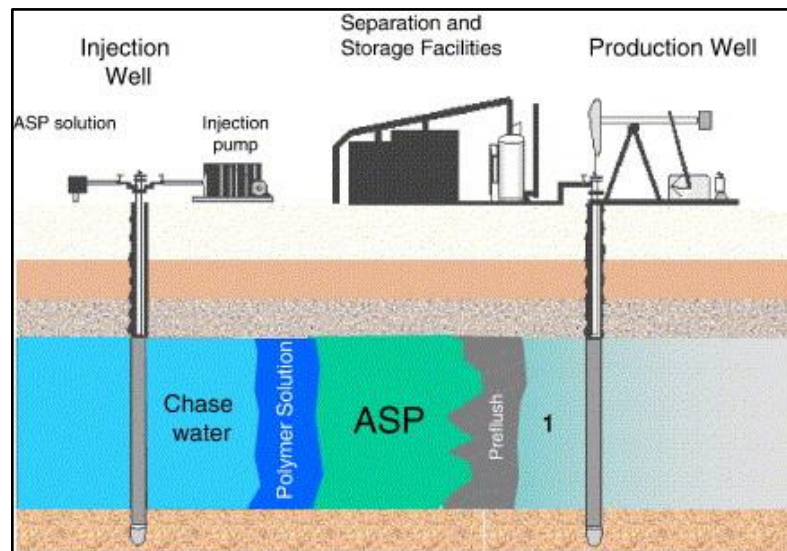
Figure I.15. Typical design of an ASP flooding process **[20]**.

c) Gas flooding (injection)

Gas is generally injected single or intermittently with water and this manner of injection called Water-Alternating Gas (WAG), has become widely practiced over all of world's oil fields. According to miscibility between gas injected and oil displaced, gas injection can be classified into two major types: miscible gas injection and immiscible gas injection. In miscible gas injection, the gas is injected at or above minimum miscibility pressure (MMP, explained in the next chapter) which causes the gas to be miscible in the oil. In contrast in immiscible gas injection, flooding by the gas is conducted below MMP. This low pressure injection of gas is used to maintain reservoir pressure to prevent production cut-off and thereby increase the rate of production. In miscible flooding, the incremental oil recovery is obtained by one of the three mechanisms: oil displacement by solvent through the generation of miscibility (i.e., zero interfacial tension between oil and solvent – hence infinite capillary number), oil swelling, and reduction in oil viscosity **[12]**. Miscible fluids are 100 % soluble in each other. The interfacial tension between miscible fluids is zero. Injection gases include:

- LPG injection
- Enriched gas miscible process
- Carbon dioxide (CO_2) injection

Carbon dioxide injection is discussed carefully in the next chapter.

I.3 Residual oil

During production, some of the oil will remain trapped in the reservoir. Typical trapped or residual oil saturation is in the range of 10% to 50% of the pore space, and it is higher in

tighter formations where the pore spaces are small. The amount of trapped oil is a function of the displacement method and conditions, making this oil a target for enhanced oil recovery (EOR) processes.

Residual oil occurs in the water-contacted portions of the reservoir trapped on small scales down to single oil droplets in individual pores. There is also the residual oil in macroscopic portions of the reservoir which were bypassed during the advance of the flood waters [21].
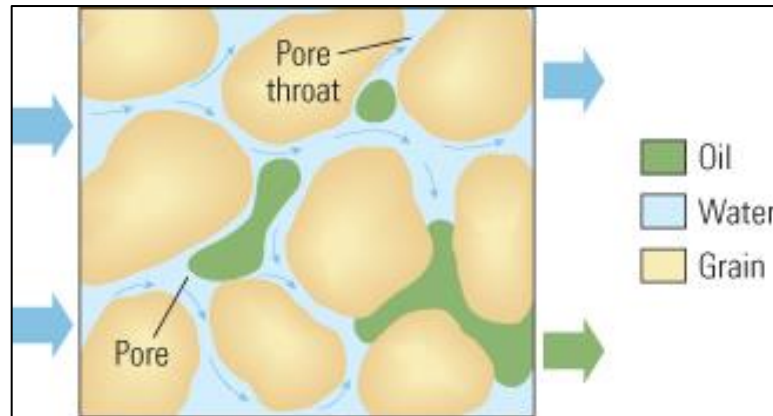
Figure I.16. Trapped oil inside the pores [21].

There are two common models describing why oil is trapped after water injection in water-wet systems is the snap-off model and the pore doublet model.

➢ **The Snap-off model**

In water-wet reservoirs, the oil will flow in the middle of the pores with a thin water film separating the oil from the pore wall. Due to capillary imbibition forces, the water film will increase in the pore throats and the oil phase will become thinner. Ultimately, the oil may snap-off and become discontinuous. The oil trapped by capillary snap-off will be left behind as immobile oil globules, as illustrated in figure (I.17) [22]:
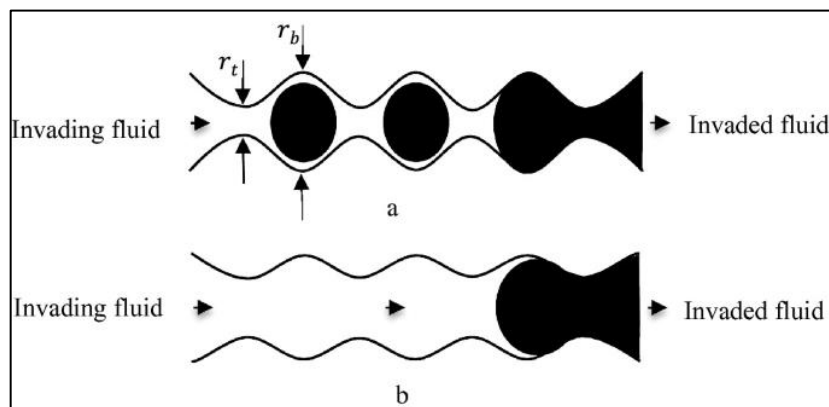
Figure I.17. Trapping of oil by capillary snap-off [23].

> **The pore doublet model**

In cases where a pore splits into two channels, the wetting phase will intrude the narrower channel more rapidly due to capillary imbibition forces. Hence, oil will be trapped in the broader pore channel, as visualized in figure (I.18) **[22]**:
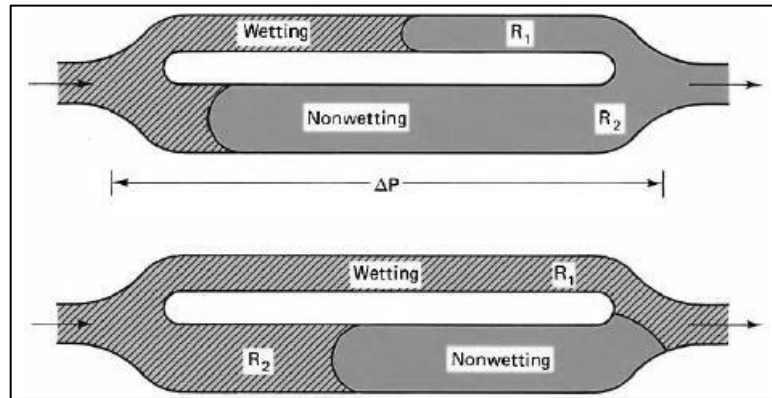
Figure I.18. Trapping of oil in a pore doublet model **[24]**.

I.4   Sweep efficiency

The ultimate goal of EOR processes is to increase the overall oil displacement efficiency E, and it is given by the product of **[21]**:

Macroscopic displacement efficiency or volumetric displacement, E_v and Microscopic displacement efficiency, E_d **[25]**.

$$E = E_v E_d \qquad\qquad (I.15)$$

Microscopic displacement efficiency is a measure of how well the oil displacing fluid moves once they are in contact **[19]**. For instance, microscopic efficiency can be increased by reducing capillary forces or interfacial tension between the displacing fluid and oil or by decreasing the oil viscosity **[21]**.

Macroscopic or volumetric displacement efficiency refers to the effectiveness of the displacing fluid (s) in contacting the reservoir in a volumetric sense. Volumetric displacement efficiency also known as conformance indicates the effectiveness of the displacing fluid in sweeping out the volume of a reservoir, both areally and vertically, as well as how effectively the displacing fluid moves the displaced oil toward production wells **[21]**. Figure (I.19) illustrates the microscopic and macroscopic sweep efficiency.
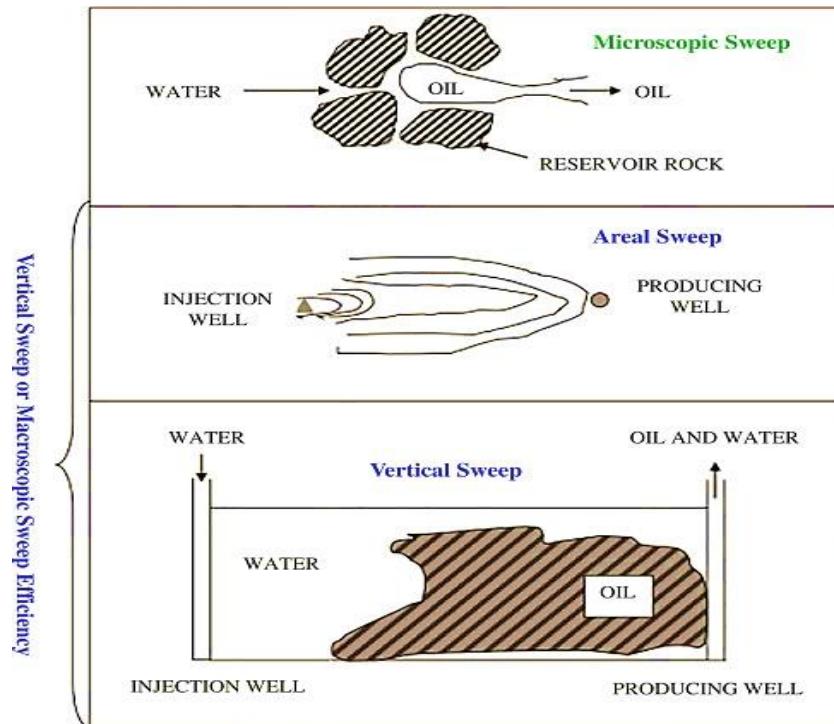
Figure I.19. Microscopic and macroscopic sweep efficiency **[26]**.

I.5   Mobility ratio

Mobility ratio is defined as the mobility of the displacing fluid (i.e. water) divided by the mobility of the displaced fluid (i.e. oil) **[25]**.

For waterflooding, this is the ratio of water to oil mobilities. The mobility ratio, M, for a waterflooding is given by the following expression **[25]**.

$$M = \frac{k_{rw}/\mu_w}{k_{ro}/\mu_o} \qquad (I.16)$$

Where

k_{rw}: relative permeability of water.

k_{ro}: relative permeability of oil.

μ_w: water viscosity.

μ_o: oil viscosity.

Volumetric sweep efficiency increases as M decreases, therefore mobility ratio is an indication of the stability of a displacement process, with flow becoming unstable (non uniform displacement front or viscous fingering) when M> 1.0. Thus, a large viscosity contrast between the displacing fluid (i.e. water) and the displaced fluid (i.e. oil) causes a large mobility ratio

(unfavourable M) which promotes the fingering of water through the more viscous oil and reduces the oil recovery efficiency. As such mobility ratio can be improved by increasing the drive water viscosity using polymers [25]. See figure (I.20).
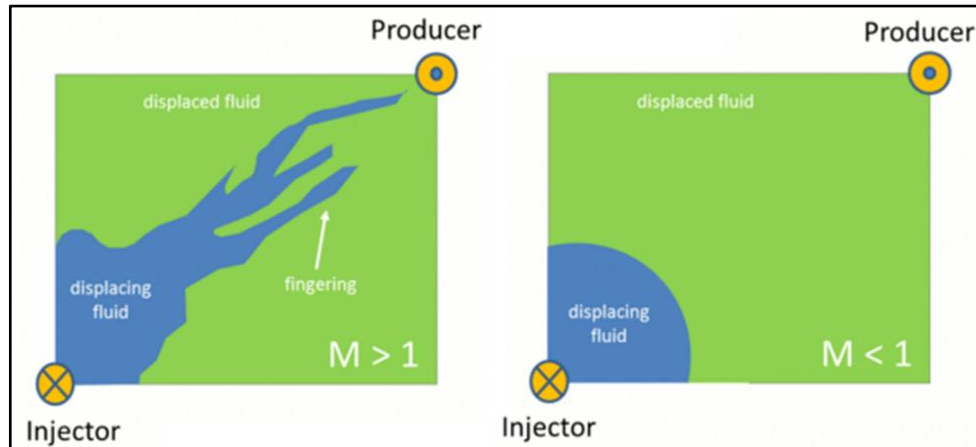
Figure I.20. Favorable and unfavorable mobility ratio [27].

I.6   Capillary number

The capillary number, N_c, is a dimensional group expressing the ratio of viscous to capillary (interfacial) forces as follows:

$$N_c = \frac{\nu \mu_w}{\sigma_{ow}} \tag{I.17}$$

Where ν is the interstitial velocity (m/s) of the displacing fluid (i.e. water), μ_w is the viscosity (Pa.s) of the displacing fluid (i.e. water), and σ_{ow} is the interfacial tension (N/m) between the oil and the displacing fluid. Capillary numbers for a mature waterflooding process are commonly in the order of 10-7 to 10-6. At the end of the waterflooding process, experience has shown that at these low capillary numbers an important amount of oil is left behind in the reservoir trapped by capillary forces at the pore scale. Thus, if the capillary number is increased through the application of EOR processes, residual oil will be mobilized and recovered. The most practical alternative to significantly increase the capillary number is through the application of CO2, surfactants or alkaline flooding (chemical flooding) [21].

I.7   Original oil in place and reserves

OOIP refers to the presence of hydrocarbons in a subsurface reservoir, while reserves refer to the portion of those hydrocarbons that can be commercially recovered.

Reserves are typically categorized based on their certainty and level of confidence, such as proven, probable and possible reserves [8].

I.7.1 Original oil in place estimation by volumetric method

The first step in a reservoir study is to accurately determine the initial hydrocarbon volume. This requires data which will allow us to calculate the size and geometry of the reservoir and the fluid volumes which the reservoir contains [8].

The original oil-in-place (OOIP) contained in a reservoir expressed in Stock Tank Barrels (STB) is designated by the symbol N and is given by the equation (field units) [8]:

$$N = \frac{7758 V_b \Phi (1 - S_{wi})}{B_{oi}} \qquad (I.18)$$

Where

V_b: Reservoir bulk volume (acre feet).

B_{oi}: initial oil formation volume factor (RB/STB).

I.7.2 Original oil in place and reserves estimation by material balance method

Material balance methods are another way of determining the initial hydrocarbon content of a reservoir.

The original oil in place at reservoir conditions is given by :

$$NB_{oi} = V_p (1 - S_{wi}) \qquad (I.19)$$

Reserves for a particular field are estimated from an analysis of the available engineering data.

➢ **For a reservoir without aquifer**

The reserves can be estimated applying the following MBE:

$$N_p B_o = NB_{oi}. C_e. \Delta P \qquad (I.20)$$

With

$$C_e = C_{wi} \frac{S_{wi}}{S_o} + C_o + \frac{C_f}{S_o} \qquad (I.21)$$

Where

$N_p B_o$: Reserves at reservoir conditions (tons).

C_e: equivalent compressibility (bar^{-1}).

C_{wi}: water compressibility (bar^{-1}).

C_o: oil compressibility (bar^{-1}).

C_f: formation compressibility (bar^{-1}).

ΔP: change in reservoir pressure (bar).

➢ **For a reservoir with aquifer**

$$N_p B_o = NB_{oi} . C_e . \Delta P + W_e \qquad (I.22)$$

With

$$W_e = C_p + C_w + V_w + \Delta P \qquad (I.23)$$

Where

W_e: water influx (m^3).

Chapter ll

Principles and

Applications of CO2-EOR

Chapter II: Principles and Applications of CO_2-EOR

This chapter delves into the fundamental principles of CO_2-EOR (Carbon Dioxide Enhanced Oil Recovery), exploring the properties of CO_2, its behavior under different reservoir conditions, and its application as a tertiary recovery method. The concept of miscibility, including the determination of Minimum Miscibility Pressure (MMP), is thoroughly explained. Additionally, the chapter discusses the advantages and disadvantages of CO_2-EOR, highlighting its potential for efficient oil recovery. Furthermore, the utilization of NMR as a monitoring tool in CO_2-EOR research is explored. CO_2 flood/injection designs are addressed, showcasing different strategies for successful implementation. Moreover, insights into ongoing CO_2-EOR projects are provided.

II.1 Carbon dioxide properties (CO2)

Carbon dioxide (CO_2) is formed from the chemical union of carbon and oxygen. It is primarily generated through the combustion of coal or hydrocarbons. CO_2 is a colorless, odorless, and non-toxic stable compound found in a gaseous state at standard conditions. In petroleum engineering application, it can be in gas or liquid state depending on the PVT conditions. The phase diagram of CO_2 is a key data to understand how CO_2 behaves under different conditions (Figure II.1) [28].
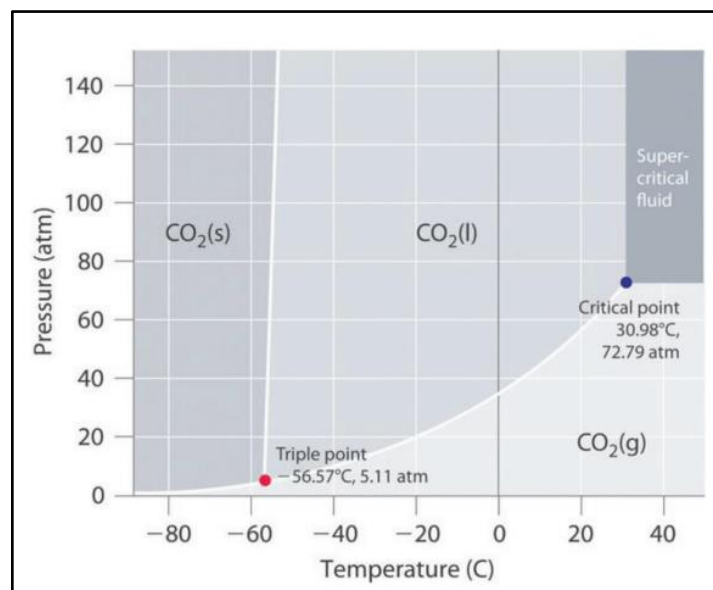
Figure II.1. CO_2 Phase diagram [28].

CO$_2$ is solid at low temperatures and pressures, but most dependent on temperature, by increasing the pressure and temperature, the liquid phase appears for the first time and coexists with the solid and vapour phases at the triple point. The liquid and the vapour phase of CO$_2$ coexist from the triple point and up to the critical point on the curve.

Below the critical temperature, CO$_2$ can exist either as a gas or as liquid. After exceeding the critical temperature, CO$_2$ exists as a gas. However when pressure is exceeding the critical pressure, the CO$_2$ becomes a supercritical fluid [28]. Table (II.1) gives the main properties of carbon dioxide.

Table II.1. Carbon dioxide properties [28].

Property	Value
Molecular weight	44 g/mol
Critical temperature	31°C
Critical pressure	73.77 bar
Critical density	467.6 kg/m3
Triple point temperature	−56.5°C
Triple point pressure	5.18 bar
Boiling (sublimation) point (1.013 bar)	−78.5°C
Solid Phase	
Density of carbon dioxide snow at freezing point	1562 kg/m3
Latent heat of vaporisation (1.013 bar at sublimation point)	571.1 kJ/kg1
Liquid Phase	
Vapour pressure (at 20 °C)	58.5 bar
Liquid density (at -20 °C and 19.7 bar)	1032 kg/m3
Viscosity (at STP)	99 µPa.s = 0.099 cp
Gas Phase	
Gas density (1.013 bar at boiling point)	2.814 kg/m3
Gas density (at STP)	1.976 kg/m3
Specific volume (at STP)	0.506 m3 /kg
Viscosity (at STP)	13.72 µPa s

II.2 Carbon capture and storage

Carbon dioxide is the most important greenhouse gas, because it is emitted into the atmosphere in large quantities. Carbon capture and storage (CCS) has been recognized as a new project around the world that should help mitigate CO_2 emissions significantly. The idea behind CCS is simple and can be divided into three steps: capture of CO_2 (e.g., from a fossil fuel power plant), transportation of the captured CO_2, and permanent storage into different geological formations (under supercritical state), with the aim of isolating CO_2 from the atmosphere (Figure II.2) [28].
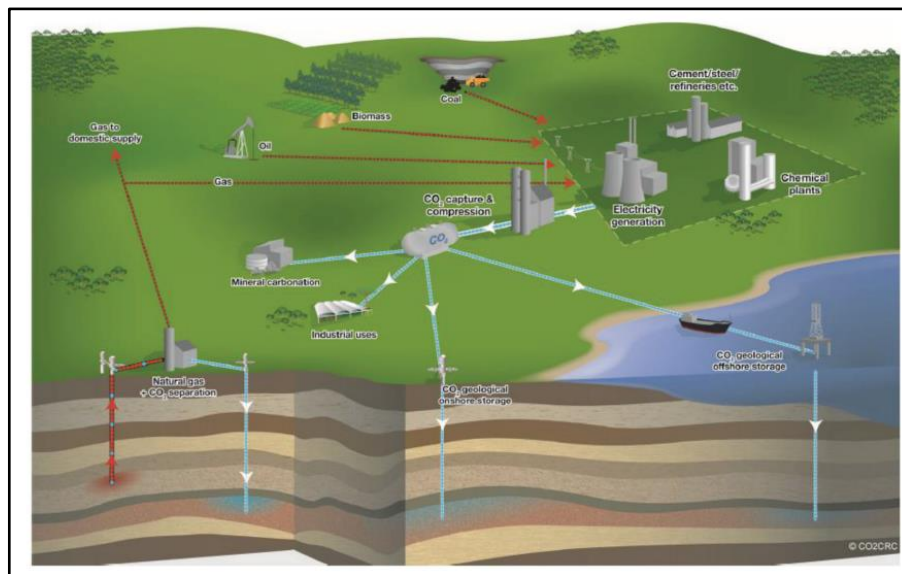
Figure II.2. A schematic diagrams of possible CCS projects [28].

Several scenarios describing the emission of greenhouse gases and models for the estimation of their influence on the global climate have been examined by the members of several association interests by this subject like as the Intergovernmental Panel on Climate Change (IPCC) and the International Energy Agency (IEA). Based on the assumptions of IPCC, the climate model global temperature increases between 1 and 6 °C were predicted by the year 2100, while some regions might benefit from higher temperatures. The IEA Agency estimates that CCS projects should contribute to about 15% to 20% of the total greenhouse gas emissions mitigation in 2050, and without application of CCS the overall costs to halve CO_2 emissions by 2050 would rise by 70% [23]. It has been estimated that geological formations worldwide are able to store more than 10000 Gt of carbon dioxide; this huge quantity is large compared to the cumulated anthropic emissions of carbon dioxide [28].

II.3 Miscibility

The term 'miscibility' refers to the ability of two or more fluids to mix in all proportions and form a single homogeneous phase **[29].**

Miscibility is a very important parameter in reservoir physics for the reason that miscibility increases the displacement efficiency and ultimate recovery, a miscible fluid can in theory displace all the oil on a microscopic scale. Miscible displacement can leave a substantial amount of residual oil behind the displacing front, this is mainly caused by two factors: instabilities caused by local heterogeneities (viscous fingering) or water shielding.

Molecules in a mixture can either be attracted to molecules of its own kind, or attracted to molecules of different kinds. Their preference towards each other depends on cohesion also known as Van der Waals forces. If for example the two fluids in place have a greater attraction towards their own kind, the fluids will be immiscible and vice versa, if the fluids have a greater attraction towards the other fluid in place, they will mix with each other and are called miscible. From experience, it is known that water and oil are immiscible fluids, while water and alcohol are miscible. There are two types of miscible displacement first and multicontact miscible displacement **[29].**

II.3.1 The first-contact miscibility

Refers to a condition wherein injected CO_2 and reservoir oil become miscible at their first ever contact. The phenomenon of achieving miscibility through first-contact process is generally exhibited by solvents like Liquefied petroleum gas (LPG) and light oils; however, CO_2 cannot achieve first-contact miscibility in most oil reservoirs within a reasonable range of pressures and reservoir temperature. In the case of a given reservoir oil and injected CO_2 system, for complete miscibility to occur, multiple contacts between the two phases are needed **[30].**

II.3.2 Multicontact miscibility process

CO_2 and various components of reservoir oil make numerous contacts by moving back and forth within the contacting phases (i.e., the CO_2-rich phase and the oil-rich phase) until a completely miscible phase (i.e., a homogeneous phase) is formed. Two mechanisms involved in a multiple contact process are condensing and vaporizing (Figure II.3). During a condensing process of rich gas and crude oil, the hydrocarbon components in the gas dissolve in the oil phase and thus generate a mixture bank that results in miscibility. For lean gas and CO_2, the mechanism is mainly vaporization, where the light and intermediate components of the oil

phase transfer into and enrich the gas phase, forming a mixture bank that eventually becomes miscible with the original oil **[30].**
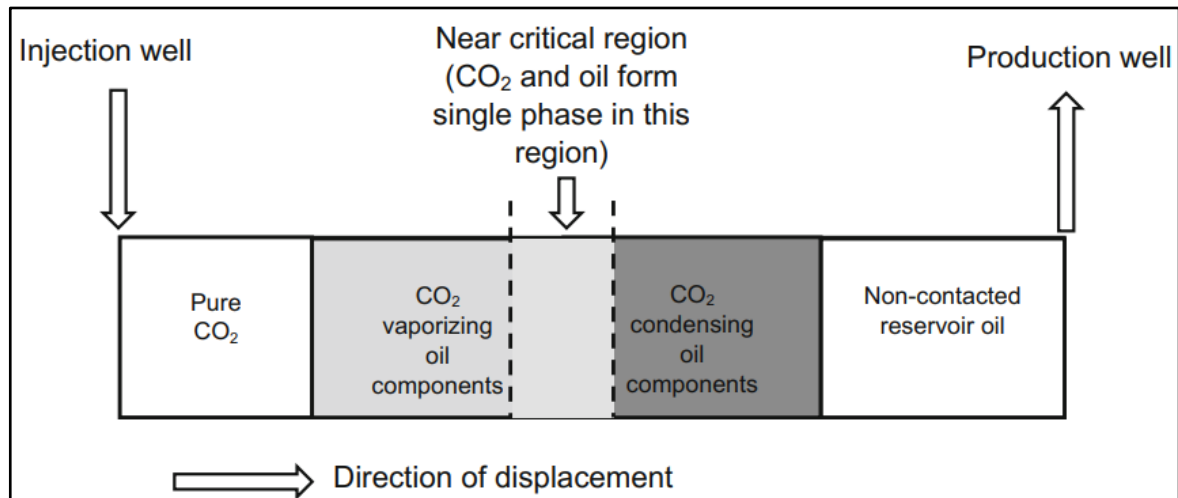
Figure II.3. One dimensional schematic of mixed drive mechanism responsible for the development of CO_2-reservoir oil miscibility in the reservoir **[31]**.

Miscible displacement can be described by a ternary phase diagram as seen in figure (II.4), where the corners represent different fluid-components. The top represents light hydrocarbon (HC), bottom right represent intermediate HC and bottom left represent heavy HC. Inside the diagram, there is a mix of the HC components. The critical line on figure (II.4) determines the type of miscible displacement. A displacement that only occurs in the one phase area is a first-contact miscible. A displacement that occurs in both two-phase and single-phase area is multimiscible. CO_2 displacement can also be immiscible. If the line crosses the two-phase region but not the critical line, it is an immiscible displacement **[31].**
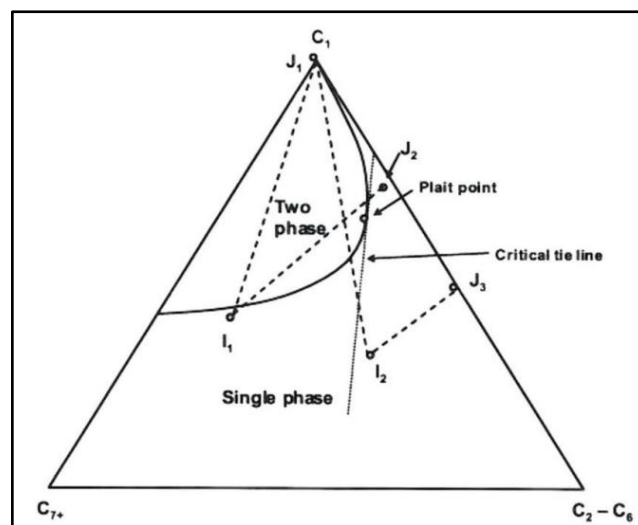
Figure II.4. Ternary phase diagram that can be used to determine the CO_2 displacement **[31]**.

II.4 Minimum miscibility pressure

The solubility of a gas in a liquid is highly dependent on two properties, pressure and temperature. The pressure at which miscibility occurs is defined as the minimum miscibility pressure (MMP) **[32].**

MMP is also dependent on the composition and properties of the gas injected. Figure (II.5) shows how MMP is determined from a slim tube experiment. The graph shows recovery measured experimentally as a function of pressure, where the MMP is characterized by the flattening of the curve **[32].**
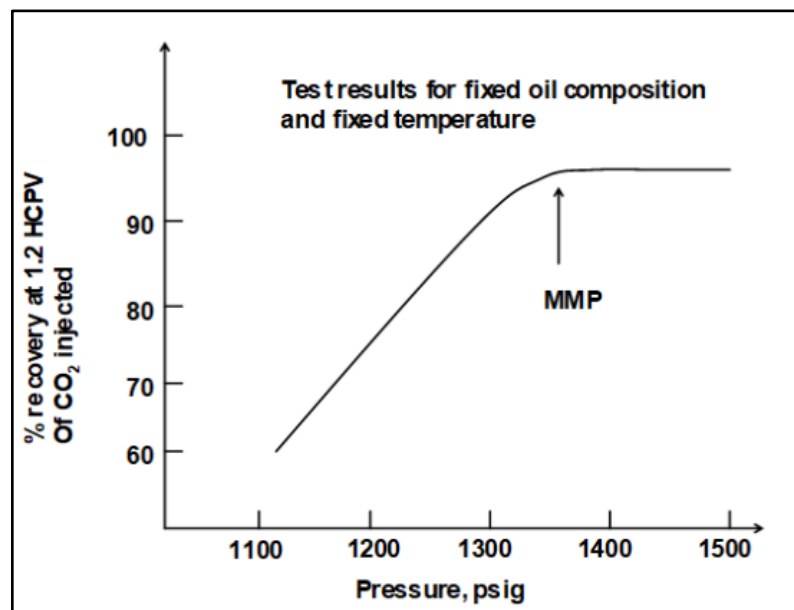
Figure II.5. Minimum miscibility pressure (MMP) determined from slim tube experiment **[32].**

II.4.1 Empirical correlation to determine MMP

Compared to experimental approaches, which are costly and time consuming and involve tedious experimental procedures, non-experimental approaches provide a relatively simple, faster, and inexpensive way for determining the MMP over a wide range of conditions.

Several researchers have attempted to build fast and robust correlations to determinate CO_2–oil MMP**,** Yellig and Metcalfe (1980)**,** presented an MMP correlation considering the effect of temperature and bubble-point pressure **[32]**. Their results suggested that MMP increases with increasing temperature, and that MMP increased 15 pounds per square inch (psi) per every increase in degree of temperature of the crude oil over a range of 95–192 °F. Until the MMP reaches a maximum value and then the trend reverses.

II.5 Oil recovery by CO2 injection

Enhanced oil recovery using CO_2 is an attractive oil recovery process that involves the injection of CO_2 to oil reservoirs and produce petroleum substances that would otherwise remain unrecoverable [37]. Typically, only around one third of the oil is produced after primary and secondary oil recovery methods. Much of the remaining oil are trapped by capillary forces as disconnected drops, surrounded by water, or as a continuous phase at low saturation with gas occupying the larger fraction of the pore space. An efficiency EOR process must mobilise these dispersed oil and form an oil bank that can move towards the production wells. This needs to be accomplished both on the microscale, at the pore level, and also on the macro-scale affecting the largest possible volume of the reservoir. EOR operations using CO_2 have been practiced for more than 50 years, the results revealed that 6 –15% of original oil in place can be recovered, whereas laboratory evaluations of CO_2 injection for EOR miscible displacement demonstrate oil recoveries over 90% of original oil in place (OOIP) [35].

Under sustainable resource development scenarios, total EOR production is forecast, by some, to increase by 2040 to about 4 million barrels per day (Figure II.6). However, this figure is highly sensitive to the oil demand and prices that materialize over the next two decades. Additional political support for carbon capture use and storage (CCUS) efforts has substantially increased interest in CO_2-EOR in recent years [33].
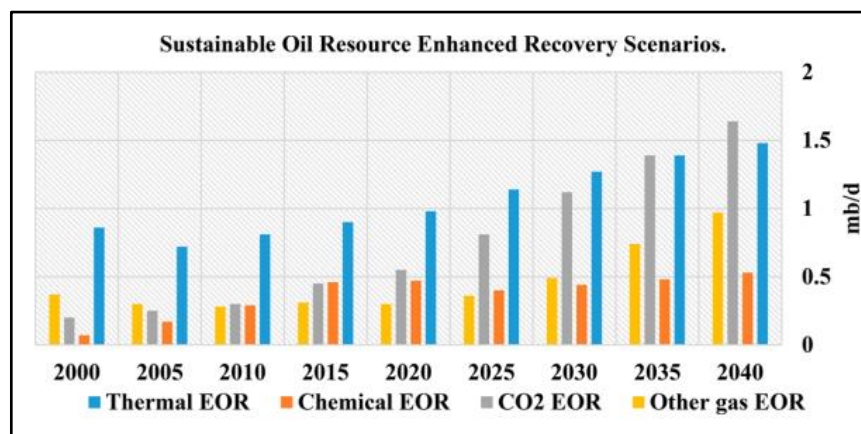
Figure II.6. Sustainable oil resource enhanced oil recovery scenarios [33].

II.6 Oil recovery mechanisms by CO2

When CO_2 is injected into the reservoir, it forms a dense or supercritical phase at typical reservoir pressure and temperature conditions (CO_2 is called "supercritical" if reservoir pressure is greater than P_c and reservoir temperature is greater than T_c, while it is called "dense" if reservoir pressure is greater than Pc but reservoir temperature is lesser than Tc). This dense or

supercritical CO_2 has a characteristic of high density and viscosity, compared to other gases, which makes the displacement front more stable by naturally mitigating gravity segregation and viscous fingering to some degree during gas injection EOR. Secondly, taking one more step further, if injected CO_2 creates a miscible flooding with the reservoir fluids by satisfying miscibility condition, then the interfacial tension becomes negligible and there is no oil trapped by capillary forces. This implies that the remaining oil saturation prior to CO_2 injection can be ideally reduced down to almost zero during miscible CO_2 flooding, boosting up the amount of oil recoverable. Lastly, if the injected CO_2 mixes with and dissolved into reservoir oils, the volume of oleic phase increases. This swelling effect, combined with pressure surge, yields more oil production **[34]**.

Figure (II.7) highlights the main oil recovery mechanisms that can take place during CO2 injection in oil reservoirs: (a) oil produced by direct CO2 displacement; (b) CO2 dissolved in the crude oil caused oil swelling; (c) vaporized oil due to CO2 extraction of light and intermediate oil components; (d) coalescing of disconnected oil ganglia by oil swelling; (e) The remaining components of crude oil after vaporization; (f) the residual oil in dead-end pores after displacing a part of swollen oil by CO2; and (g) the improvement in oil recovery due to various CO2 mechanisms. The dark color and the grey color represent the original oil and the oil after interaction with the injected CO2, respectively.
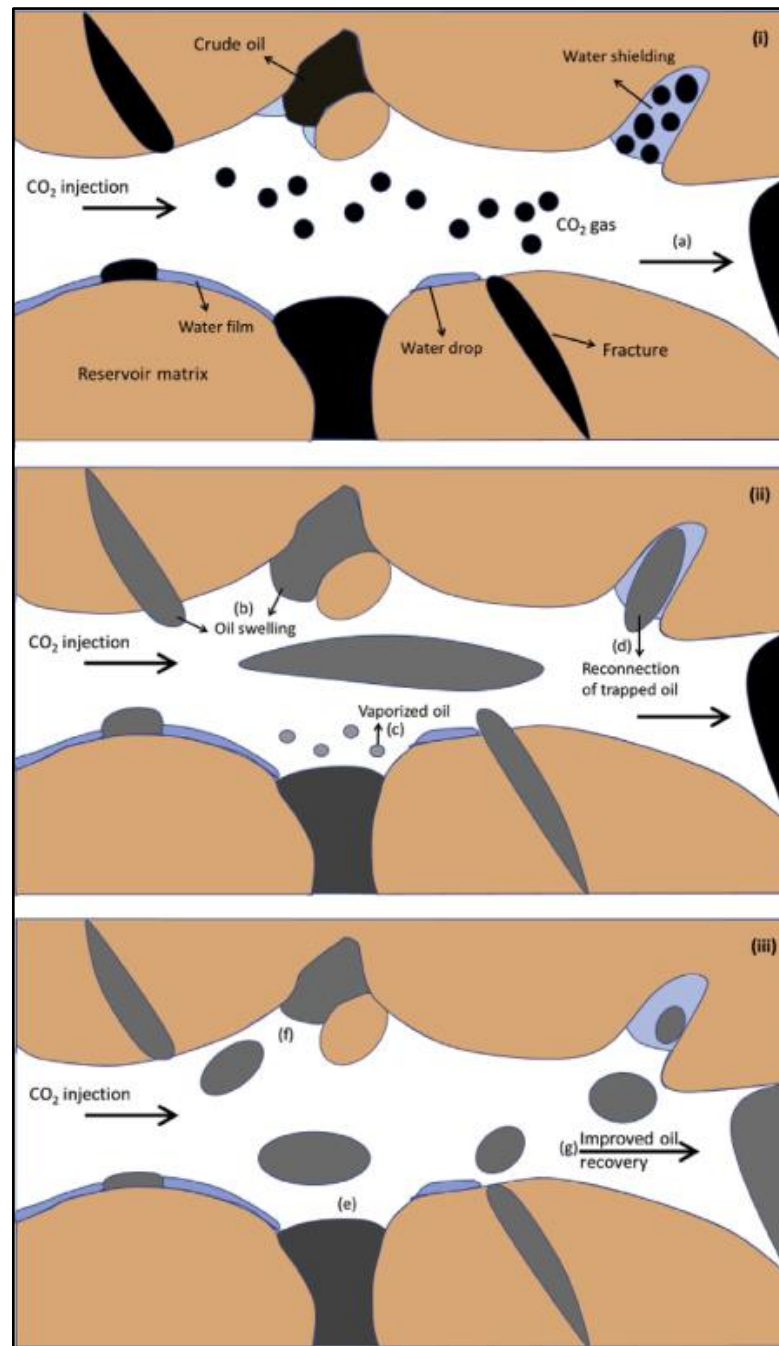
Figure II.7. The main oil recovery mechanisms during CO2 injection in oil reservoirs **[34].**

II.7 CO2 Flood/Injection Designs

Depending on the reservoir geology, fluid and rock properties, timing relative to water flooding, and well-pattern configuration, the CO_2-EOR flood may use one of several recovery methods as described below and shown in figure (II.8) **[35].**

II.7.1 Continuous CO_2 injection

This process requires continuous injection of a predetermined volume of CO_2 with no other fluid. Sometimes a lighter gas, such as nitrogen, follows CO_2 injection to maximize

gravity segregation. This approach is implemented after primary recovery and is generally suitable for gravity drainage of reservoirs with medium to light oil as well as reservoirs that are strongly water-wet or are sensitive to water flooding.

II.7.2 Continuous CO_2 injection followed with water

This process is the same as the continuous CO_2 injection process except for chase water that follows the total injected CO_2 slug volume. This process works well in reservoirs of low permeability or moderately homogenous reservoirs.

II.7.3 Conventional water-alternating-gas followed with water

In this process, a predetermined volume of CO_2 is injected in cycles alternating with equal volumes of water. The water alternating with CO_2 injection helps overcome the gas override and reduces the CO_2 channeling thereby improving overall CO_2 sweep efficiency. This process is suitable for most of the reservoirs with permeability contrasts among various layers.

II.7.4 Tapered water-alternating-gas

This design is similar in concept to the conventional WAG but with gradual reduction in the injected CO_2 volume relative to the water volume. With an objective to improve CO_2 utilization, tapered WAG is the method most widely used today because this design improves the efficiency of the flood and prevents early breakthrough of the CO_2, thus less recycled CO_2 and better oil recoveries. The CO_2 utilization is the volume of CO_2 used to produce a barrel of oil and is reported either as a gross volume, including the recycled CO_2, or a net volume.

II.7.5 WAG followed with gas

This process is a conventional WAG process followed by a chase of less expensive gas (for example air or nitrogen) after the full CO_2 slug volume has been injected.
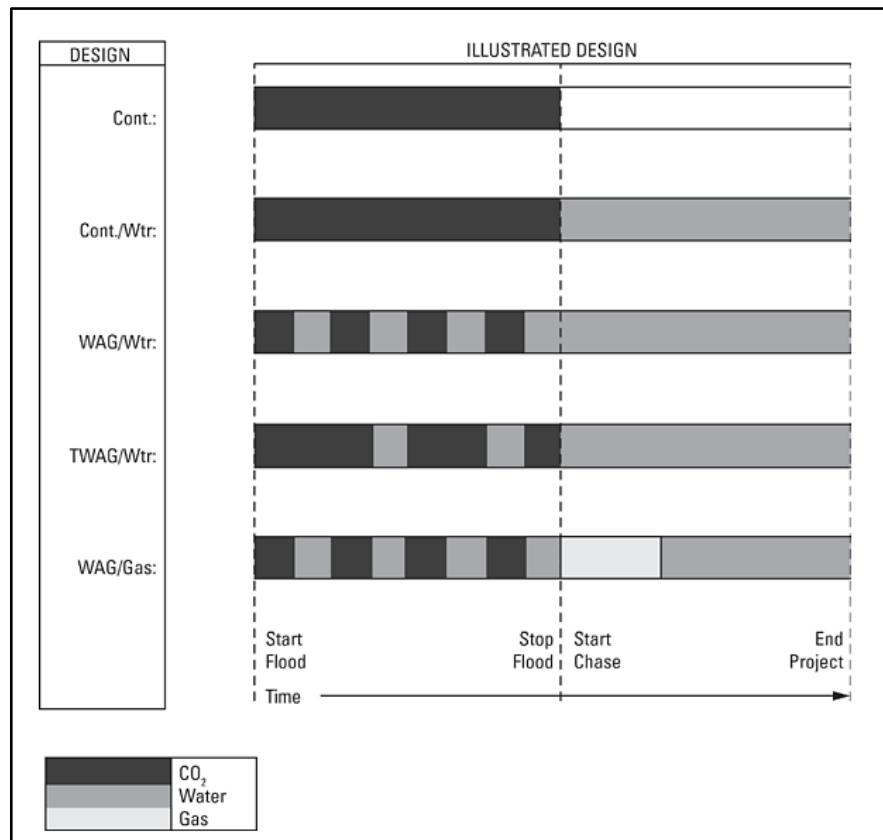
Figure II.8. Schematic of various carbon dioxide (CO_2) flood-injectant designs in oil reservoirs **[35]**.

II.8 Advantages and disadvantages of using CO2

CO_2 is regarded to be an excellent solvent for miscible CO_2 floods. But still there are both advantages and disadvantages to take into consideration when considering an EOR project **[29].**

II.8.1 Advantages

The greatest difference compared to other gases is that CO_2 can extract heavier components up to C30. The solubility of CO_2 in hydrocarbon oil causes the oil to swell. CO_2 expands oil to a greater extent than methane does. The swelling depends on the amount of methane in the oil. Because the CO_2 does not displace all of the methane when it contacts a reservoir fluid, the more methane there is in the oil, the less is the swelling of oil. CO_2 has the following characteristics in a flood process:

- It promotes swelling.
- It reduces oil viscosity.
- It increases oil density.
- It is soluble in water.
- It can vaporize and extract portions of the oil.

- It achieves miscibility at pressures of only 100 to 300 bar.
- It reduces water density.
- It reduces the difference between oil and water density, and then reduce the change for gravity segregation.
- It reduces the surface tension of oil and water, and result in a more effective displacement.

II.8.2 Disadvantages

In a gravity stable injection gases such as methane has a more favorable density difference than CO_2. CO_2 has acidic properties which can cause corrosion of equipment. With today's technology, CO_2 is expensive to capture. It is also expensive to separate CO_2 from the produced oil, especially if the CO_2 content becomes too high. There are natural CO_2 reservoirs; these are however, not always located nearby an oil field. CO_2 has an unfavorable mobility ratio, which causes viscous fingering through the oil. This can lead to early break through and very low macroscopic sweep efficiency. The unfavorable mobility ratio can also cause the CO_2 to flow through high permeable zones, leaving low permeable zones unswept (channeling). The density difference between CO_2 and oil in horizontal flooding can cause gravity segregation, so that the CO_2 only reaches the attic oil. This effect can be reduced if there are higher permeable layers in the bottom than the top of the given formation. Low vertical permeability can also delay the segregation process. Although diffusion effects are very effective on a microscopic scale, on a field scale it might not be effective enough to offset the negative effects of bypassed oil due to the unfavorable mobility and density difference **[29]**.

- Gravity override.
- Fingering and early gas breakthrough.
- CO_2 corrosion.
- Asphaltene deposition
- Availability.

II.9 On-going CO2-EOR projects

The first project of CO_2-EOR at industrial scale was started in 1972 in SACROC field in the USA. A large number of CO_2 EOR projects have started since then. Based on the 2014 EOR survey by the Oil and Gas Journal there are more than 140 of CO_2-EOR projects worldwide. Nearly all of them are miscible CO_2-EOR projects were implemented in the USA. Table (II.2) shows the production of active CO_2-EOR projects and their production rates in 2014 with the outlook of these projects in 2020 for United State by region. These projects produced cumulatively approximately 300000 barrels of oil per day at the start of year 2014 by injecting over than 68 million tonnes of CO_2 per year. This rate of oil production has grown steadily for the past 30 years. Given the new volumes of CO_2 supplies and the numerous announced CO_2-EOR projects, A. Kuuskraa and M.Wallace envision strong growth in near-term oil production and CO_2 utilization from CO_2-EOR, their analysis shows that incremental oil production from CO_2-EOR operations is likely to double to 638000 barrels of oil per day in 2020 **[36]**..

Table II.2 Projected CO_2-EOR production **[36].**

Region	CO2-EOR production rates (bbl/day)	
	2014	**2020**
Permian Basin	199000	323000
Gulf Coast	47000	152000
Rocky Mountains	39000	103000
Midcontinent	14000	59000
Other	1000	1000
Total	300000	638000

The use of CO_2 injection for oil recovery has been slow to catch some exception on outside of the US. One notable exception is Weyburn oil field, where in Canad and Apache have field-wide CO_2-EOR projects. Additional exceptions include the injection of CO_2 into Bati Raman heavy oil field in Turkey and the use of CO_2 in a series of heavy oil fields in Trinidad. Recently, the interests have emerged several CO_2 injection projects in Algeria (In Salah Gas), Abu Dhabi, Brazil, China, Malaysia, the North Sea, and other areas for purpose of enhanced oil recovery or CO_2 storage (Figure II.9) **[36]**.
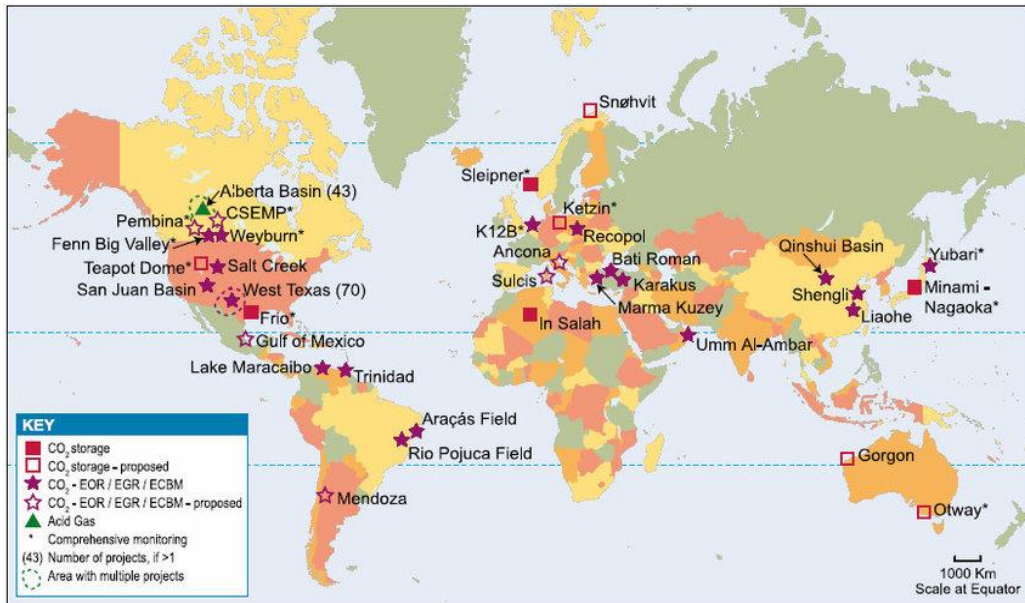
Figure II.9. Location of sites where activities relevant to CO_2 storage are planned or under way **[36].**

In Salah Gas is a joint venture of Sonatrach, British Petroleum (BP), and Statoil, which started in July 2004, for producing natural gas to sale in Europe. The natural gas contains up to 10% of CO_2 concentration, which has to be reduced to 0.3% before the gas is sold. Hence, 1 million tonnes/year of CO_2 is produced and re-injected into the Krechba Carboniferous Sandstone reservoir via two horizontal wells at a depth of 1900 metres for combined between CO_2 geological storage and enhanced gas recovery. The height of this geological formation is 20m, its porosity is 16% and its permeability is 10 md (Figure II.10). This joint venture is the first industrial-scale project in the world to store CO_2 in the water leg of a gas reservoir **[37, 38].**
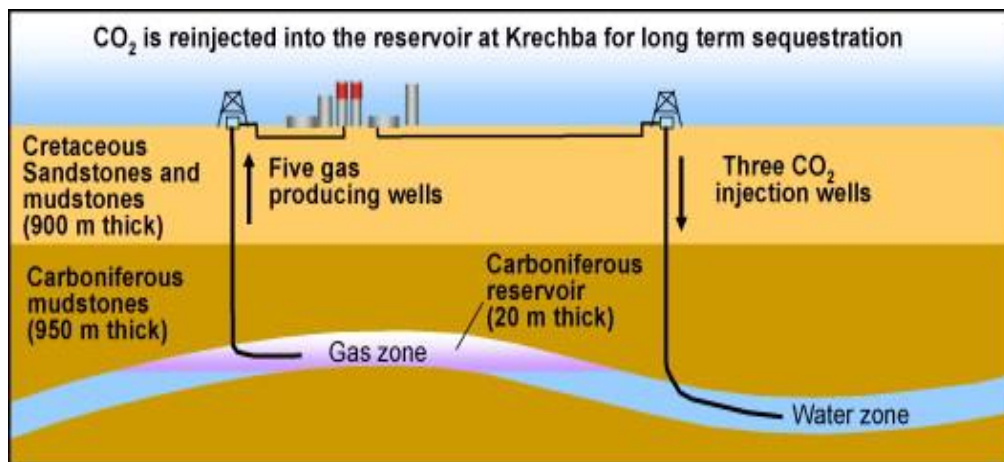
Figure II.10 Schematic of CO_2 storage strategy at Krechba field (In Salah Gas project) **[38].**

II.10 Nuclear magnetic resonance

Nuclear magnetic resonance (NMR) is a phenomenon in which some nuclear nucleus with a spin magnetic moment absorbs electromagnetic waves of a specific frequency under an external magnetic field, thereby changing the energy state. The nuclear magnetic resonance technology is widely applied in petroleum exploration and development field recently [39]. Through nuclear magnetic resonance testing of rock samples, the physical properties and fluid parameters of the formation such as reservoir permeability, porosity, oil saturation, percentage of movable fluid and mobile water saturation can be quickly obtained, which is benefit for the division, evaluation and identification of the effective reservoirs [40].

After the fluid (oil or water) is contained in the pores, the force between the fluid molecules and the surface of the pore solids is generated, and the strength of the force is related to the pore size, morphology, mineral composition, surface properties, fluid type and viscosity, etc. When performing nuclear magnetic resonance measurement on a core sample containing fluid (oil or water), the obtained T2 spectrum indicates the pore size distribution inside the core [41]. Within the T2 plot, the abscissa indicates the T2 relaxation time, and the ordinate indicates the fluid component occupancy share of different T2 relaxation times in the core. The T2 relaxation time is characterized by the strength of the surface of the fluid molecule and the pore solid [42].

The fluid in the tiny pore is strongly affected by the surface of the pore solid. The T2 relaxation time of the fluid is small, and the fluid is in a restrained or immobile state. It is called a restraint fluid or a non-movable fluid. The fluid in the larger pores is weakly affected by the surface of the pore solid, the T2 relaxation time of the fluid is large, and the fluid is in a free or movable state, called a free fluid or a movable fluid. Given the T2 cutoff at the T2 spectrum, the fluid in the right pore of the T2 cutoff is a movable fluid, and the fluid in the left pore is a non-movable fluid, Through using the magnitude and distribution characteristics of the T2 relaxation time in the nuclear magnetic resonance T2 spectrum of the fluid in the rock sample, the state of the fluid in the pore can be analysed [43]. T2 distribution, can be interpreted in terms of pore size and the composition of the fluid residing in the pore (Figure II.11).
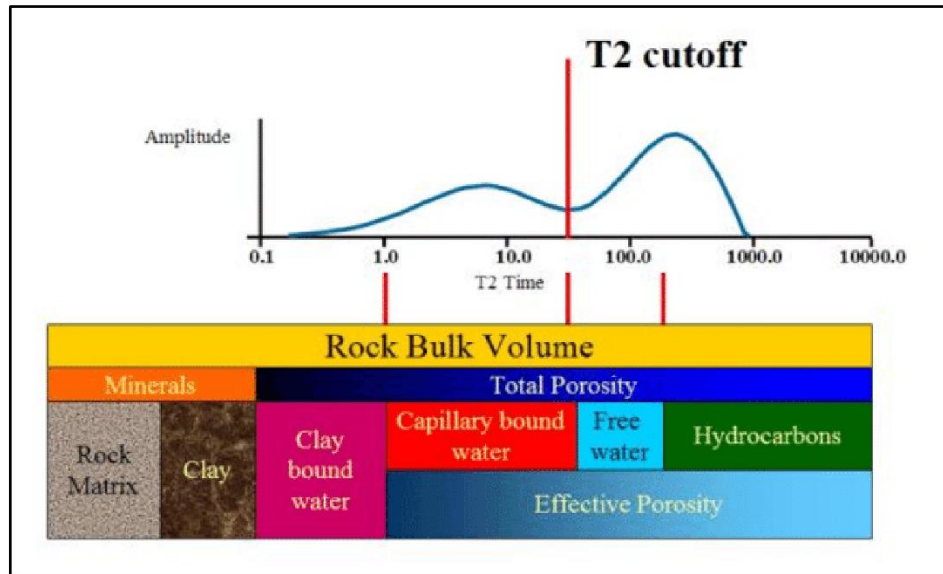
Figure II.11 T2 distribution in relation to pore size and fluids **[40].**

The recovery potential of the supercritical CO_2 flooding process was investigated, and the resulting recovery factor was analyzed. To verify the obtained results, the NMR T2 spectrum was applied and interpreted in detail to assess the effectiveness of the flooding process.

Conclusion

CO_2-EOR has proven to be a highly efficient method for oil extraction, particularly with light oil where miscible displacement is achieved, which is characteristic of Algeria's oil reserves. The miscibility of CO_2 with light oil enhances the recovery process. Ongoing projects and research have demonstrated the potential to achieve significant increases, approximately 20% or more, in oil recovery using CO_2-EOR strategies. Additionally, the integration of CO_2-EOR with Carbon Capture, and Storage (CCS) technologies presents a dual benefit of enhanced oil recovery and mitigating carbon emissions. This combination offers a promising avenue for sustainable and responsible oil extraction practices in Algeria and beyond, contributing to both economic growth and environmental stewardship.

Chapter lll

Experimental Work

Chapter lV

Results and discussion

Conclusions and Recommendations

Conclusions

This experimental study on CO2 miscible injection for enhanced oil recovery in a sandstone core sample with moderate permeability (3.64 md), homogeneous characteristics, and water-wet nature has provided the following insights:

- Our findings also revealed the limitations of conventional waterflooding, which only resulted in the extraction of approximately 30% of the OOIP. This emphasizes the need for alternative methods, such as CO2 injection, to mobilize the remaining 70% of the oil that cannot be recovered through conventional means.

- During the waterflooding process, an early breakthrough of water occured due to the significant capillary forces, necessitating an increase in the injection pressure to overcome these forces.

- Furthermore, the noticeable increase in oil acidity after extraction indicates the interaction of CO2 with the oil, leading to the formation of acidic compounds. This chemical reaction can potentially contribute to the oxidation of the oil or the degradation of the equipment, posing a corrosive challenge.

- We have also highlighted the significance of utilizing NMR (Nuclear Magnetic Resonance) technology in core-flooding experiments for accurate measurements and analysis. Compared to the conventional visual reading monitoring method, NMR technology eliminates errors associated with dead volume considerations and provides precise data for EOR experiments and scale analysis.

Recommendations

- In this study, all experiments were conducted using supercritical CO_2, obtained from an empirical correlation developed for predicting the minimum miscibility pressure (MMP). However, it is recommended to consider not only the temperature but also the oil composition and utilize experimental determination of MMP to accurately determine the optimum injection pressure.

- It is recommended to repeat all experiments in order to achieve good reproducibility and validate the results obtained in this thesis.

- Further investigation is needed to simulate the behavior of oil-wet rock, as this thesis primarily focused on water-wet rock samples.

- We recommend conducting relative permeability tests to gain a better understanding of CO_2 mobility and its potential for fingering and early breakthrough. Additionally, exploring the use of foam as a means to optimize mobility and improve sweep efficiency is suggested. This will provide valuable insights into enhancing the overall performance of CO_2 injection for enhanced oil recovery.

- It is recommended to incorporate a flow meter at the outlet of the injection system to accurately detect CO2 breakthrough and measure the quantity of injected and produced CO2. To determine the amount of CO2 sequestered in the reservoir.

- Apart from optimizing the reservoir performance, economic performance of the CO2-EOR projects has to be evaluated.

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Appendixes

Appendixe A: Full diameter core

Appendixe B: Coreflooding Sytem 350 from Vinci technology.

Appendixe C: Side view of the Coreflooding System 350.

Appendixe D: Oxford Geospec2 Core NMR Scanner.